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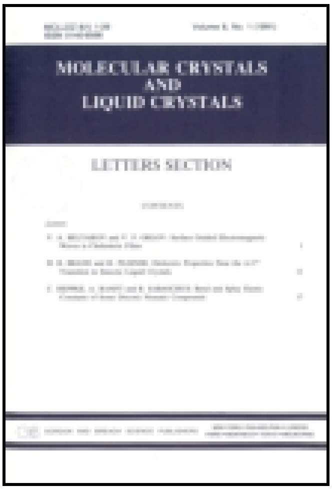

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# Ternary Solar Cells Based on the Benzo [1,2-*b*:4,5-*b*′]dithiophene-Containing Polymer and Small Molecule

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*Two benzo[1,2-b:4,5-b']dithiophene and thiophene-based materials, a small molecule (SM-BDT) and a polymer (P-BDT), were synthesized and their photovoltaic properties were investigated by fabricating their binary and ternary cells. The introduction of the ternary blend system effectively enhanced device performance. The power conversion efficiency (PCE) of the ternary SM-BDT:P-BDT:[6,6]-phenyl-C61-butyric acid methyl ester (PCBM) film (0.19%) was nearly double that of the pristine binary films of SM-BDT:PCBM and P-BDT:PCBM. The optical and electrochemical properties were investigated to explain the improved photovoltaic properties of the ternary blended cells.*

**Keywords** Organic photovoltaic cells; solar cells; benzodithiophene; ternary

## Introduction

The field of organic photovoltaic cells (OPVs) has progressed remarkably in terms of both device performance and overall understanding of the governing physical processes. Recently, there have been many reports on ternary organic photovoltaic cells in an attempt to improve device performance [1,2]. Hwang et al. reported that the power conversion efficiency (PCE) of poly(3-hexylthiophene) (P3HT):[6,6]-phenyl-$C^{61}$-butyric acid methylester (PCBM) could be improved by incorporating a dibenzo[*f,h*]thieno[3,4-b]quinoxaline-based dye (TQTFA) additive. In doing so, a PCE of 4.5% was achieved due to both the broader absorption profile and the energetic cascade between components [3]. More recently, the addition of a low band gap small molecule DPP-CN (10%) into the P3HT:PCBM system resulted in an improved PCE, going from 3.23% to 4.7% [4]. Our group also reported the improved photovoltaic performance of P3HT:PCBM cells by addition of a low band gap oligomer based on thiophene and benzothiadiazole due to improved UV-vis absorption and increased P3HT crystallinity [5]. In the present study, we introduced two benzo[1,2-*b*:4,5-*b*′]dithiophene (BDT)-thiophene–based materials into the ternary blended cells. Compared to the binary blend films, the ternary blend films can result not only in a broader absorption spectrum but also in a better energy-level offset between donor and acceptor.

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## Experimental

### *Measurements*

The molecular weight of polymer was measured by gel permeation chromatography (GPC). UV-vis spectra were obtained using a Shimadzu UV/vis. Spectrometer. The optical energy band gaps ($E_g$) were estimated from the absorption onset wavelengths of the UV-vis spectra ($E_g = 1240/\lambda_{onset}$ (eV)) of the films. The electrochemical properties of the materials were characterized by cyclic voltammetry (CV). The films were prepared by dip-coating the polymer solution onto Pt wire and the measurements were calibrated using the ferrocene value of −4.8 eV as the standard. The highest occupied molecular orbital (HOMO) levels of the materials were obtained 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) [6]. The lowest unoccupied molecular orbital (LUMO) levels were calculated from the HOMO and the optical band gap ($E_g$). Film thicknesses were measured using a TENCOR surface profiler.

### *Materials and Synthesis*

The syntheses of small-molecule–based BDT (SM-BDT) and poly(benzo[1,2-*b*:4,5-*b′*]dithiophene-alt-bithiophene) (P-BDT) were carried out using well-known palladium-catalyzed Suzuki and Stille coupling reactions, respectively. 2,6-Bis(trimethyltin)-4,8-didodecyloxybenzo[1,2-*b*;3,4-*b′*]dithiophene was prepared according to the literature [7,8]. 2,2-Bithiophene-5-boronic acid pinacol ester and 5,5′-bis(tributylstannyl)-2,2′-bithiophene were purchased from Aldrich. All reagents purchased commercially were used without further purification, except for the toluene used as a solvent, which was distilled.

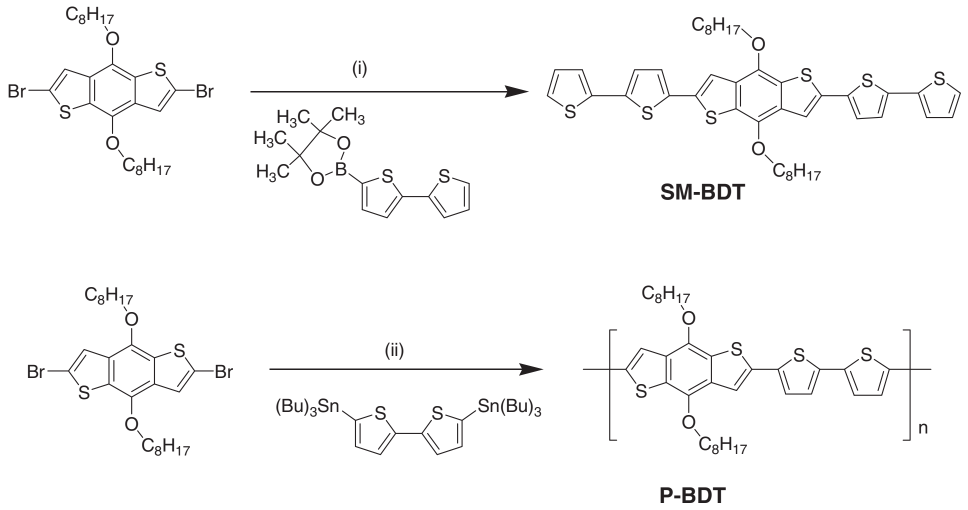
### *Device Fabrication*

The OPVs were fabricated with the configuration ITO/PEDOT:PSS (40 nm)/active layer/Al (100 nm). The PEDOT:PSS layer was spin-coated on the cleaned ITO-coated glass substrate (3000 rpm, 30 s) and annealed at 120°C for 20 min. The active layer consisting of donor and acceptor was spin-coated from a 1,2-dichlorobenzene solution. The devices were completed by evaporating Al metal electrode. The area of the device was 4 mm$^2$. The current–voltage (*J–V*) characteristics were measured with a Keithley 2400 source-measure unit under white light illumination of AM 1.5 (100 mW/cm$^2$).

## Results and Discussion

### *Synthesis and Characterization*

Two BDT-thiophene–based materials (SM-BDT and P-BDT) were synthesized for use as donors in OPVs; they were synthesized by the Suzuki and Stille coupling reactions, respectively. The two materials were designed to have the same backbones of BDT and thiophene, which could make them well mixed for the ternary blended system having two donors in OPVs. The weight-average ($M_w$) and number-average ($M_n$) molecular weights of P-BDT were 10,045 and 3,700, respectively. The synthetic schemes to produce SM-BDT and P-BDT are shown in Scheme 1.



**Scheme 1.** Synthetic schemes toward SM-BDT and P-BDT: (i) $Pd(PPh_3)_4$, toluene, Aliquat, $Na_2CO_3$(aq), 80 °C, 72 hour, $N_2$. (ii) $Pd(PPh_3)_4$, toluene, 80 °C, overnight, $N_2$.

The optical and electrochemical properties of SM-BDT and P-BDT were studied. The SM-BDT and P-BDT films showed UV-visible absorption maxima at around 400 and 445 nm, respectively [8]. On adding P-BDT into SM-BDT:PCBM, the UV absorption of the ternary (i.e., SM-BDT:P-BDT:PCBM) film was slightly red-shifted than that of the binary SM-BDT:PCBM film. Moreover, the PL emission quenching was more enhanced in the ternary SM-BDT:P-BDT:PCBM film compared to the binary SM-BDT:PCBM film. In other words, the charge transfer from donor to acceptor is more effective in the ternary system, obtained by addition of the third component, P-BDT, into the binary SM-BDT:PCBM system.

The $E_g$ of SM-BDT and P-BDT were 2.39 and 1.97 eV, respectively. P-BDT has a longer conjugation length compared to SM-BDT and showed a lower band gap. The electrochemical properties of the materials were also studied by CV. The HOMO/LUMO levels of SM-BDT and P-BDT were −5.30/−2.91 and −5.06/−3.09 eV, respectively and these can be seen in Figure 1.

## *Organic Photovoltaic Properties*

The OPVs were fabricated with the configuration ITO/PEDOT:PSS/active layer/Al. Figure 2 shows the current–density versus voltage (J–V) curves for photovoltaic devices

**Table 1.** The optimized device performance of OPV cells

| | ratio | thickness (nm) | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (V) | FF (%) | PCE (%) |
|---|---|---|---|---|---|---|
| SM-BDT:PCBM | 1:1 | 90 | 0.73 | 0.47 | 0.27 | 0.09 |
| P-BDT:PCBM | 1:3 | 40 | 0.68 | 0.50 | 0.28 | 0.10 |
| SM-BDT:P-BDT:PCBM | 2:1:2 | 60 | 1.23 | 0.59 | 0.26 | 0.19 |

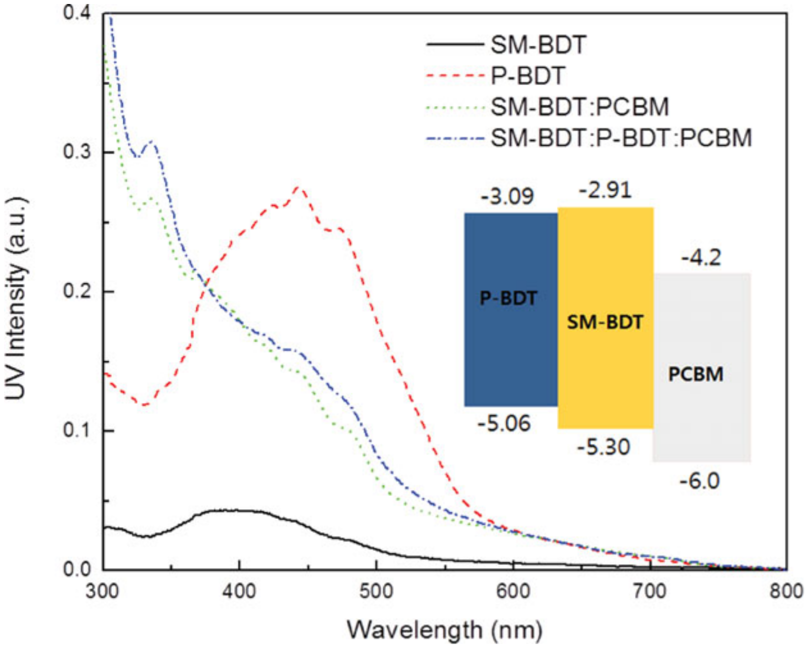


**Figure 1.** UV absorption spectra of the materials (Inset: HOMO and LUMO energy levels of the SM-BDT and P-BDT with PCBM).

measured in air under white light AM 1.5 illumination (100 mW/cm$^2$), and the photovoltaic properties of the blend films are summarized in Table 1. Three types of devices were fabricated: two binary cells of SM-BDT:PCBM and P-BDT:PCBM and a ternary cell of SM-BDT:P-BDT:PCBM. The highest PCE was achieved in the ternary blended cells. Devices fabricated using a 2:1:2 SM-BDT:P-BDT:PCBM blend showed an enhanced performance with a PCE of 0.19% compared to its parent binary devices, SM-BDT:PCBM

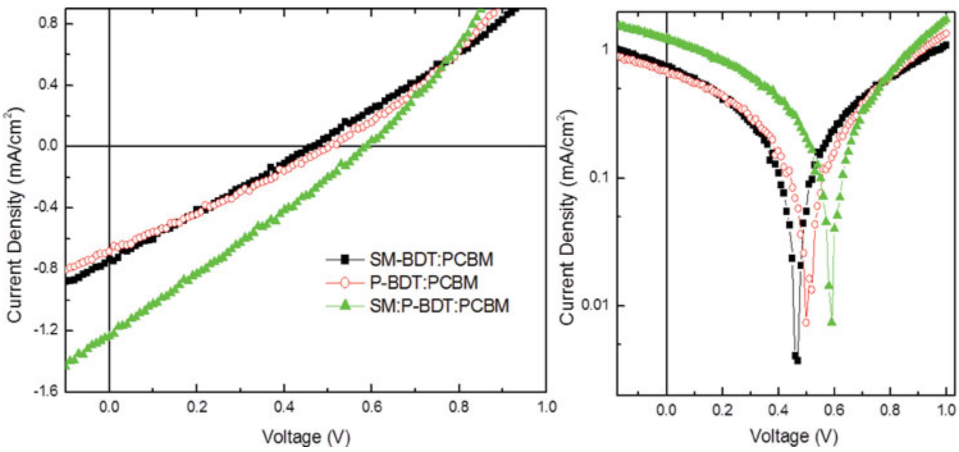


**Figure 2.** *J–V* curves of SM-BDT:PCBM, P-BDT:PCBM, and SM-BDT:P-BDT:PCBM blend films (left) and semilogarithmic plot of *J–V* curves (right).

(0.09%) and P-BDT:PCBM (0.1%). The PCE was nearly doubled by the addition of the third component to the binary films. The improvement was attributed to the increase in both the short-circuit current ($J_{SC}$) and the open-circuit voltage ($V_{OC}$), which can be explained in terms of the UV absorption and the well-matched cascade energy levels. As mentioned above, the absorption of the ternary SM-BDT:P-BDT:PCBM blend film is slightly red-shifted compared to that of the binary film of SM-BDT:PCBM. The additional shoulder at 450 nm, originating from P-BDT, broadens the absorption spectrum of the ternary film. Moreover, the well-matched energy levels between components also play an important role in improving the device performance of the ternary cells. The favorable energy cascade of the HOMO and LUMO energy levels between components resulted in an increased $J_{SC}$ through more effective charge separation at the donor/acceptor interfaces [1,3]. The $V_{OC}$ of the ternary cells is also higher than those of the binary cells. There have been many reports on the tunable $V_{OC}$ of ternary blend photovoltaic cells, in which the $V_{OC}$ value of OPVs could be varied by various parameters, such as the composition of the active layer and the energy-level offset between donor and acceptor [2,9]. Further improvements in photovoltaic characteristics could be achieved by optimizing the fabrication conditions.

## Conclusion

In this paper, we have introduced a ternary blended system for OPV applications. The enhanced photovoltaic properties of ternary cells could be explained by improved UV-visible absorption and the well-matched cascade energy levels between the three components.

## Funding

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