A comparative study of Perylene derivatives in organic bulk heterojunction solar cells

Yingyot Infahsaeng[1]*, Karnjana Oncheurn[1], Kitsalanun Kitsakul[1], Khathawut Lohawet[2], Pisist Kumnorkaew[2], Wiyada Saennawa[3], Vinich Promarak[3]

[1]Division of Physics, Faculty of Science and Technology, Thammasat University, Khlong Nueng, Khlong Luang, Pathum-Thani, Thailand
[2]National Nanotechnology Center, 111 Thailand Science Park, Phahonyothin, Khlong Nueng, Khlong Luang, Pathum Thani, Thailand
[3] Vidyasirimedhi Institute of Science and Technology, School of Molecular Science and Energy, Wangchan, Rayong, Thailand

*E-mail: yingyot.infahsaeng@gmail.com

Abstract. Perylene derivative were used as electron acceptor in non-fullerene organic solar cells using the structure of ITO/PEDOT:PSS/PCDTBT:Acceptor/TiO_x/Al. Using a new perylene structure, PCDTBT:Perylene diimide photoactive device showed a low power conservation efficiency (PCE), compared to a PCDTBT:$PC_{70}BM$ photoactive device. This result has been observed in reduced short circuit current (I_{sc}) and open circuit voltage (V_{oc}). The devices with electron acceptors as bis-perylene diimide-1 and bis-perylene diimide-2 all showed excellent efficiency of 0.27%, with weight ratio of PCDTBT:acceptor (1:2). In addition, the morphologies and optical properties of PCDTBT:acceptor thin films were investigated. The high roughness and low absorbance due to the perylene derivatives were consistent with the low efficiency of solar cells.

1. Introduction

Organic solar cells offer a clean and renewable energy source that can potentially solve the problems of energy crisis. This is also due to their easy processing and low fabrication cost [1]. In organic bulk heterojunction (BHJ) solar cells, fullerene derivatives such as [6,6]-phenyl C_{71} -butyric acid methyl ester ($PC_{70}BM$) have been widely used as electron acceptor. High internal quantum efficiency approaching 100% have been achieved with the structure of ITO/PEDOT:PSS/donor:acceptor/TiO_x/Al [2]. The photoactive layer of such device used the alternating co-polymer, poly[N-9''-hepta-decanyl-2,7-carbozole-alt-5,5-(4',7'-di-2-thienyle-2',1',3'-benzothiadiazole) (PCDTBT) and $PC_{70}BM$ as electron donor and acceptor, respectively. However, fullerene acceptors have some drawbacks such as the difficulty of electronic structure tuning, the NIR regions absorption enhancement, and the high commercial value for large scale application [3]. Thus, the alternative acceptor materials must be developed and proposed with the favorable electron transporting and good visible-NIR absorption. Among of alternative acceptors, perylene diimides (PDIs) are widely interested due to their chemical, thermal, and photochemical stability. Moreover, PDI molecules exhibit large optical absorption in the visible to NIR spectral region [4,5].

PDI molecules is the small organic semiconductor molecule that can be used as electron acceptor in BHJ solar cells. By using the bay-substitution of perylene diimide molecule with fused aromatic rings, the enhancement of P3HT/PDI solar cells can be achieved approaching 1% [6]. Later, several studied on perylene acceptors have been examined with the growth of power conversion efficiency (PCE) in the range of 1-6% [7–9]. Recently, difference PDI structures as two donor-acceptor-donor have exhibited the balanced electron and hole carrier transport and their morphology which affect the conversion efficiency [7,10]. Moreover, the perylene structure have modified by bridging at difference position that can enhance the conversion efficiency more than 5% [11,12]. Among which, the high-power conversion efficiency (>6%) of the PDI-based non-fullerene solar cells has been acquired [13,14]. Recently, the performance limitation of PDI-based solar cells has been revealed which primarily attributed to the weak absorption in near-UV region, less charge generation, and unbalanced charge transport [15]. In this work, bis-PDI derivatives were tested and compared as electron acceptor in BHJ solar cells with PCDTBT as the donor. The optical and morphological properties of the photoactive films, the solar cells characteristics are examined.

2. Material and methods

2.1 Materials

PCDTBT and $PC_{70}BM$ was purchased from 1-Material and Ossila, respectively, and were used as received. All solvents were anhydrous and purchased from Sigma-Aldrich. The bis-PDI molecules were synthesized and received from Vidyasirimedhi Institute of Science and Technology (VISTEC) (unpublished work). The chemical structures of 5,5'-(9,10-dioxo-9,10-dihydroanthracene-2,6-diyl) bis(2,9-bis(2-ethylhexyl) anthra[2,1,9-def:6,5,10-d'e'f'] diisoquinoline-1,3,8,10(2H,9H)-tetraone) (bis-PDI-1) and 5,5'-(9-benzyl-9H-carbazole-2,7-diyl) bis(2,9-bis(2-ethylhexyl) anthra[2,1,9-def:6,5,10-d'e'f'] diisoquinoline-1,3,8,10(2H,9H)-tetraone) (bis-PDI-2) are shown in figure 1(a) and 1(b), respectively.

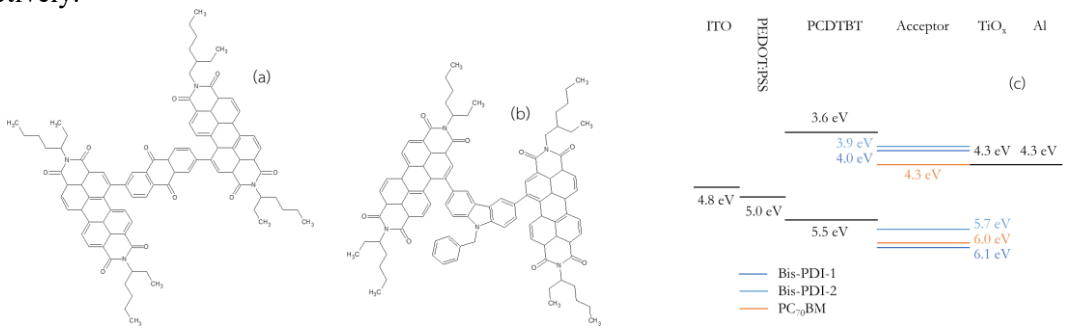

Figure 1. Molecular structure of (a) bis-PDI-1 and (b) bis-PDI-2 and energy level diagram of the BHJ device structure.

2.2 Preparation and characterization of the solar cells

The structure of the BHJ devices was prepared with the structure of ITO/PEDOT:PSS/PCDTBT: Acceptor/TiO_x/Al. The pre-patterned glass-indium tin oxide (ITO) substrates (Geomatec, 10 Ωsq^{-1}) were ultrasonically cleaned with Alconox detergent, deionized water, and isopropyl alcohol for every 30 min. The glass-ITO substrates were treated with oxygen plasma treatment for 1.5 min. PEDOT:PSS was coated by rapid convective deposition onto the ITO substrates at 3000 µm s^{-1} solution volume at 20 µl with two time coating. The PEDOT:PSS film was annealed at 120 ºC for 20 min under the atmospheric conditions. A series of solution containing total donor:acceptor blending 40 mg/ml in o-dichlorobenzene (DCB) with the weight ratio of 1:4 PCDTBT:$PC_{70}BM$, 1:1 PCDTBT:bis-PDI-1, 1:2 PCDTBT:bis-PDI-1, 1:1 PCDTBT:bis-PDI-2, 1:2 PCDTBT:bis-PDI-2, and 1:3 PCDTBT:bis-PDI-2. The solutions were stirred at 70 ºC for 60 min under the nitrogen atmosphere. The solution with the volume of 10 µl was deposited on the dried PEDOT:PSS at a deposition rate of 750 µm/s. Later the TiO_x sol-gel was deposited on the photoactive layer at the rate of 1250 µm/s and then dried at 80 ºC for 30 min under the

atmospheric conditions. Finally, the sample was transferred to thermal-evaporator to deposit aluminum electrode, then sealed with covering glass. The cell active area of the devices is 0.1 cm^2. The J-V characteristics were examined under AM 1.5G solar simulator (ABET Technology) The external quantum efficiency (EQE) was also measured. Moreover, the UV-vis absorption spectra and morphology of PCDTBT:acceptors thin films were investigated by spectrophotometer (Shimadzu UV-2600) and scanning probe microscope (Olympus OLS4500), respectively.

3. Results and discussion

The current density-voltage (J-V) characteristics of difference acceptor and blending ratio devices are shown in figure 2(a). The performance of PCDTBT:$PC_{70}BM$ (1:4) device is clearly exhibit the highest open circuit voltage (V_{oc}) and short circuit current density (J_{sc}) lead to the high PCE of 4.80%. However, all PCDTBT:perylene acceptor devices exhibit rather low V_{oc} (0.28 – 0.73 V) and J_{sc} (0.35 – 1.22 mA cm^{-2}). The devices performances are summarized in table 1. It shows that the highest performances of peryelene-based BHJ solar cells at 0.27% can be achieved from both bis-PDI-1 and bis-PDI-2 at donor:acceptor ratio of 1:2. Slightly difference fill factor from both devices can be observed, which may attributed to the series and shunt resistances. While the series resistances of all devices are rather high which reduced the fill factor (FF), the high shunt resistances can be observed in perylene based device which should indicate the low power loss compared with $PC_{70}BM$ based device. Thus, the low PCE of perylene based device may attributed to the inefficient charge generation that can be observed in low current density and external quantum efficiency as depicted in figure 2(b). The EQE of all perylene based devices showed a maximum intensity of less than 10% at all wavelength. Interestingly, the EQE of perylene based device cannot achieve up to the NIR region as the $PC_{70}BM$ based device can reach. Although the HOMO and LUMO levels of $PC_{70}BM$, bis-PDI-1, bis-PDI-2 are not dramatically difference as shown in figure 1(c), the absorption spectra of PCDTBT:acceptor blend thin film are rather difference as shown in figure 2(c). Note that the PCDTBT:perylene acceptors with the ratio of 1:3 for bis-PDI-1 and of 1:4 for both PDI can not be prepared due to their high viscosity. To investigated the morphology of PCDTBT:acceptors thin films, the topographic (1 μm × 1 μm) of films which measured by scanning probe microscope (SPM) were observed as shown in figure 3.

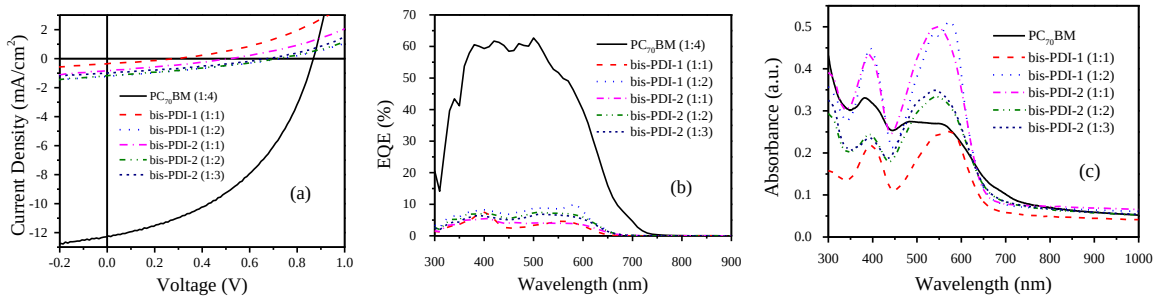

Figure 2. (a) Current density-voltage (J-V) characteristics and (b) external quantum efficiency (EQE) of organic BHJ solar cells. (c) UV-vis absorption spectra of PCDTBT:acceptors thin films.

Table 1. The parameters extracted from the J-V characteristics of PCDTBT:acceptors devices with difference acceptors

Acceptor	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	PCE (%)	R_S (Ω)	R_{SH} (Ω)
$PC_{70}BM$ (1:4)	12.25	0.87	45.05	4.80	1681.18	181.11
Bis-PDI-1 (1:1)	0.35	0.28	30.84	0.03	4204.44	11772.44
Bis-PDI-1 (1:2)	1.22	0.73	30.70	0.27	1731.24	2102.22
Bis-PDI-2 (1:1)	0.84	0.51	31.64	0.14	2452.59	4905.18
Bis-PDI-2 (1:2)	1.18	0.72	31.27	0.27	5351.11	6540.24
Bis-PDI-2 (1:3)	0.99	0.66	33.06	0.22	1783.70	9055.72

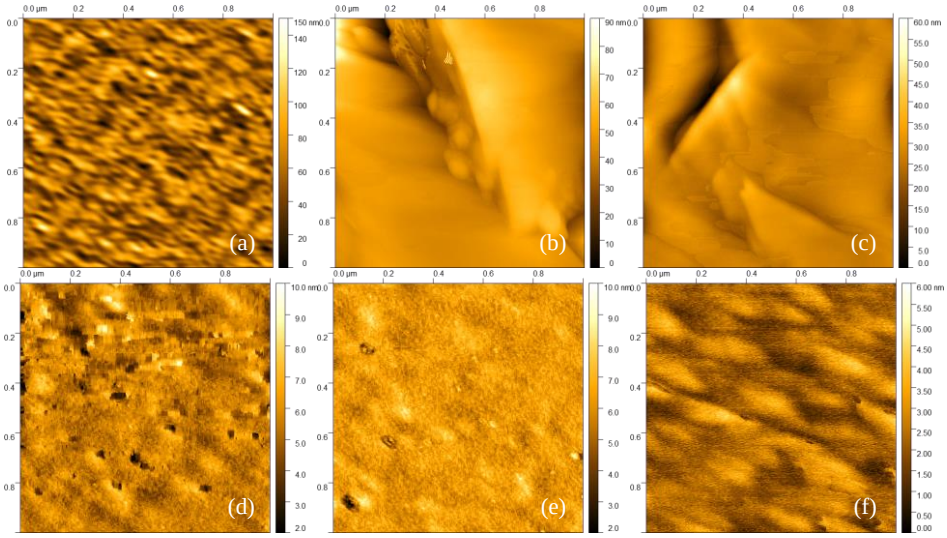

Figure 3. SPM morphology of thin films with the acceptor of (a) $PC_{70}BM$ (1:4), (b) bis-PDI-1 (1:1), (c) bis-PDI-1 (1:2), (d) bis-PDI-2 (1:1), (e) bis-PDI-2 (1:2), and (f) bis-PDI-2 (1:3).

As shown in figure 3, high roughness of 14.2 nm is achieved for PCDTBT:$PC_{70}BM$ (1:4) film. However, the uniform morphology can be observed by confocal optical microscope. Interestingly, the crystalline structure can be clearly discovered for bis-PDI-1 acceptor as shown in figure 4. The surface topographic of crystalline structure with the roughness of 6.75 nm and 3.32 nm for the blend ratio of (1:1) and (1:2), respectively, are shown in figure 3(b-c). Although, a smooth morphology with a roughness of 0.64 nm, 0.48 nm, and 0.53 nm can be obtained as shown in figure 3(d-f) for the PCDTBT:bis-PDI-2 ratio of (1:1), (1:2), and (1:3), respectively, some defect and crystalline seed can be observed by optical microscope as shown in figure 4. The crystalline domains are attributed to the self-organization of perylene derivative, which is drawback for charge separation and transport in organic solar cells. This result lead to the low current density and EQE, which lead to the low performance efficiency of perylene-based solar cells.

Figure 4. Confocal optical microscope of (a) PCDTBT:$PC_{70}BM$ (1:4), (b) PCDTBT:bis-PDI-1 (1:1), and (c) PCDTBT:bis-PDI-2 (1:1) thin films.

4. Conclusions

In summary, a novel bis-PDE acceptor was tested for bulk heterojunction solar cells. The low power conversion efficiency can be observed due to low current density and external quantum efficiency. The presence of crystalline structure in polymer:bis-PDI film lead to non-uniform morphology, which may limit the charge separation and transport in solar cells. The BHJ solar cells with electron acceptors of bis-PDI-1 and bis-PDI-2 all showed highest efficiency of 0.27%, with PCDTBT:acceptor ratio of (1:2).

Acknowledgements
This work has been financial supported by the Thailand Research Fund (TRF) (MRG5980192) and the Young Scientist and Technologist Programme or YSTP (SCA-CO-2560-4669-TH) of the National Science and Technology Development Agency, Thailand.

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