Tetraphenyldibenzoperiflanthene as sensitizer for enhancing the performance in dinaphthothienothiophene-based photovoltaics with and without fullerene

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In this work, various interlayers were inserted between the donor and acceptor in a dinaphthothienothiophene (DNTT)/C₆₀ planar heterojunction (PHJ) to sensitize the performance. The power conversion efficiency is enhanced from 1.16% for the DNTT/C₆₀ PHJ cell to 2.23% by inserting a 5-nm-thick tetraphenyldibenzoperiflanthene (DBP) interlayer because of the greatly improved photocurrent and open-circuit voltage (V_{OC}). To achieve high V_{OC} , fullerene-free PHJs of DNTT/boron subphthalocyanine chloride (SubPc) (donor/acceptor) were fabricated, and V_{OC} is further improved by doping various fractions of DBP into the SubPc layer. The V_{OC} clearly increases from 0.82 V to 1.24 V by 70 wt%-DBP doping and is accompanied by a slight increase in photocurrent. The bipolar transfer characteristics of SubPc and DBP are investigated by field-effect transistors and show that both can transport electrons, indicating their potential as acceptors in photovoltaic devices. When another 5-nm-thick SubPc layer was included in the fullerene-free

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DNTT/SubPc:DBP PHJ cell, the power conversion efficiency further increases to 1.32%. These results indicate that DBP is a promising sensitizer for enhancing the performance of DNTT-based photovoltaics.

Keywords: Dinaphthothienothiophene; Sensitize; Alternative acceptor; DBP-doped-SubPc; Contact modification

1. Introduction

Tremendous research effort has been made in the field of organic photovoltaics (OPVs) regarding the designing of novel materials and exploring the physical mechanisms governing the operation of devices. The performance of bilayer planar heterojunction (PHJ) OPVs is often limited by the short exciton diffusion length in comparison with the optical absorption length, and bulk heterojunctions (BHJs) or cascade structures with multiple donors offer possible routes to overcome this problem [1-3]. Even with the variety of available device structures, most research to date focuses on devices prepared with a wide range of traditional and new donor molecules while the acceptor materials are often fullerene derivatives. Although fullerenes and their soluble derivatives are efficient electron acceptors, they generally have weak absorption and poorly-matched energy levels that can limit photocurrent and open-circuit voltage (V_{OC}). Furthermore, restricting the acceptor to fullerenes prevents a wider range of donor/acceptor (D/A) combinations, which could have different characteristics and help to further understand the key operation principles of these devices, from being studied.

Successful D/A heterojunctions are thought to depend on well-tuned highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels, so materials that are traditionally thought of as donors or acceptors may also be able to serve as acceptors or donors as long as the energy level offset in the D/A systems can overcome the exciton binding energy and the charge transport is sufficient. For example, the traditional acceptor material indene- C_{60} bisadduct (ICBA) could be employed as donor because of its bipolar transfer

characteristics and shallow HOMO and LUMO energy levels [4]. Additionally, to get higher V_{OC} , it has been recently demonstrated that some materials that have been traditionally used as donors and possess deep HOMO levels, such as boron subphthalocyaninechloride (SubPc) and diindenoperylene (DIP), could be used as acceptors [5, 6]. The efficient combination of fullerene-free acceptors in a cascade-energy-level (CEL) structure has achieved a high efficiency of 8.4% [7]. The expansion of available acceptors will allow for additional tuning of properties such as absorption, V_{OC} , and mobility.

The organic semiconductor tetraphenyldibenzoperiflanthene (DBP) has shown a wide range of applications in organic electronic devices, such as serving as the donor in bilayer PHJ OPVs [8-10], as the main active layer in a DIP-templated cascade structure [11], and as a red-emitting dopant in organic light-emitting diodes [12]. On the other hand, dinaphthothienothiophene (DNTT) is a promising donor with high hole mobility, and DNTT has been used in OPVs in only a few reports [13,14]. Considering the energy-level matching between the wide band-gap DNTT and multiple donor molecules including SubPc and DBP, we fabricate CEL structures of DNTT/interlayer/ C_{60} including various donors as interlayer to improve performance. We also introduce DNTT-based fullerene-free PHJs using SubPc as an alternative acceptor and optimize the performance by doping DBP into SubPc. The bipolar transfer characteristics of SubPc and DBP are investigated using field-effect transistors to better understand the carrier flow in the devices.

2. Experimental

All chemicals were purchased commercially, and DNTT (Luminescence Technology Corp., Taiwan), DBP (Luminescence Technology Corp., Taiwan) and SubPc (Aldrich, USA) were used after once purification by vacuum gradient sublimation (purity of about 99%). Clean ITO-coated glass substrates with a sheet resistance of 15 Ω /square were treated for 15 min in an ultraviolet-ozone chamber, followed immediately by spin-coating of a 20-nm-thick layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Clevios PVP. AI 4083)

at 3000 rpm for 60 s. After annealing for 10 min at 200 °C in air, the substrates were loaded into a vacuum chamber for deposition. Organic and metal layers were sequentially deposited on the PEDOT:PSS films via shadow masks to form devices with an area of 0.04 cm². The evaporation rates of the organic and metal layers were about 0.03 nm/s and 0.2 nm/s, respectively.

Current density vs. voltage (*J-V*) characteristics in the dark and under the illumination of an AM1.5 G (1000 W/m²) solar simulator (Bunko Keiki SRO-25GD, Bunko Keiki Co., Japan) were measured in air without encapsulation. To measure the external quantum efficiency (EQE) spectra, monochromatic light was generated using a Xe arc lamp in conjunction with a monochromator (Bunko Keiki M25-T), and intensity was measured with a calibrated Si solar cell. For mobility measurements of DBP and SubPc, field-effect transistors (FETs) were prepared on heavily doped n-Si substrates coated with a 300-nm-thick SiO₂ dielectric layer. The device configuration was Si/SiO₂/hexamethyldisilazane (HMDS)/organic layer (50 nm)/Mg (50 nm)/Au (50 nm) with a channel width/length of 50 μm/2000 μm. The characteristics of the FETs were measured with a semiconductor parameter analyzer (Agilent, B1500A). The photoluminescence (PL) spectra were recorded using a spectrofluorometer (Fluoro Max-4, Horiba Co., Japan). HOMO levels were measured by ultra-violet photoelectron spectroscopy (AC-2, Riken Keiki Co.), and the LUMO energies were determined by the low-energy optical absorption edge positions relative to the HOMO.

3. Results and discussion

3.1 DNTT/ interlayer/C₆₀ cascade PHJs

The effect of various interlayers acting as sensitizers on the performance of bilayer PHJs of DNTT/C₆₀ was first studied using a device configuration of ITO (150 nm)/PEDOT:PSS (20 nm)/MoO₃ (5 nm)/DNTT (40 nm)/interlayer (5 nm)/C₆₀ (30 nm)/bathocuproine (BCP) (10 nm)/Ag (100 nm), as shown in Fig. 1a. Here, PEDOT:PSS is used to reduce leakage current, MoO₃ acts as a hole-extraction layer, DNTT and C₆₀ act as donor and acceptor, respectively, the interlayer between donor

and acceptor modifies the junction properties, BCP works as a hole blocker and an electron-transport layer, and Ag is the cathode. DBP, SubPc, DIP, and chloroaluminum phthalocyanine (ClAlPc) were selected as interlayers because they have appropriate HOMO and LUMO energy levels positioned between those of DNTT and C₆₀ (Fig. 1b). Similar to a CEL cell with multiple donors, the interlayers can function both as an electron and energy acceptor for excitons generated in DNTT and C₆₀, respectively [7], and achieve bipolar carrier transport. Although there are some research reports about various CEL structures [1, 7], these CEL cells consist of multi-donors or multi-acceptors with the same HOMO or LUMO energy levels. However, here the CEL cell is composed of three active layers with completely different HOMO and LUMO energy levels. There is no report about a CEL cell with DNTT as donor, and the wide band-gap of DNTT and the narrow band-gaps of the interlayers such as SubPc and DBP achieve complementary absorption.

The *J-V* characteristics and EQE spectra of the DNTT/C₆₀ devices with and without interlayers are shown in Fig. 2, and the device performance is summarized in Table 1. Except for the short-circuit current (J_{SC}) with DIP, the V_{OC} , J_{SC} , and power conversion efficiency (η_{PCE}) are improved for all of the PHJ devices with interlayers relative to those of the reference DNTT/C₆₀ PHJ cell. The V_{OC} enhancement is attributed to the deeper HOMO level of the interlayers than DNTT, as the V_{OC} in cascade cells is mainly determined by the energy offset between the HOMO level of the interlayer and the LUMO level of C₆₀ [1], and not by the charge transfer state between DNTT and C₆₀. The J_{SC} enhancement is ascribed to the additional absorption from the interlayers that is much stronger and wider than that of DNTT. On the other hand, there is no consistent change in fill factor (FF) by including the interlayer.

Among these devices, the cell including a thin DBP interlayer achieves the largest enhancement in η_{PCE} over that of the reference cell, with an increase of 92% from η_{PCE} of 1.16% to 2.23%, because of the greatly increased J_{SC} and slightly enhanced V_{OC} . While the EQE of the reference cell is mainly located in the range of 300-550 nm, the addition of thin interlayers of DBP, SubPc, and ClAlPc greatly increases the EQE from 530-900 nm, as seen in Fig. 2b. Although the 5-nm-thick ClAlPc layer yields the

highest J_{SC} of 5.60 mA/cm² because of its near infrared absorption, the DBP interlayer leads to the highest η_{PCE} . The evident enhancement of J_{SC} suggests fluent bipolar carrier transport in the DBP and ClAlPc films. These results demonstrate that a thin DBP interlayer could sensitize the J_{SC} and V_{OC} , thus increasing the η_{PCE} of the DNTT/C₆₀ PHJ cell.

3.2 Fullerene-free DNTT PHJs

Based on the deeper HOMO and LUMO levels of SubPc and DBP relative to DNTT, fullerene-free OPVs were fabricated with DNTT as donor and either SubPc or DBP as an alternative acceptor. Firstly, SubPc layers with thicknesses of 13, 20 or 30 nm were used as acceptor in devices with a configuration of ITO (150 nm)/PEDOT:PSS (20 nm)/MoO₃ (5 nm)/DNTT (40 nm)/SubPc (X nm)/BCP (10 nm)/Ag (100 nm) and compared to the device with a 20-nm-thick C₆₀ layer as acceptor. Here, DNTT and SubPc act as donor and acceptor, respectively, and all other layers work the same way as mentioned in Section 3.1. The 20-nm-thick SubPc layer achieves the highest FF of 0.439 and J_{SC} of 2.73 mA/cm² for a maximum η_{PCE} of 0.98%. The higher V_{OC} (0.82 V) in the 20-nm-SubPc-based PHJ contributes to the higher η_{PCE} compared to that (0.6%) of the DNTT/C₆₀ (20 nm) PHJ cell (Table 2). By using SubPc as acceptor, absorption can be increased at longer wavelengths and V_{OC} can be raised relative to C₆₀.

Next, the potential for DBP to be used as acceptor with DNTT as donor was explored because of the matching of their HOMO and LUMO levels (Fig. 3a). When the SubPc layer in the DNTT/SubPc (D/A) PHJ cell is replaced with 20-nm-thick DBP, the highest V_{OC} of 1.29 V is achieved. The higher V_{OC} for DBP can be attributed to the shallower LUMO level of DBP (3.5 eV) relative to SubPc (3.6 eV) together with the horizontal orientation of DBP. The molecular orientation has been reported to slightly affect the actual HOMO and LUMO level of organic materials in devices [15], and the horizontal orientation of DBP could suppress the charge recombination at the DNTT/DBP interface to yield higher V_{OC} [16].

However, although DBP contributes to a higher V_{OC} , it also results in a low FF of 0.285 and a relatively low J_{SC} . Low J_{SC} and FF are often attributed to poor exciton

dissociation or low mobility preventing carriers from being collected before recombination. To explore if charge mobility is a limiting factor, the transfer characteristics of DBP and SubPc FETs were measured and are shown in Fig. 3b. Both DBP and SubPc exhibit bipolar transfer characteristics and higher hole mobilities than electron mobilities (μ_e), with μ_e of $8.15 \times 10^{-6} \text{ cm}^2/\text{Vs}$ and $9.26 \times 10^{-6} \text{ cm}^2/\text{Vs}$ for SubPc and DBP, respectively. The similar μ_e suggests that a difference in μ_e is not what leads to a reduction of J_{SC} when DBP is used as acceptor.

Instead, the low J_{SC} is attributed to poor exciton dissociation indicated by the slightly enhanced PL intensity of 5 wt%-DNTT-doped DBP compared to a pristine DBP film, as shown in the inset of Fig. 4b. Weak exciton dissociation at the DNTT/DBP can lead to a low photocurrent that is dominated by free charges generated in the donor or acceptor bulk [4]. Furthermore, the estimated threshold voltage (81 V) of the DBP transistor is much larger than that (32 V) of SubPc transistor, suggesting a higher concentration of trap states and weaker electron-injection into DBP than SubPc [17, 18]. These results imply that DBP is not suitable as a pristine acceptor layer in fullerene-free DNTT PHJs although a very high V_{OC} could be achieved.

In order to enhance the V_{OC} of the DNTT/SubPc (D/A) PHJ cell while trying to maintain J_{SC} , DBP was doped into an acceptor layer of SubPc, as shown in Fig. 3a, with a device configuration of ITO (150 nm)/PEDOT:PSS (20 nm)/MoO₃ (5 nm)/DNTT (40 nm)/DBP:SubPc (X wt%, 20 nm)/BCP (10 nm)/Ag (100 nm). Fig. 4 demonstrates the J - V characteristics and EQE spectra for devices using acceptor layers of DBP-doped-SubPc with the DBP content from 0 wt% to 100 wt%.

Doping only 10 wt%-DBP into SubPc decreases the FF from 0.439 for neat SubPc to 0.332, resulting in an S-shape in the J - V characteristics, while increasing the V_{OC} by almost 0.3 V. It has been reported that S-shaped J - V curves could occur due to imbalanced hole and electron mobility [19] or carrier injection or extraction barriers [20]. By doping 90 wt%-DBP into the SubPc layer, the V_{OC} could be increased from 0.82 V for neat SubPc to 1.28 V, while maintaining a relatively high J_{SC} of 2.0 mA/cm^2 . The highest η_{PCE} of 1.18% is obtained for a DBP:SubPc ratio of 7:3 (w/w),

which is 1.2 and 4.9 times the η_{PCE} of the cells with only SubPc or DBP as the acceptor layer, respectively. The EQE spectra indicate that doping 70 wt%-DBP into the SubPc layer broadens the EQE spectrum near 620 nm. Thus, doping an appropriate concentration of DBP into SubPc can enhance the V_{OC} and J_{SC} as a result of the shallower LUMO level and the slightly broader absorption for DBP than SubPc, respectively.

3.3 Fullerene-free DNTT p-i-n structures

However, although the V_{OC} could be increased by doping DBP into SubPc, the FF is still only 0.333 in the device with a DBP:SubPc (7:3, w/w) blend layer as acceptor. If carrier extraction barriers are the cause of the low FF and S-shaped kink (Fig. 4a), then modifying the cathode contact may possibly improve the FF. A thin SubPc layer was inserted between the DBP:SubPc blend and BCP layer to fabricate fullerene-free p-i-n junction (p, i, and n denote the donor, blend, and acceptor layer, respectively), as shown in Fig. 5a, with the structure of ITO (150 nm)/PEDOT:PSS (20 nm)/MoO₃ (5 nm)/DNTT (40 nm)/DBP:SubPc (70 wt%, 20 nm)/SubPc (5 or 10 nm)/BCP (10 nm)/Ag (100 nm). Here, DNTT/DBP:SubPc/SubPc acts as a p-i-n structure, and all other layers work the same way as mentioned in Section 3.1.

The J - V characteristics and photovoltaic parameters of the p-i-n structures are shown in Fig. 5b and Table 3. Inserting a 5-nm-thick SubPc yields a higher J_{SC} and a further enhanced η_{PCE} of 1.32%, but the FF could not be increased. The increase in J_{SC} can probably be ascribed to the DBP:SubPc/SubPc interface providing an additional exciton-dissociation interface while also modifying the contact by preventing DBP from touching the BCP layer. When the SubPc thickness increases to 10 nm, both J_{SC} and V_{OC} are reduced, which is attributed to the limited efficacy of cascaded energy heterojunctions and increased geminate charge recombination in thick cascade layers (≥ 10 nm) [21]. Thus, FF could not be easily improved by modifying the cathode contact.

Reconsidering the blend acceptor, the fact that doping only 10 wt%-DBP can greatly affect the J - V characteristics is somewhat surprising. From the dark characteristics (as shown in Fig. 3c), the turn-on voltage (the intersect of the

asymptotes in the J - V plots) clearly shifts to much higher voltages after DBP doping. Thus, even though the DBP concentration is low, the electronic processes in the PHJ are changed enough to lower the reverse saturation current, perhaps by changing the electron injection barrier at the cathode. However, the photocurrent for the devices with a blend acceptor (DBP:SubPc=1:9, w/w) layer appears to be a superposition of those of the SubPc- and DBP-only devices (as shown in Fig. 4a), with the photocurrent following that of the SubPc-only device from -0.5 V to ~0.7 V and that of the DBP-only device from 0.8 V to 1.1 V.

The kink in the J - V characteristics could be explained by field-dependent photocurrent [22, 23]. Field-dependent photocurrents have previously been attributed to the external field counteracting the internal field, making polaron pair dissociation unfavorable and increasing recombination of charges before extraction. Both SubPc and DBP can separate excitons at low external fields, but the photocurrent from SubPc decreases more quickly with increasing voltage compared to that from DBP, as indicated by the lower V_{OC} [24].

Thus, the photocurrent at low forward bias follows that of the SubPc-only device since the contribution from DBP is small. At higher forward bias, the internal field is still sufficient to separate excitons contributed by the DBP, so the photocurrent follows that of the DBP-only device until V_{OC} is reached. Although SubPc can increase the J_{SC} , the field-dependence of the photocurrent generation from SubPc could not be broken, so the devices ultimately suffer a low FF.

4. Conclusions

In conclusion, various organic materials were inserted into a DNTT/C₆₀ PHJ to fabricate CEL cells, and a DBP interlayer is found to greatly improve the η_{PCE} because of the evidently enhanced V_{OC} and J_{SC} . However, PL spectra suggest that DBP is not suitable as a single acceptor in fullerene-free DNTT PHJs even DBP achieves an ultrahigh V_{OC} of 1.29 V. An appropriate doping of DBP into SubPc could improve the V_{OC} and J_{SC} of a fullerene-free DNTT/SubPc PHJ because of the shallower LUMO level and bipolar transporting property of DBP. Thus DBP is a promising sensitizer

for enhancing the performance of DNTT based photovoltaics. Finally, the power conversion efficiency could be further enhanced by including an additional SubPc layer in a DNTT/DBP:SubPc/SubPc p-i-n cell.

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Table 1

The photovoltaic characteristics of CEL cells of ITO (150 nm)/PEDOT:PSS (20 nm)/MoO₃ (5 nm)/DNTT (40 nm)/interlayer (5 nm)/C₆₀ (30 nm)/BCP (10 nm)/Ag (100 nm)

Interlayer	$J_{SC}/\text{mA cm}^{-2}$	V_{OC}/V	FF	$\eta_{PCE}/\%$
none	3.13	0.60	0.624	1.16
DBP	5.11	0.70	0.626	2.23
DIP	3.04	0.66	0.648	1.30
SubPc	3.67	0.61	0.588	1.31
ClAlPc	5.60	0.63	0.590	2.08

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Table 2

The photovoltaic parameters of ITO/PEDOT:PSS (20nm)/MoO₃ (5 nm)/DNTT (40 nm)/acceptor (20 nm)/BCP (10 nm)/Ag (100 nm)

Acceptor	J_{SC}	V_{OC}	FF	η_{PCE}
(20 nm)	(mA/cm ²)	(V)		(%)
C ₆₀	2.29	0.54	0.485	0.60
SubPc	2.73	0.82	0.439	0.98
DBP	0.65	1.29	0.285	0.24
DBP:SubPc (1:9)	2.69	1.14	0.332	1.02
DBP:SubPc (1:1)	2.79	1.22	0.302	1.03
DBP:SubPc (7:3)	2.84	1.24	0.333	1.18
DBP:SubPc (9:1)	2.00	1.28	0.336	0.87

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2 **Table 3**

3 The photovoltaic parameters of DNTT p-i-n structures of ITO (150 nm)/PEDOT:PSS
 4 (20 nm)/MoO₃ (5 nm)/DNTT (40 nm)/DBP:SubPc (70 wt%, 20 nm)/n layer/BCP (10
 5 nm)/Ag (100 nm).

n layer	J_{SC}	V_{OC}	FF	η_{PCE}
(nm)	(mA/cm ²)	(V)		(%)
SubPc (5)	3.42	1.26	0.306	1.32
SubPc (10)	2.75	1.09	0.311	0.93
None	2.84	1.24	0.333	1.18

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Fig. 1. (a) Schematic representation of the CEL architecture. (b) Energy-level diagram of the active layers with HOMO and LUMO energies in electronvolts.

Fig. 2. (Color online) (a) *J-V* characteristics and (b) EQE spectra of the DNTT/C₆₀ PHJ devices with and without interlayers between DNTT and C₆₀.

Fig. 3. (Color online) (a) Energy-level diagram of active layers in fullerene-free PHJs. (b) Bipolar transfer characteristics of DBP and SubPc FETs. (c) Dark current density versus voltage plots of ITO/PEDOT:PSS (20 nm)/MoO₃ (5 nm)/DNTT (40 nm)/DBP:SubPc (X wt%, 20 nm)/BCP (10 nm)/Ag (100 nm) structures.

Fig. 4. (Color online) (a) J - V characteristics of ITO/PEDOT:PSS (20 nm)/MoO₃ (5 nm)/DNTT (40 nm)/C₆₀ (20 nm) or DBP:SubPc (X wt%, 20 nm)/BCP (10 nm)/Ag (100 nm) structures. (b) EQE spectra of the corresponding devices. The inset shows the PL spectra of 20-nm pristine DBP and 5%-DNTT-doped DBP films (20-nm) excited at 400 nm.

Fig. 5. (Color online) (a) Schematic energy level diagrams of active layers in DNTT p-i-n structures. (b) J - V characteristics of the DNTT p-i-n structures.

Small molecule DBP was added as an interlayer for a DNTT cascade PHJ cell, or was used as a dopant in the SubPc layer in a fullerene-free DNTT PHJ cell to enhance the performance.