Improved photovoltaic performance of P3HT:PCBM cells by addition of a low band-gap oligomer†

Eunhee Lim,* Sungkoo Lee and Kyeong K. Lee

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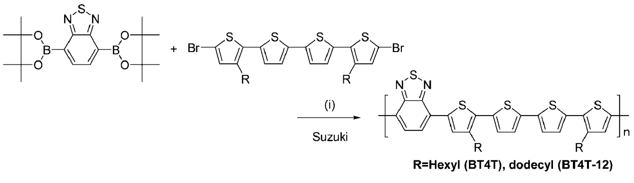
The introduction of a low band-gap oligomer, oligo(benzo[1,2,5]thiadiazole-*alt*-3,3‴-dihexylquaterthiophene) (BT4T) improved the performance of P3HT:PCBM bulk heterojunction organic photovoltaic cells due to improved UV-vis absorption and increased P3HT crystallinity.

Organic photovoltaic cells (OPVs) are promising sources of electrical power that have attracted considerable attention because of their efficiency, low cost, and potential for use in renewable energy applications.[1] During the last decade, the field of OPV research has progressed remarkably both in terms of device performance and overall understanding of the governing physical processes. To date, most efforts have been devoted to developing bulk-heterojunction polymer solar cells composed of polymer donors and soluble fullerene acceptors because of the easy fabrication and low cost of such cells.[2] The prototypical system comprising poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C_{61}-butyric acid methylester (PCBM) is nearing its theoretically optimal device performance limit.[3] P3HT systems principally harvest photons with wavelengths shorter than 650 nm, and new conjugated materials with low band gaps are being actively developed to enable efficient harvesting of solar energy over a broader spectrum. The alternating arrangement of electron–donor and electron–acceptor units along the conjugated backbone is the most successful approach to synthesizing low band-gap materials.[4] At the same time, several reports have described improvements in the power conversion efficiencies (PCE) of P3HT:PCBM systems by incorporating additives *via* ternary mixing. The addition of polymers, such as electron-donating polymer or regiorandom P3HT, has led to increases in the open-circuit voltage (V_{OC}).[5] More recently, Jeong *et al.* reported that the PCE of a P3HT:PCBM device could be improved by incorporating discotic liquid crystal (DLC) additives with self-assembly properties.[6] Despite the low absorbance of DLCs, devices containing DLCs showed remarkable improvements in the short-circuit current (J_{SC}) due to increased ordering of the P3HT chains.

In the present study, we introduced low band-gap materials into polymer photovoltaic cells as additives to provide a simple method for improving the properties of the active layers. The incorporation of low band-gap materials can result not only in a broader absorption spectrum, but also in improved P3HT ordering. Here, low band-gap materials based on benzothiadiazole and thiophene (**BT4Ts**) were synthesized, and the general properties of the oligomers, including their thermal, electrochemical, and optical properties, were investigated. The effects of **BT4T**s on the photovoltaic properties of P3HT:PCBM films were systematically investigated by UV-vis absorption spectroscopy, thin-film X-ray diffraction (XRD) studies, and atomic force microscopy (AFM), which characterized the surface morphologies of the films.

We synthesized new conjugated oligomers based on thiophene and benzothiadiazole, oligo(benzothiadiazole-*alt*-3,3‴-dihexyl-2,2′:5′,2″:5″,2‴-quaterthiophene) (**BT4T**) and oligo(benzothiadiazole-*alt*-3,3‴-didodecyl-2,2′:5′,2″:5″,2‴-quaterthiophene) (**BT4T-12**), *via* the Suzuki coupling reaction.[7] Scheme 1 outlines the synthetic route to the **BT4T**s. The number-average molecular weights (M_n) of **BT4T** and **BT4T-12**, determined by gel permeation chromatography (GPC) using tetrahydrofuran (THF) as the eluent and polystyrene as the standard, were 2100 and 2590 (M_w/M_n = 1.1–1.2), respectively. This result revealed that **BT4T** and **BT4T-12** comprised 3–4 repeating units, indicative of an oligomer. The relatively low molecular weights may have been due to the rigid oligomer backbone and the low solubility of the oligomer. In addition, high-temperature GPC using trichlorobenzene as the eluent (135 °C) resulted in an M_n for **BT4T** of 5070 (eight repeat units). The thermal characteristics of the oligomers were studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Weight losses of 5%, from **BT4T** and **BT4T-12**, occurred at 295 and 255 °C, respectively, indicating that the **BT4T**s were sufficiently thermally stable for use in OPV applications. As shown in Fig. 1, the DSC thermogram of **BT4T-12** showed liquid crystalline characteristics with two endotherms, at 62 and 230 °C, corresponding to the crystalline-to-liquid crystalline and liquid crystalline-to-isotropic phase transitions, respectively, similar to the well-known liquid-crystalline polymer, poly(3,3‴-didodecylquaterthiophene) (PQT-12).[8] No apparent transition was observed in **BT4T** up to 170 °C, probably due to the rigid backbone of the compound. Therefore, **BT4T** may have been present in an amorphous glassy state below 120 °C, whereas a crystalline **BT4T-12** film



Scheme 1 Synthetic procedure of **BT4T** and **BT4T-12**: (i) $Pd(PPh_3)_4$, Na_2CO_3 (aq, 2 M), Aliquat®, toluene, N_2, 80 °C, 72 h.

Korea Institute of Industrial Technology (KITECH), Cheonan, Chungnam 331-825, Republic of Korea. E-mail: ehlim@kitech.re.kr; Fax: (+82)-41-589-8580; Tel: (+82)-41-589-8467

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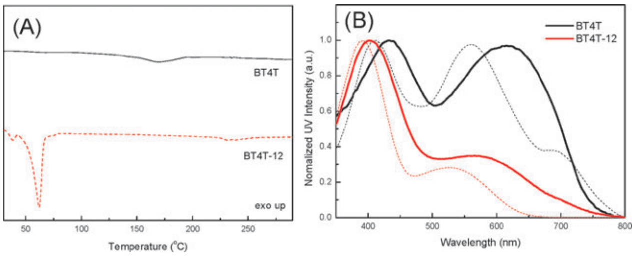

Fig. 1 DSC curves upon heating (A) and UV-vis absorption spectra of **BT4T**s in solution (dashed line) and film (solid line) (B).

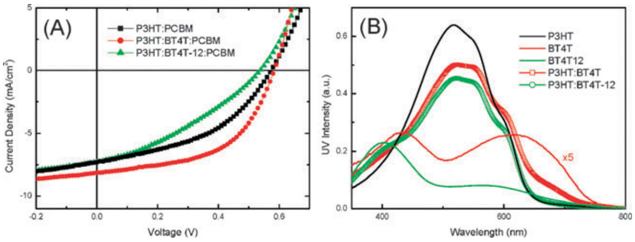

Fig. 2 *J*–*V* curves of OPVs (A) and UV-vis absorption spectra of P3HT:**BT4T** (or **BT4T-12**) blend films, together with the spectra of the pristine P3HT and **BT4T** films (B).

Table 1 Photovoltaic properties of OPV devices

	J_{SC}/mA cm^{-2}	V_{OC}/V	FF (%)	PCE (%)
BT4T:PCBM	3.14	0.64	0.30	0.61
BT4T-12:PCBM	2.02	0.51	0.30	0.31
P3HT:PCBM	7.28	0.57	0.44	1.83
P3HT:**BT4T**:PCBM	8.13	0.58	0.53	2.52
P3HT:**BT4T-12**:PCBM	7.27	0.54	0.34	1.33

may have been achieved by cooling after annealing at 120 °C, the temperature at which the device is annealed.

Fig. 1 shows the UV-visible absorption spectra of **BT4T**s; both showed two absorption bands (*e.g.*, λ_{max}(**BT4T-12**) = 392, 530 nm) which were assigned to the π–π* transition of the conjugated backbone and intramolecular charge transfer (ICT) interaction between the thiophene donor and the benzothiadiazole acceptor units, respectively.[9] The absorption spectrum of **BT4T** in chloroform was slightly red-shifted with respect to that of **BT4T-12**, showing three absorption bands at 410, 560 and 692 nm. In the film state, the absorption band at longer wavelengths was more intense, and the absorption spectra of the oligomer films showed very broad absorption bands that extended up to 800 nm (λ_{max}(**BT4T**) = 432, 616 nm and λ_{max}(**BT4T-12**) = 402, 575 nm), providing favorable light harvesting properties.[10] Therefore, the optical band gaps (E_g) of the **BT4T** and **BT4T-12**, estimated from the absorption onset wavelength (at 10% of the maximum absorption),[11] were as low as 1.67 and 1.77 eV, respectively. These low band gaps suggest that **BT4T**s may be candidate materials for use in OPVs. The electrochemical properties of the **BT4T**s were studied by cyclic voltammetry (CV). The films were prepared by dip-coating the oligomer solution onto Pt wire and the measurements were calibrated using ferrocene value of −4.8 eV as the standard. The anodic scan showed that the onset of oxidation for **BT4T** or **BT4T-12** occurred at 0.71 or 0.73 V (*vs.* SCE), respectively, which corresponded to the highest occupied molecular orbital (HOMO) levels −5.10 and −5.12 eV, according to the empirical relationship proposed by Leeuw *et al.* (I_p(HOMO) = (E_{onset} + 4.39) (eV), where E_{onset} is the onset potential of oxidation).[7] The lowest unoccupied molecular orbital (LUMO) levels of **BT4T** and **BT4T-12**, calculated from the HOMO levels and the optical band gaps, were −3.43 and −3.35 eV, respectively.

The OPVs were fabricated with the configuration ITO/PEDOT:PSS (40 nm)/polymer:PCBM (60 nm)/Al (100 nm). Fig. 2A shows the current–density *vs.* voltage (*J*–*V*) curves measured in air under white light AM 1.5 illumination (100 mW cm^{-2}), and the photovoltaic properties of the films are summarized in Table 1. In our system, the P3HT:PCBM (1 : 0.8, 3.6 wt%) control device showed a moderate performance of 1.83%. Despite their low band gap and broad UV absorption properties, **BT4T** (or **BT4T-12**):PCBM blend films (1 : 3, 2 wt%) showed relatively low photovoltaic efficiencies of 0.3–0.6%. Such low efficiencies probably arose from the poor quality and homogeneity of the films as a result of the poor solubility of the oligomers. According to the literature, similar copolymers based on benzothiadiazole and thiophene have shown OPV performances in the range 0.9–1.0%.[12] Therefore, the device efficiencies of the **BT4T**s may theoretically be improved by increasing molecular weights and/or optimizing the device fabrication conditions. However, more interesting results were obtained by blending these low band-gap oligomers with P3HT. Devices fabricated using P3HT:**BT4T**:PCBM (7 : 3 : 8, 3.6 wt%) blends showed considerably enhanced performance with a PCE of 2.52% compared to the P3HT:PCBM control device. Thus, the addition of **BT4T** increased the PCE from 1.83 to 2.52%, a ~38% improvement. The performance improvement from the P3HT:PCBM to the P3HT:BT4T:PCBM systems was mainly attributed to the increase in both J_{SC} (from 7.28 to 8.13 mA cm^{-2}) and the fill factor (FF, from 0.44 to 0.53). However, similar devices comprising P3HT:**BT4T-12**:PCBM showed a lower performance (1.33%) than P3HT:PCBM, mainly due to the decreased FF.

The improvement in OPV performance upon addition of **BT4T** can be explained in terms of the UV absorption and thin film morphological studies. Fig. 2B shows the UV-vis absorption spectrum of the P3HT:**BT4T** film together with the spectra of P3HT and **BT4T** films. For comparison, the polymer solutions (3.6 wt%) were spin-coated onto glass according to the OPV fabrication procedure (1500 rpm, 60 nm). The relatively low absorption intensity of the **BT4T** film itself reduced the absorption intensity of the P3HT:**BT4T** blend film relative to that of the P3HT film. However, the P3HT:**BT4T** film showed three vibronic absorption shoulders originating from P3HT that were more pronounced in the presence of **BT4T**, indicating a higher degree of ordering.[13] The absorption maximum of the P3HT:**BT4T** film (λ_{max} = 524 nm) was red-shifted relative to that of P3HT film (λ_{max} = 518 nm). The red shifts have been widely observed in more ordered films because high degrees of crystalline ordering usually entail longer conjugation lengths and, hence, the absorption spectra shift to lower energies.[14] Moreover, the additional shoulder at 680 nm, originating from the **BT4T**, may broaden the absorption spectrum of the P3HT:BT4T blend

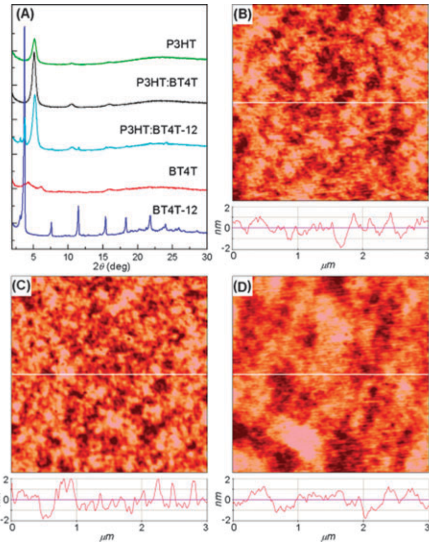

Fig. 3 XRD patterns (A) and AFM morphologies of annealed films of P3HT (B), P3HT:**BT4T** (C) or P3HT:**BT4T-12** (D).

film into the lower energy region. The absorption spectrum of P3HT was not improved by addition of **BT4T-12** to the P3HT:**BT4T-12** film, in agreement with the reduced OPV performance observed upon addition of **BT4T-12**. The thin film morphologies of the P3HT:**BT4T**s and pristine P3HT and **BT4T** films were characterized by XRD and AFM analyses. The AFM images were obtained by annealing the blend films on PEDOT-coated glass substrates for the purpose of preparing conditions identical to those used in devices. The extent of polymer aggregation increased upon addition of **BT4T**, as can be seen in the AFM image shown in Fig. 3. The P3HT:**BT4T**:PCBM films showed increased surface roughness (rms = 0.86 nm) compared to the P3HT:PCBM films (rms = 0.62 nm). The film roughness increased by ~40% upon addition of **BT4T**. A rough surface is the signature of polymer self-organization, which, in turn, indicates the formation of more extensively ordered structures in thin films. XRD analysis provided insight into the molecular arrangement of the blend films. The films were prepared on glass by spin-coating P3HT:**BT4T** and **BT4T** solutions followed by annealing at 120 °C for 30 min. As shown in Fig. 3A, the annealed P3HT film displayed characteristic peaks at $2\theta \approx 5.2$, 10.5 and 15.8°, assigned to (100), (200) and (300) reflections, respectively.[15] Compared to the broad diffraction peaks of **BT4T** at 3.8, 4.2 and 6.1°, **BT4T-12** showed a series of multiple reflections with a strong (100) reflection peak at 3.8°, indicative of d spacing of 23.7 Å. The long dodecyl group may enhance the intermolecular ordering of **BT4T-12**. The interchain distance of 23.7 Å was somewhat longer than the layer periodicities reported previously in PQT-12.[8] The strong (100) reflection of **BT4T-12** was also observed in the P3HT:**BT4T-12** blend film, although the characteristic peaks of **BT4T** were not observed in the P3HT:**BT4T** blend film, in which the intensity of P3HT peak is increased. In other words, the crystallinity of P3HT increased upon addition of **BT4T**, which, in turn, enhanced the values of J_{SC}, FF, and, ultimately, the PCE of the device. A similar effect was reported for P3HT:PCBM OPVs prepared with liquid crystal additives.[6] In contrast, crystalline **BT4T-12** in the P3HT:**BT4T-12** blend would be expected to decrease carrier transport at the grain boundaries and reduce the FF and device performance. Therefore, the thin film morphology in XRD and AFM studies as well as the UV-vis absorption spectra revealed that introduction of **BT4T** effectively enhanced device performance (*e.g.*, J_{SC} and FF) in P3HT:PCBM films by improving the crystallinity of P3HT. Introduction of an appropriate low band-gap material into conjugated polymers (*i.e.*, a ternary mixing system) can be a good strategy for enhancing the performance of conventional photovoltaic devices. Future work will include optimization of the device fabrication conditions, for example, the annealing temperature and the blend ratio, and introduction of this strategy into other photovoltaic polymer systems.

In summary, we have developed a new strategy for improving the device performances of polymer photovoltaic cells through the addition of a low band-gap material. The introduced low band-gap oligomer (**BT4T**) improved the molecular ordering of **P3HT** and the UV-vis absorption spectra of P3HT:PCBM blend films.

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