1. Introduction

Solution-processed organic photovoltaics (OPVs) have emerged as a promising renewable energy technology due to their potential to form light-weight, flexible, and inexpensive manufacturing methods [1,2]. Generally, OPV adopts the bulk heterojunction (BHJ) with the p-type conjugated polymer donors and the fullerene derivatives as an electron acceptor. The power conversion efficiencies (PCEs) of polymer OPVs surpassed over 10% in the single junction [3]. In comparison with the polymer semiconducting material, the small molecules (SMs) have been considered as an impeccable alternative in OPVs due to their advantages such as well-defined molecular structure, high purity, no end-group contamination, and good batch-to-batch consistency [4,5]. To date, the development of photosensitive materials employing organic small molecules (SMs) has led to record power conversion efficiencies (PCEs) of over 10% in OPVs [6–8]. Thus, the use of SMs in OPVs has dramatically increased over the past few years [5]. In general, these π-conjugated SMs are used as donors, and the derivatives of fullerene are widely employed as acceptors in OPVs. In order to improve the PCE of SMs based on OPVs, the SMs-donor materials should satisfy the following requirements: (i) broad absorption bands; (ii) suitable electronic energy levels; and (iii) high charge carrier mobility [9–11]. One of the effective strategies to design the SMs donors with the long range absorption (small band gap) is to incorporate the electron-rich and electron-deficient moieties in π-conjugated SMs [12,13].

More specifically, the use of strong electron-deficient moieties is a commonly employed method to narrow the band-gap of SMs [14–16]. For example, the diketopyrrolopyrrole (DPP) derivatives have been employed for the construction of high-performance conjugated polymers and SMs due to their ameliorate optical-electronic properties and thermal stability [17,18]. Peng and co-workers reported the new conjugated DPP-porphyrin SMs with the PCE of 8.08%, where the blend films were annealed and processed with the pyridine additive [19]. In addition, Wang et al. demonstrated a narrow band-gap DPP-based SM that provides the PCE of 8.50% [20]. Most OPVs utilizing small band gap SMs exhibit large photocurrent density (J_{SC}) and low open circuit voltage (V_{OC}). Because the electron deficient groups used in SMs reduce the band gap of the SMs and shift E_{HOMO} (energy level of highly occupied molecular orbital) closely to the vacuum level. Therefore, it is still required to design a new SM for OPV exhibiting both large J_{SC} and...
high $V_{OC}$ to improve the PCE.

The introduction of the B←N unit to π-conjugated SMs could increase the $E_{HOMO}$ of SMs and enable contraction of SM based OPV exhibiting large $J_{SC}$ and high $V_{OC}$. Recently, Yamaguchi and coworkers developed a thienylthiazole skeleton containing B←N unit as a new π-conjugated bridge for electron-transporting materials [21]. A few years later, Wang and coworkers introduced new n-type semiconducting polymer acceptors containing B←N bridged thienylthiazole moieties with high electron mobility and low-lying $E_{HOMO}$ [22,23]. Together, they demonstrated that B←N bridged thienylthiazole moieties can be used for photosensitive materials.

Thus, based on the preceding investigations, we herein designed and synthesized new type of SMs (Fig. 1) having small band gap and low-lying $E_{HOMO}$ by incorporating the B←N bridged thienylthiazole and DPP derivatives. To the best of our knowledge, the use of B←N bridged thienylthiazole moieties with DPP linked at the sides has not been explored as active materials for OPVs.

2. Experimental section

2.1. Materials and characterization methods

All chemical reagents and solvents were purchased from commercial suppliers and were used without further purification. All reactions were carried out in oven-dried glassware equipped with a magnetic stir bar. Reactions were monitored by thin-layer chromatography (TLC) with 0.25 mm pre-coated silica gel plates (Kieselgel 60F254). Yields refer to chromatographically and spectroscopically pure compounds unless otherwise noted. $^1$H and $^{13}$C spectra were recorded on a 300 MHz spectrometer.

Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF) spectra were obtained on a Bruker Autoflex III mass spectrometer. Ultraviolet-visible (UV-vis) absorption spectra were measured on a Scinco 300 spectrophotometer. Cyclic voltammetry (CV) data were collected on a BAS 100B electrochemical analyser at room temperature inside a glove box. Current density-voltage (J-V) curves of OPVs were recorded using a Keithley 2400 Source meter. Atomic force microscopy (AFM) images were obtained in a non-contact mode using an XE-70 (Park Systems Corp., Korea) atomic force microscope. Grazing incidence wide-angle X-ray scattering (GIWAXS) was performed at the beamline PLS-II 9A U-SAXS in the Pohang Accelerator Laboratory (South Korea). The operating conditions were fixed at an X-ray wavelength of 1.121 Å, an incidence angle of $\sim 0.12^\circ$, and a sample-to-detector distance of 224 nm. GIWAXS patterns were recorded using a 2D CCD detector (Rayonix, SX-165, USA) with an exposure time of 5–10 s.

2.2. Device fabrication and characterization of organic solar cells

The organic solar cells were fabricated with inverted architectures of indium ITO/ZnO/active layer/MoO3/Ag. The cell devices were prepared on patterned glass indium-tin oxide (ITO) substrates. The substrates were thoroughly cleaned in an ultrasonic bath with soapy-water, water, isopropyl alcohol, acetone, and isopropyl alcohol for 10 min each, and then dried in an oven. The substrates were then exposed to UV-ozone for 20 min. The ZnO precursor was prepared according to published literature sol-gel procedures [24]. The solution was spin-coated on top of the ITO-glass substrate. The films were annealed at 230 °C for 1 h. The ZnO-coated substrates were transferred into a glove box. A solution comprising a mixture of B←N units containing SM: PC71BM (1:1.5 mass ratio) in a mixed solvent (0.8–1% v/v additive in chloroform) was prepared with a concentration of 12 mg/mL. The solution was spin-coated onto the ZnO layer at 4000 rpm. The substrate was then dried on a hot-plate at 90 °C for 10 min. The devices were completed by deposition of a 10 nm layer of MoO3 followed by a 100 nm Ag layer. This layer was thermally evaporated at a pressure of $\sim 3 \times 10^{-6}$ Torr at room temperature.

2.3. Molecular synthesis

Schemes 1 and 2 show the synthetic routes for the preparation of TBDPPOT, TBDPPEH, and TBDPPEHT4. Initially, bis(tributylstannyl) coupling reagent 2 was prepared from the diiodide 1 [20] by treatment with n-BuLi in the presence of tributylchloride. Organostannane 2 was directly used in the next step without further purification. The Pd-catalyzed coupling reactions of 2 and the corresponding mono-brominated-DPPs 3, 4, or 5 provided TBDPPOT, TBDPPEH, and TBDPPEHT4 in 43%, 61% and 61% yield, respectively. These SMs were characterized by $^1$H NMR, $^{13}$C NMR, $^{11}$B NMR and MALDI-TOF.

2.3.1. Synthesis of compound 6

In a dried flask, monobrominated-DPP 4 (1 g, 1.65 mmol), monoborurate T4 (0.81 g, 2.15 mmol), Pd(PPh3)$_4$ (191 mg, 0.17 mmol, 10 mol %), and K$_2$CO$_3$ (16.5 mmol) were dissolved in an 8 mL mixture of THF:H$_2$O (3:1 v/v). The reaction mixture was then stirred at 70 °C for 24 h under Ar. After cooling down to room temperature, the reaction mixture was filtered through Celite with EtOAc and the solution was

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Fig. 1. The chemical structures of small molecules.
removed in vacuo. The residue was purified by flash column chromato-
graphy on silica gel using hexane/dichloromethane (1:1, v/v), pro-
viding pure 6 (550 mg, 0.84 mmol, 51%) as a dark red solid, with a
melting-point temperature (T_mel) of 120–124 °C and refractive index
(R_n) of 0.34. ^1^H NMR (300 MHz, CDCl_3): δ 8.96 (d, J = 4.2 Hz, 1H),
8.88 (d, J = 3.9 Hz, 1H), 7.61 (d, J = 4.8 Hz, 1H), 7.42 (s, 1H), 7.31 (d,
J = 3.9 Hz, 1H), 7.28 (d, J = 3.9 Hz, 1H), 6.94 (s, 1H), 4.11–3.97 (m,
4H), 2.89 (t, J = 7.5 Hz, 2H), 1.93–1.83 (m, 2H), 1.77–1.68 (m, 2H),
1.44–1.18 (m, 26H), 0.94–0.83 (m, 15H). ^1^C NMR (75 MHz, CDCl_3): δ
161.6, 161.4, 150.6, 143.9, 139.7, 139.5, 139.3, 138.3, 137.0, 136.0,
135.3, 130.6, 130.1, 128.8, 128.0, 124.7, 117.6, 116.6, 108.4, 108.3,
46.2, 39.5, 39.3, 32.1, 31.7, 31.5, 30.6, 30.5, 29.9, 29.6, 29.5, 29.3,
28.8, 28.6, 23.9, 23.8, 23.4, 23.3, 22.9, 14.34, 14.33, 14.3, 10.8, 10.7.
MALDI-TOF (m/z): [M^+^] calcd for C_40_H_36_Br_N_2_O_2_S_4 850.0996; found
775.1374.

2.3.2. Synthesis of compound 5

In a dried flask, compound 6 (520 mg, 0.67 mmol) was dissolved in
anhydrous CHCl_3 (10 mL) under Ar. The mixture was cooled down to
0 °C and N-bromosuccinimide (120 mg, 0.67 mmol) was added. After
being stirred at room temperature for 7 h under Ar, the reaction mix-
ture was quenched with H_2O and extracted with chloroform (10 mL, 3
times). The combined organic layer was dried over MgSO_4 and the
solvent was removed in vacuo. The residue was purified by flash column
chromatography on silica gel using hexane/dichloromethane (1:1, v/v) provided pure 5 (480 mg, 0.56 mmol, 84%) as a dark blue
solid, with a melting-point temperature (T_mel) of 138–140 °C and re-
fractive index (R_n) of 0.28. ^1^H NMR (300 MHz, CDCl_3): δ 8.98 (d,
J = 4.2 Hz, 1H), 8.64 (d, J = 4.2 Hz, 1H), 7.39 (s, 1H), 7.27 (d, J = 1.8 Hz, 1H), 7.19 (d, J = 4.2 Hz, 1H), 6.92 (s, 1H), 4.0–3.9 (m,
4H), 2.88 (t, J = 7.5 Hz, 2H), 1.93–1.83 (m, 2H), 1.78–1.68 (m, 2H),
1.45–1.30 (m, 26H), 0.95–0.87 (m, 15H). ^1^C NMR (75 MHz, CDCl_3): δ
161.6, 161.2, 150.8, 144.3, 140.3, 139.5, 138.4, 138.0, 137.3, 135.9,
135.1, 131.8, 131.6, 127.9, 124.8, 118.7, 117.9, 116.6, 108.5, 107.9,
46.2, 39.5, 39.3, 32.1, 31.7, 31.5, 30.6, 30.5, 29.9, 29.6, 29.5, 29.3,
28.8, 28.6, 23.9, 23.8, 23.4, 23.3, 22.9, 14.34, 14.33, 14.3, 10.8, 10.7.
MALDI-TOF (m/z): [M^+^] calcd for C_48_H_49_Br_N_3_O_S_4 854.0996; found
854.4575.

2.3.3. Synthesis of TBDPPPOT

To a solution of diiodide 1 (100 mg, 0.15 mmol) in THF, n-BuLi
(2.5 M in hexane, 0.21 mL, 0.34 mmol) was added dropwise at –78 °C.
After being stirred for 1 h at –8 °C under Ar, tributyltin chloride
(0.1 mL, 0.42 mmol) was slowly added. The reaction mixture was then
slowly warmed up to room temperature and stirred overnight. The re-
action mixture was quenched by adding ethyl acetate, which was was-
shed with ammonium chloride solution and water. The combined or-
ganic layer was dried over MgSO_4 and the solvent was removed in
vacuo. The crude product 2 was used in the next step without further
purification. To a mixture of 2 (125 mg, 0.12 mmol) and mono-
 brominated-DPP 3 (100 mg, 0.17 mmol), Pd[PPh_3]_4 (19 mg,
0.017 mmol, 10 mol %) and 2.6 mL of anhydrous toluene were added.
The mixture was then stirred at 120 °C for 18 h under Ar. After cooling
down to room temperature, the reaction mixture was filtered through
Celite with EtOAc and the solution was removed in vacuo. The residue
was purified by flash column chromatography on silica gel using hexane/dichloromethane (1:1, v/v), providing pure TBDPPPOT
(134 mg, 0.09 mmol, 61%) as a dark blue solid, with a melting-point
temperature (T_mel) of 206–208 °C and refractive index (R_n) of 0.26. ^1^H
NMR (300 MHz, CDCl_3): δ 8.98–8.94 (m, 3H), 8.88 (d, J = 4.2 Hz, 1H),
7.83 (s, 1H), 7.67–7.65 (m, 2H), 7.43 (s, 1H), 7.37 (d, J = 4.2 Hz, 1H),
7.30–7.27 (m, 3H), 6.72 (s, 4H), 4.02–3.95 (m, 8H), 2.22 (s, 6H),

![Scheme 1. Synthetic routes of small molecules TBDPPPOT, TBDPPEH, TBDPPEH74.](image-url)

![Scheme 2. Synthesis of monobrominated-DPP 5.](image-url)
1.97–1.94 (m, 12H), 1.42–1.26 (m, 36H), 0.93–0.86 (m, 24H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 164.0, 161.7, 161.5, 145.3, 141.2, 140.3, 140.2, 139.4, 136.7, 136.0, 135.8, 135.4, 134.8, 133.5, 131.1, 130.7, 130.1, 129.7, 129.5, 129.3, 128.6, 128.5, 126.8, 126.5, 126.3, 109.1, 108.6, 108.0, 45.9, 39.3, 39.1, 30.3, 30.2, 29.7, 28.3, 24.3, 23.6, 23.5, 23.1, 20.8, 14.0, 10.6, 10.5. $^{11}$B NMR (500 MHz, CDCl$_3$): $\delta$ –3.98. MALDI-TOF (m/z): $[\text{M}^+]$ calcd for C$_{85}$H$_{102}$BN$_5$O$_4$S$_6$ 1460.9515; found 1460.9609.

2.3.4. Synthesis of TBDPPEH

To a mixture of 2 (142.0 mg, 0.14 mmol) and monobrominated-DPP 4 (180 mg, 0.31 mmol), Pd(PPh$_3$)$_4$ (35 mg, 0.031 mmol, 10 mol %) and 2.3.5. Synthesis of TBDPPEHT4

To a mixture of 2 (150 mg, 0.14 mmol) and monobrominated-DPP 4 (180 mg, 0.31 mmol), Pd(PPh$_3$)$_4$ (35 mg, 0.031 mmol, 10 mol %) and TBDPPEH (582 mg, 0.68 mmol), Pd(PPh$_3$)$_4$ (78 mg, 0.068 mmol, 10 mol %) and TBDPPO (134 mg, 0.09 mmol, 61%) as a viscous oil was removed in vacuo. The residue was purified by flash column chromatography on silica gel using hexane/dichloromethane (1:1, v/v), providing pure TBDPPEH, TBDPPEHT4, and TBDPPEH (solution) and in thin film (open symbol).

2.6 mL of anhydrous toluene were added. The mixture was then stirred at 120 °C for 18 h under Ar. After cooling down to room temperature, the reaction mixture was filtered through Celite with EtOAc and the solution was removed in vacuo. The residue was purified by flash column chromatography on silica gel using hexane/dichloromethane (1:1, v/v), providing pure TBDPPEHT4 (121 mg, 0.06 mmol, 41%) as a dark blue solid, with a melting-point temperature ($T_{mp}$) of 208–210 °C and refractive index (R$_p$) of 0.1. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 9.00 (q, $J$ = 4.2 Hz, 2H), 8.93 (d, $J$ = 4.2 Hz, 1H), 8.86 (d, $J$ = 4.2 Hz, 1H), 7.81 (s, 1H), 7.43 (s, 1H), 7.34 (s, 2H), 7.24–7.22 (m, 3H), 7.12 (d, $J$ = 4.2 Hz, 1H), 6.90 (d, $J$ = 3.9 Hz, 2H), 6.73 (s, 4H), 4.01–3.99 (m, 8H), 2.90–2.86 (m, 4H), 2.23 (s, 6H), 1.98 (s, 12H), 1.93–1.92 (m, 6H), 1.75–1.71 (m, 4H), 1.36–1.25 (m, 48H), 0.94–0.87 (m, 32H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 163.8, 161.6, 161.2, 150.5, 145.4, 144.2, 143.7, 142.2, 141.5, 140.5, 140.2, 139.7, 139.2, 139.1, 138.1, 137.5, 136.2, 135.8, 135.7, 134.8, 130.2, 129.8, 129.4, 127.7, 127.5, 126.7, 126.2, 124.4, 117.5, 116.3, 109.3, 109.2, 108.0, 108.6, 108.2, 106.0, 93.8, 31.8, 31.4, 31.3, 30.3, 29.7, 29.3, 29.2, 29.1, 28.5, 24.5, 23.7, 23.1, 22.7, 20.8, 14.1, 10.6. $^{11}$B NMR (500 MHz, CDCl$_3$): $\delta$ –3.62. MALDI-TOF (m/z): $[\text{M}^+]$ calcd for C$_{113}$H$_{138}$BN$_5$O$_4$S$_{10}$ 1961.7969; found 1961.5891.

2.4. DFT calculation method

To find out the optimized molecular geometry and energy level of HOMO and LUMO, density functional theory (DFT) calculation was conducted on TBDPPO, TBDPPEH, and TBDPPEHT4, respectively. DFT calculation used the B3LYP functional with the 6-31G (d,p) basis set in Gaussian 09. The calculation was proceeded in gas phase.

3. Results and discussion

3.1. Optical properties

The UV-vis absorption spectra of TBDPPO, TBDPPEH and TBDPPEHT4 in dilute chloroform solutions and thin films are shown in Fig. 2. The maximum absorption wavelength ($\lambda_{max}$), absorption edge wavelengths ($\lambda_{edge}$), and determined optical band gaps ($E_{opt}$) are summarized in Table 1. All the materials exhibit a broad spectral coverage in absorbance band in the range of 300–800 nm. The strong absorption peak at $\lambda_{max}$ of 611, 611 and 678 nm was observed for TBDPPO, TBDPPEH and TBDPPEHT4, respectively. The intramolecular charge transfer (ICT) between the electron rich and electron deficient units in the SMs broaden the absorption of SMs up to 800 nm [25–27]. The absorbance spectra of the solid films are red-shifted compared to that of the spectrum taken in solutions for all three SMs. This implies that the SMs were planarized while they formed as a solid film with increased inter molecular stacking of SMs. The $\lambda_{max}$ of TBDPPO and TBDPPEH is similar, while the TBDPPEHT4 is shifted to the longer wavelength. This conjectures two important things: at first, the alkyl side chain does not influence the conjugation length of the SMs; and secondly, the planar thienothiophene unit in TBDPPEHT4 increases the conjugation length of the SMs [28]. This confirms and

Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>UV-Vis $\lambda_{max}$ (nm)</th>
<th>LUMO (eV)</th>
<th>E$_{onset}$ (V)</th>
<th>E$_{HOMO}$ (eV)</th>
<th>$\Delta E_{opt}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBDPPO</td>
<td>611° (618)$^a$</td>
<td>–1.07</td>
<td>–3.67</td>
<td>0.86</td>
<td>–5.60$^c$</td>
</tr>
<tr>
<td>TBDPPEH</td>
<td>611° (623)$^a$</td>
<td>–1.06</td>
<td>–3.68</td>
<td>0.87</td>
<td>–5.62$^c$</td>
</tr>
<tr>
<td>TBDPPEHT4</td>
<td>678° (745)$^a$</td>
<td>–1.03</td>
<td>–3.71</td>
<td>0.74</td>
<td>–5.48</td>
</tr>
</tbody>
</table>

$^a$ In solution CHCl$_3$ at 1.0 × 10$^{-5}$ M.

$^b$ film by spin coating.

$^c$ Calculated by CV (cyclic voltammetry) in CH$_2$Cl$_2$. (E$_{onset}$ = reductive potential; E$_{HOMO}$ = oxidative potential).

$^d$ Energy gap estimated from optical absorption.
supports the strategy of our molecular design for conjugated SMs in OPV applications.

3.2. Electrochemical properties

The HOMO and LUMO (lowest unoccupied molecular orbitals) energy levels of these SMs (TBDPPOT, TBDPPEH and TBDPPEHT4) were investigated using cyclic voltammetry (CV) with a standard three-electrode configuration. A Pt electrode (diameter of 1.6 mm) and Pt coiled wire electrodes were used as the working and counter electrode, respectively. An Ag/AgNO₃ electrode was used as a reference electrode. All the potentials were converted into the saturated calomel standard electrode (SCE) by measuring the ferrocene/ferrocenium (Fc/Fc⁺) redox systems (Fig. 3). The electronic properties of SMs are summarized in Table 1 and Fig. 3. Since the backbone structures of TBDPPOT and TBDPPEH are similar except the alkyl side chains, both these SMs have shown similar redox potentials in CV (Eox = −1.07 V; Ered = 0.87 V) leads to the similar HOMO and LUMO energy levels. The HOMO and LUMO band edges were calculated by the empirical formula EHOMO = −e( Eox + 4.74) (eV) and ELUMO = −e( Ered + 4.74) (eV) [29]. Interestingly, the incorporation of thienothiophene group significantly reduces the oxidation potential that destabilizes the HOMO energy level (−5.48 eV) and decreases the band gap (1.77 eV) of TBDPPEHT4. Although the introduction of the thienothiophene unit facilitates the
reduction of the band gap, it also weakens the anti-oxidation property of the SM due to the lower HOMO energy level. However, the $E_{\text{HOMO}}$ of TBDPPEHT4 is deeper than that of the thienothiophene-containing SM without the B←N bridge, because the B←N bridged core increases the HOMO energy level of the SM. This suggests that the combined effect of incorporations of the thienothiophene unit along with the B←N bridges could simultaneously reduce the band gap with enhanced the anti-

<table>
<thead>
<tr>
<th>Compound</th>
<th>LUMO Exp (eV)</th>
<th>LUMO Calc (eV)</th>
<th>HOMO Exp (eV)</th>
<th>HOMO Calc (eV)</th>
<th>$E_{\text{gap}}$ Exp (eV)</th>
<th>$E_{\text{gap}}$ Calc (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBDPPOT</td>
<td>-3.67</td>
<td>-2.99</td>
<td>-5.60</td>
<td>-4.87</td>
<td>1.80</td>
<td>1.88</td>
</tr>
<tr>
<td>TBDPPEH</td>
<td>-3.68</td>
<td>-3.02</td>
<td>-5.62</td>
<td>-4.90</td>
<td>1.80</td>
<td>1.88</td>
</tr>
<tr>
<td>TBDPPEHT4</td>
<td>-3.71</td>
<td>-2.99</td>
<td>-5.48</td>
<td>-4.70</td>
<td>1.68</td>
<td>1.72</td>
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Table 2
Comparison between experiment and calculation results of each small molecule.

Table 3
Solar cell parameters of OPVs.

<table>
<thead>
<tr>
<th>Photo-active layer</th>
<th>Additive</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA/cm²)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBDPPOT: PC71BM</td>
<td>None</td>
<td>0.90</td>
<td>5.45</td>
<td>0.32</td>
<td>1.59</td>
</tr>
<tr>
<td>TBDPPOT: PC71BM</td>
<td>DIH 0.8 wt%</td>
<td>0.87</td>
<td>5.96</td>
<td>0.49</td>
<td>2.52</td>
</tr>
<tr>
<td>TBDPPEH: PC71BM</td>
<td>None</td>
<td>0.73</td>
<td>3.05</td>
<td>0.37</td>
<td>0.82</td>
</tr>
<tr>
<td>TBDPPEH: PC71BM</td>
<td>DIH 0.8 wt%</td>
<td>0.92</td>
<td>6.78</td>
<td>0.51</td>
<td>2.21</td>
</tr>
<tr>
<td>TBDPPEHT4: PC71BM</td>
<td>None</td>
<td>0.84</td>
<td>8.12</td>
<td>0.34</td>
<td>2.35</td>
</tr>
<tr>
<td>TBDPPEHT4: PC71BM</td>
<td>DPE 1.0 wt%</td>
<td>0.84</td>
<td>8.00</td>
<td>0.38</td>
<td>2.56</td>
</tr>
</tbody>
</table>

oxidation ability of an SM. This reduced bang gap and higher anti-oxidation properties are the key requirements for the materials to be used as an active layer in OPVs.

Fig. 6. $J$-$V$ curves and EQE spectra of OPVs utilizing small molecule based photo-active layer processed with additive (solid symbol) and without additive (open symbol).
3.3. Structure optimization and molecular orbital calculation by DFT calculation

To find out optimized molecular geometry and energy level of HOMO and LUMO, density functional theory (DFT) calculation was conducted on TBDPPOT, TBDPPEH, and TBDPPEHT4, respectively. Fig. 4 shows optimized structure of molecules. The π conjugated backbone looks fairly flat. In case of TBDPPOT and TBDPPEH, the most distorted dihedral angle is about 14°. Especially, in TBDPPEHT4 case, the most distorted dihedral angle is less than 10°. The width of SMs are measured 33.56 Å, 33.47 Å, and 62.88 Å for TBDPPOT, TBDPPEH, and TBDPPEHT4.

The energy and surface plot of HOMO and LUMO of TBDPPOT, TBDPPEH, and TBDPPEHT4 are presented in Fig. 5. For all molecules, electron density in HOMO and LUMO is well delocalized through the π-conjugated backbone. The calculated molecular orbital energies, especially HOMO-LUMO energy gap, were well matched to experimental values measured with cyclic voltammetry (See Table 2).

3.4. Photovoltaic properties

The solution processed OPVs were fabricated using TBDPPOT, TBDPPEH and TBDPPEHT4 as a donor and the PC71BM as an acceptor. The inverted OPV device structure of ITO/ZnO/photoactive layer/MoO3/Ag has been employed for device fabrication. The thickness of MoO3 layer was maintained between 90 and 120 nm. The charge-transport characteristics of the SMs: PC71BM were investigated by using the space-charge-limited current (SCLC) model. The measured SCLC hole mobilities of TBDPPOT, TBDPPEH and TBDPPEHT4 were found to be 2.73 × 10−6, 1.97 × 10−6 and 4.04 × 10−5 cm2 V−1 s−1, respectively. The electron mobilities were found to be diﬀerent. This might be ascribed to diﬀerent morphology between SMs and PC71BM; which reduces the charge transport kinetics [31–33]. Since TBDPPOT and TBDPPEH are consisting of similar backbone with different alkyl chain variance, there is no signiﬁcant diﬀerence in energy level and light absorbance properties. However, the EQE and JSC values were found to be different. This might be ascribed to diﬀerent morphology between ﬁlms.

The charge-transport characteristics of the SMs: PC71BM were investigated by constructing hole-only device with structure of ITO/PEDOT:PSS/SM/PC71BM/MoO3 (7 nm)/Al (100 nm). Their charge-carrier mobilities were obtained by using the space-charge-limited current (SCLC) model. The measured SCLC hole mobilities of TBDPPOT, TBDPPEH and TBDPPEHT4 were found to be 2.73 × 10−6, 1.97 × 10−6 and 4.04 × 10−5 cm2 V−1 s−1, respectively. The carrier mobility was found to be higher for TBDPPEHT4 SMs with thienothiophene conjugated side units (4.04 × 10−5 cm2 V−1 s−1), which is one order of magnitude higher than that of the molecules without thienothiophene units (TBDPPOT and TBDPPEH). The electron mobility values were lower than the electron mobility values for all three devices, indicating charge unbalance is one of main factor for low

Fig. 7. Grazing incidence wide angle X-ray scattering (GIWAXS) images. GIWAXS images of pristine small molecule films (a) (g), without additive (b) (e) (h) and with additive (c) (f) (i), and small molecule: PC71BM blend films show the images for TBDPPOT, TBDPPEH and TBDPPEHT4.
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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2017.11.060.

References


