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# Highly crystalline new benzodithiophene-benzothiadiazole copolymer for efficient ternary polymer solar cells with energy conversion efficiency over 10%

Vellaiappillai Tamilavan,<sup>a,†</sup> Yanliang Liu,<sup>a,†</sup> Jihoon Lee,<sup>a</sup> Yun Kyung Jung,<sup>b</sup> Semo Son<sup>c</sup>, Junghyun Jeong,<sup>a</sup> and Sung Heum Park<sup>\*a</sup>

A new alternating polymer P(BDTSi-DFBT), poly(4,8-bis(triisopropylsilylethynyl)-benzo[1,2-b:4,5-b']dithiophene-*alt*-5,6difluoro-4,7-bis(4-octylthiophen-2-yl)benzo[c][1,2,5]thiadiazole), was prepared via Stille polymerization. The determined absorption maximum and optical band-gap ( $E_g$ ) of P(BDTSi-DFBT) were 590 nm and 1.74 eV, respectively. The calculated highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of P(BDTSi-DFBT) were –5.45 eV and –3.71 eV, respectively. The X-ray diffraction (XRD) analysis confirmed that P(BDTSi-DFBT) is a crystalline polymer. The binary-polymer solar cells, ITO/PEDOT:PSS/P(BDTSi-DFBT):PC7<sub>0</sub>BM (1:1.5 wt%)+3 vol% DIO/Al, made from P(BDTSi-DFBT) gave a power conversion efficiency (*PCE*) of 5.02% with a open-circuit voltage ( $V_{oc}$ ) of 0.81 V, a short-circuit current ( $J_{sc}$ ) of 11.68 mA/cm<sup>2</sup>, and a fill factor (*FF*) of 53%. Conversely, the ternary-polymer solar cells, ITO/PEDOT:PSS/PTB7-Th:P(BDTSi-DFBT):PC7<sub>0</sub>BM (0.8:0.2:1.5 wt%)+3 vol% DIO/Al, made with synthesized medium bandgap P(BDTSi-DFBT) and low band-gap PTB7-Th, offered a maximum *PCE* of 10.05%, with a  $V_{oc}$  of 0.79 V, a  $J_{sc}$  of 17.92 mA/cm<sup>2</sup>, and a *FF* of 71%.

#### 1. Introduction

Organic solar cells (OSCs), fabricated via solution-processed printing techniques using a blend of electron-donating polymers and electron-accepting fullerene derivatives or  $\pi$ conjugated organic small molecules, have attracted great interest as promising low-cost, lightweight, and large-area devices on flexible substrates for solar-to-electrical energy conversion.<sup>1-23</sup> The conventional binary-polymer solar cells (PSCs) made from polymer and [6,6]-phenyl C<sub>71</sub> butyric acid methyl ester (PC<sub>70</sub>BM) offered a maximum power conversion efficiency (PCE) of ~11%.1-9 On the other hand, ternary-PSCs, made from wide- or medium band-gap polymer 1, a low bandgap polymer 2, and PC<sub>70</sub>BM, gave an improved PCE of ~12%.<sup>10-</sup> <sup>18</sup> Recently, OSCs made by using a blend of polymer and  $\pi$ conjugated organic small molecules have also displayed an impressive PCE over ~13%.19-23 It is well documented that the properties of the  $\pi$ -conjugated material used on the photoactive layer of the solar cell devices (PSCs and OSCs) are crucial determining factors of the device performance.1-23 Therefore, a new efficient  $\pi$ -conjugated material, such as

#### electron-donating polymers and electron-accepting organic small molecules, is required to further enhance the performance of PSCs and OSCs devices. We have been interested in preparing a new polymeric donor material, because an efficient polymeric material is required for all three types of solar cells mentioned above.

The literature suggests that the electron-deficient benzo[c][1,2,5]thiadiazole (BT)<sup>24,25</sup> derivatives are promising building blocks to prepare efficient polymeric donor materials for solar cell applications. The broad absorption in the entire visible part of the solar spectrum and the relatively high PCE achieved for BT-based polymers have pushed researchers to tune the photo-physical properties of BT-based polymers via side or main chain engineering. Consequently, various electron donor and acceptor units were inserted into the BT backbone.<sup>26-41</sup> Interestingly, the substituents on the 5 and 6<sup>th</sup> positions of BT and the 4<sup>th</sup> position of the thiophene attached with BT greatly alter the properties and photovoltaic performance of resulting BT-based polymers.<sup>24-41</sup> Among them, the fluoro substituent is found to be the best choice for the 5 and 6<sup>th</sup> positions of BT and alkyl groups are more suitable for the 4<sup>th</sup> position of the thiophene attached with BT to obtain high energy converting BT-based polymers.<sup>42-51</sup> Consequently, 5,6-difluoro-4,7-bis(4-octylthiophen-2we chose yl)benzo[c][1,2,5]thiadiazole (DFBT) as an electron accepting unit to prepare new donor-acceptor (D-A) polymers for PSCs. Several studies have shown that DFBT-based polymers offer a maximum PCE over 10% in binary-PSCs.42-51 Fig. 1a shows the

<sup>&</sup>lt;sup>a</sup> Department of Physics, Pukyong National University, Busan 608-737, Republic of Korea. Fax: 82-51-629-5549; Tel: 82-51-629-5774; \*E-mail: spark@pknu.ac.kr

<sup>&</sup>lt;sup>b.</sup> School of Biomedical Engineering, Inje University, Gimhae 50834, Republic of Korea.

<sup>&</sup>lt;sup>c.</sup> Department of Graphic Arts Information Engineering, Pukyong National University, Busan 608-737, South Korea

<sup>+</sup> These two authors contributed equally to this work.

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different positions of the BT derivatives for an easy and clear understanding.

On the other hand, the rigid and planar structured benzo[1,2-b:4,5-b']dithiophene (BDT) is an efficient electron rich unit used to prepare high energy converting D-A polymers.<sup>52-54</sup> Many D–A polymers incorporating BDT and DFBT units have been reported for PSCs.<sup>16,17,44-46</sup> These careful studies suggest that the substituents on the  $4^{\text{th}}$  -and  $8^{\text{th}}$ position of the BDT unit significantly affect the properties of the resulting polymers.<sup>24,25,52-54</sup> The 4- and 8-positions of the BDT unit are also shown in Fig. 1a. For example, the 4,8alkoxy-substituted BDT unit offered a relatively low band-gap and highly crystalline polymer when it was copolymerized with the DFBT derivative compared to that of the 4,8-thienylsubstituted BDT unit. As a result, a large difference was observed in their photovoltaic performances.<sup>51</sup> The chemical structure of the respective DFBT-based polymers P(BDT-DFBT) and P(BDTT-DFBT) are shown in Fig. 1b.



Fig. 1. (a) The different positions of BT and BDT units for substitution. (b) The chemical structure of the DFBT-based polymers P(BDT-DFBT) and P(BDTT-DFBT).

It is widely known that the bulky triisopropylsilylethynyl (TIPS) on acene derivatives improves the solubility, oxidative stability, and crystallinity of  $\pi$ -conjugated materials, as well as the  $\pi$ -orbital overlap between  $\pi$ -conjugated molecules.<sup>55,56</sup> Consequently, the 4,8-triisopropylsilylethynyl-substituted BDT (BDTSi) derivative was copolymerized with a variety of electron-deficient units, such as benzo[c][1,2,5]oxadiazole (BO),<sup>57</sup> diketopyrrolo[3,4-c]pyrrole (DPP),<sup>58</sup> quinoxaline (QX),<sup>59</sup> benzo[d][1,2,3]triazole (BTz),<sup>60</sup> thieno[3,4-b]thiophene (TT),<sup>61</sup> and thiazolo[5,4-d]thiazole (TTz)<sup>62</sup> derivatives and explored in PSCs. However, the combination of BDTSi and DFBT has not yet been studied, though DFBT is a more promising acceptor unit than the above-mentioned acceptor units. Here, we report the synthesis, optical, electrochemical, and photovoltaic

properties of the new polymer, P(BDTSi-DFBT), excentaining BDTSi and DFBT. DOI: 10.1039/C8TC00817E

#### 2. Experimental section

#### 2.1 Materials and measurements.

We obtained the required chemicals and reagents from Sigma-Aldrich. A Varian Mercury Plus spectrometer (300 MHz) was used for nuclear magnetic resonance (NMR) analysis. Gel permeation chromatography (GPC) was performed on the Agilent 1200 Infinity Series separation module. The JASCO V-570 spectrophotometer and a CH Instruments Electrochemical Analyzer were used to obtain the absorption spectrum and cyclic voltammogram (CV) of the polymer. The X-ray diffraction (XRD) and small-angle X-ray scattering (SAXS) analysis were performed on the XPert-MPD (Philips, Netherland) with sealed proportional counter and X'celerator PSD for high speed data collection detector. The XRD and SAXS instruments were calibrated using standard silicon crystal. The incident photon to current efficiency (IPCE) was measured as a function of the wavelength in the wavelength range 300 to 1000 nm using a xenon lamp as the light source, and the calibration was performed by using a silicon reference cell. Atomic force microscopy (AFM) and transmission electron microscopy (TEM) were performed using Seiko instruments SPI 3800N-SPA 400 and Hitachi H-7500, respectively.

#### 2.2. PSC device fabrication and characterization.

The PSCs were fabricated with a device structure of ITO-coated glass substrate/PEDOT:PSS/P(BDTSi-DFBT):PC70BM/Al. The precleaned ITO-coated glass substrate was dried overnight in an oven. A 40-nm thick layer of PEDOT:PSS (Baytron PH) was spincasted from an aqueous solution on to an ITO-coated glass substrate. The substrate was dried for 10 min at 140°C in air and then transferred to a glove box to spin-cast the photoactive layer. A solution containing a mixture of P(BDTSi-DFBT):PC70BM (1:1.5 wt%) in chlorobenzene (CB):1,8diiodooctane (DIO) at a volumetric ratio of 97:3 (CB :DIO) was then spin-casted on top of the PEDOT/PSS layer. The film was then dried for 30 min at RT in a glove box. Subsequently, an aluminum (Al, 100 nm) electrode was deposited by thermal evaporation in a vacuum of approximately  $3 \times 10^{-6}$  Torr. The current density-voltage (J-V) characteristics of the PSC devices were measured using a Keithley 2400 Source Measure Unit. The solar cell performance was determined using an Air Mass 1.5 Global (AM 1.5 G) using a Peccell (PEC-L01) solar simulator with an irradiation intensity of 1000 Wm<sup>-2</sup>. The spectral mismatch factor was calculated by comparing the solar simulator spectrum with the AM 1.5 spectrum at RT.

#### 2.3. Synthesis of P(BDTSi-DFBT) [polymer poly(4,8bis(triisopropylsilylethynyl)-benzo[1,2-b:4,5-b']dithiophene-alt-5,6-difluoro-4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole)]

A solution of BDTSi  $^{59}$  (0.26 g, 0.30 mmol) and DFBT $^{63}$  (0.22 g, 0.30 mmol) in chlorobenzene (15 mL) was purged well with argon for 20 min. Pd\_2(dba)\_3 (7 mg) and P(o-tol)\_3 (15 mg) were

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then added in one portion. The entire mixture was stirred and refluxed for 18 h under argon atmosphere. Subsequently, the reaction mixture was cooled to RT and then added dropwise into vigorously stirred methanol (200 mL). The precipitates were recovered by filtration, and the crude polymer was extracted with methanol and acetone for 24 h in a Soxhlet apparatus. The pure polymer P(BDTSi-DFBT) was obtained as a deep blue solid. Yield (0.30 g, 91%). Anal. Calc. for  $C_{62}H_{82}F_2N_2S_5Si_2$ : C, 67.10; H, 7.45; N, 2.52; S, 14.45. Found: C, 66.21; H, 6.87; N, 2.12; S, 13.93.

#### 3. Results and discussions

#### 3.1 Synthesis and characterization

The monomers, 2,6-bis(trimethyltin)-4,8bis(triisopropylsilylethynyl)-benzo[1,2-b:4,5-b']dithiophene (BDTSi)59 and 4,7-bis(5-bromo-4-octylthiophen-2-yl)-5,6difluorobenzo[c][1,2,5]thiadiazole (DFBT),63 were prepared as shown in Scheme 1. The Stille copolymerization between BDTSi and DFBT using the procedure described in the experimental section resulted in the new polymer P(BDTSi-DFBT). The synthetic route for the synthesis of P(BDTSi-DFBT) is outlined in Scheme 1. Polymer P(BDTSi-DFBT) exhibited excellent solubility in most common chlorinated organic solvents like chloroform (CF), chlorobenzene (CB), and dichlorobenzene (DCB). The determined weight average molecular weight  $(M_w)$ , number average molecular weight ( $M_n$ ), and polydispersity for P(BDTSi-DFBT) were 4.30 x 10<sup>4</sup> g/mol,  $2.22 \times 10^4$  g/mol and 1.93, respectively.

#### 3.2 Opto-electrical properties





Scheme 1. Synthetic route for P(BDTSi-DFBT).

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XRD spectrum for P(BDTSi-DFBT) exhibited several peaks at  $2\theta \approx 14.18^{\circ}$ , 18.02°, 24.17° and 39.14°, as well as in the SAXS spectrum at  $2\theta \approx 3.75^{\circ}$  and  $5.45^{\circ}$ . The presence of these peaks confirm that P(BDTSi-DFBT) is a crystalline polymer. It is worth noting that the DFBT-based polymers, P(BDT-DFBT) and P(BDTT-DFBT), incorporating alkoxy- or thienyl-substituted BDT units, showed only two peaks at  $2\theta \approx 4^{\circ}$  and  $24^{\circ}$  in their XRD spectrum; on the other hand, P(BDTSi-DFBT) displayed several peaks. These results proved that triisopropylsilylethynyl substituents significantly alter the crystallinity of the resulting polymer compared to that of the frequently used alkoxy and thienyl substituents.<sup>51</sup> The calculated in-plane spacing between polymer backbones (d<sub>1</sub> and d<sub>2</sub>-spacings) of P(BDTSi-DFBT) are 23.54 Å and 16.20 Å. In contrast, the estimated p-stacking distance, d<sub>3</sub>-d<sub>6</sub>-spacings, for P(BDTSi-DFBT) are 6.24 Å, 4.92 Å, 3.68 Å and 2.30 Å.

#### 3.4 Binary-polymer solar cell properties

Fig. 4. shows the PSC device structure (a), the energy level diagram (b), the current-voltage (J-V) curves (c) and the incident photon to the current efficiency (IPCE) spectra (d) of the PSCs prepared by using a P(BDTSi-DFBT):PC70BM (1:1.5 wt%) blend. The device made with 3 vol% DIO displayed an improved power conversion efficiency (PCE) of 5.02% with an open-circuit voltage ( $V_{oc}$ ) of 0.81 V, a short-circuit current ( $J_{sc}$ ) of 11.68 mA/cm<sup>2</sup>, and a fill factor (FF) of 53% compared to that of the device made without additives (PCE  $\approx$  1.01%, V<sub>oc</sub>  $\approx$  0.68 V,  $J_{sc} \approx 4.58 \text{ mA/cm}^2$ , and  $FF \approx 32\%$ ). As seen in Fig. 4d, both devices made with and without 3 vol% DIO showed quite broad IPCE response from 300 nm to 720 nm. However, the maximum IPCE values significantly increased when the device was processed with DIO. The IPCE responses for the device made without any additives were over 20% in the range of 350-620 nm, with a maximum IPCE of 27% at 410 nm. While the device made with 3 vol% DIO showed an increased IPCE maximum of 67% at 410 nm, with responses found to be over 50% in the range of 360-650 nm.

The dissimilar performances of the PSC devices are attributed to the difference in the surface morphology of their photoactive layers. The atomic force microscopy (AFM) and transmission electron microscopy (TEM) images of the films processed using the P(BDTSi-DFBT):PC70BM (1:1.5 wt%) blend with and without 3 vol% DIO are shown in Fig. 5. The films processed without additives showed a uniform size of cluster formation between polymer and PC70BM. However, the cluster formation was significantly decreased with the use of 3 vol% DIO. The root mean square (RMS) values of the films made with and without 3 vol% DIO were found to be quite similar. The 3D topology images reveal that the grain size notably altered when the film was processed under different conditions, such as with and without 3 vol% DIO. Overall, the film processed with DIO shows better morphology for efficient carrier transport than the film processed without DIO. We think that the high crystalline nature of P(BDTSi-DFBT) could be a possible reason for the high roughness obtained. The TEM



**Fig. 2.** (a) Absorption spectra of P(BDTSi-DFBT) in CB and as thin film on glass. (b) The cyclic voltammogram of P(BDTSi-DFBT).



#### 3.3 X-ray diffraction analysis

The powder X-ray diffraction (XRD) and small-angle X-ray scattering (SAXS) analyses were performed with P(BDTSi-DFBT) to study the nature of P(BDTSi-DFBT). The XRD and SAXS spectra of P(BDTSi-DFBT) are shown in Fig. 3. Interestingly, the

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# images presented in Fig. 5 firmly support our argument. The dark color observed on the TEM image arises from $PC_{70}BM$ and white color is related to P(BDTSi-DFBT). In this instance, the $PC_{70}BM$ aggregation was clearly observed for the film made without DIO and a much-improved nanoscale network between P(BDTSi-DFBT) and $PC_{70}BM$ was observed for the film made with 3 vol% DIO.

The overall *PCE* for P(BDTSi-DFBT) is comparable with that of P(BDTT-DFBT) but lower than that of P(BDT-DFBT).<sup>51</sup> The maximum *PCE* reported for P(BDTT-DFBT) and P(BDT-DFBT) was 4.46% ( $V_{oc} \approx 0.68$  V,  $J_{sc} \approx 11.87$  mA/cm<sup>2</sup>, and *FF*  $\approx 55\%$ ) and 8.30% ( $V_{oc} \approx 0.78$  V,  $J_{sc} \approx 15.38$  mA/cm<sup>2</sup>, and *FF*  $\approx 69\%$ ), respectively.<sup>51</sup> The P(BDTSi-DFBT)-based device showed reasonable  $V_{oc}$  values compared to P(BDT-DFBT)-value P(BDTTFE DFBT)-based devices. However, the low PPJ\_state of the P(BDTSi-DFBT)-based device resulted in a performance within 5.1%. The device made with a lower concentration of P(BDTSi-DFBT) gave relatively higher *FF* ( $\approx$  58%) but the J<sub>sc</sub> value was significantly lower ( $\sim$  8.50 mA/cm<sup>2</sup>) and consequently, there was no improvement on the *PCE*. We think that the blue-shifted absorption and the relatively high RMS value might be the reasons for the moderate performance of P(BDTSi-DFBT). Nevertheless, the photovoltaic parameters obtained for P(BDTSi-DFBT) are quite similar to those of the DFBT-based polymers incorporating 2D  $\pi$ conjugated BDT units.<sup>24,25</sup>



Fig. 4. The PSC device structure used in this study (a), the energy level diagram for the materials used for PSC fabrication (b), the J-V curves (c) and IPCE spectra (d) of the binary-PSCs prepared using the P(BDTSi-DFBT):PC70BM (1:1.5 wt%) blend without and with 3 vol% DIO.



Fig. 5. Topology AFM and TEM images of the films made from P(BDTSi-DFBT):PC<sub>70</sub>BM (1:1.5 wt%) blend without and with 3 vol% DIO.

#### 3.5 Ternary-polymer solar cell properties

The high crystallinity of P(BDTSi-DFBT) allows its application as co-absorber along with low band-gap PTB7-Th in ternary-PSCs. A recent study suggests that the addition of the highly crystalline  $\pi$ -conjugated small molecule p-DTS(FBTTH<sub>2</sub>)<sub>2</sub> on the PTB7-Th:PC<sub>70</sub>BM blend resulted in a improvement of absorption, crystallinity and the face-on orientation of the ternary blend. Consequently, the J<sub>sc</sub> and FF of ternary-PSCs are considerably enhanced, and the overall performance of ternary-PSCs greatly increased compared to binary-PSCs made

from p-DTS(FBTTH<sub>2</sub>)<sub>2</sub>:PC<sub>70</sub>BM and PTB7-Th:PC<sub>70</sub>BM blends.<sup>64</sup> In this instance, the use of crystalline P(BDTSi-DFBT) along with the PTB7-Th:PC<sub>70</sub>BM blends is also expected to improve the *PCE* of binary-PSCs prepared from the PTB7-Th:PC<sub>70</sub>BM blend. The chemical structure (a), the energy level diagram for the materials used for ternary PSC fabrication (b), and normalized absorption spectra of P(BDTSi-DFBT) and PTB7-Th (c), the *J-V* curves (d) and *IPCE* spectra (e) of the ternary PSCs prepared using PTB7-Th:P(BDTSi-DFBT):PC<sub>70</sub>BM (at various ratio) + 3 vol% DIO blends are shown in Fig. 6.

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**Fig. 6.** The chemical structure of polymers used for ternary PSCs (a), the energy level diagram for the materials used for ternary-PSC fabrication (b), and the normalized absorption spectra of the polymers P(BDTSi-DFBT) and PTB7-Th (c), the *J-V* curves (d) and *IPCE* spectra (e) of the ternary-PSCs prepared using PTB7-Th:P(BDTSi-DFBT):PC<sub>70</sub>BM (at various ratio) + 3 vol% DIO blends.

Table 1. Photovoltaic properties of PSCs made with the device structure of ITO/PEDOT:PSS/PTB7-Th:P(BDTSi-DFBT):PC70BM (at different ratio) + 3 vol% DI	O/Al.
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Ternary blend ratio	J <sub>sc</sub> (mA/cm²)ª / (Ave. Value) <sup>f</sup>	[cal] J <sub>sc</sub> (mA/cm <sup>2</sup> ) <sup>b</sup>	V <sub>oc</sub> (V) <sup>c</sup> / (Ave. Value) <sup>f</sup>	FF (%) <sup>d</sup> / (Ave. Value) <sup>f</sup>	PCE (%) <sup>e</sup> / (Ave. Value) <sup>f</sup>
1.0 : 0.0 : 1.5	16.43 (16.30±0.21)	16.09	0.76 (0.75±0.01)	68 (67±1)	8.49 (8.22±0.27)
0.9:0.1:1.5	17.16 (16.95±0.25)	16.89	0.77 (0.76±0.01)	69 (68±1)	9.12 (8.83±0.29)
0.8 : 0.2 : 1.5	17.92 (17.71±0.32)	17.40	0.79 (0.78±0.01)	71 (70±2)	10.05 (9.70±0.35)
0.7:0.3:1.5	16.54 (16.10±0.46)	15.96	0.79 (0.78±0.01)	67 (65±2)	8.75 (8.30±0.45)
0.6:0.4:1.5	15.69 (15.20±0.53)	15.10	0.80 (0.79±0.01)	63 (60±3)	7.91 (7.32±0.59)
0.0:1.0:1.5	11.68 (10.85±0.91)	11.40	0.81 (0.80±0.01)	53 (50±3)	5.02 (4.60±0.42)
<sup>a</sup> Short-circuit current de obtained from 15 devices	nsity. <sup>b</sup> Calculated Short-circuit	current density from IPCE.	<sup>c</sup> Open-circuit voltage. <sup>d</sup> Fill	factor. <sup>e</sup> Power conversion	efficiency. <sup>f</sup> Average values

As indicated in Fig. 6c, the polymers P(BDTSi-DFBT) and PTB7-Th showed better complementary absorption between 300 and 800 nm. In addition, the HOMO levels of P(BDTSi-DFBT) and PTB7-Th (see Fig. 6b) are found to be similar and therefore expected to have better charge transport on the ternary systems. A recent study indicated that the matched HOMO levels of the two donor polymers are favorable to get high FF, via the improved carrier mobility, and PCE for ternary-PSCs.65 Consequently, combined effects such as improved absorption via complementary absorption, and high carrier mobility via the improved crystallinity, are expected for the ternary-PSCs made from the PTB7-Th:P(BDTSi-DFBT):PC70BM blend. The photovoltaic parameters obtained for the ternary-PSCs are summarized in Table 1. The ternary-PSC made with 0.8:0.2:1.5 wt% blend offered a maximum PCE of 10.05% with a  $V_{oc}$  of 0.79 V, a  $J_{sc}$  of 17.92 mA/cm<sup>2</sup>, and a FF of 71%. The overall PCE of ternary-PSCs is 20% higher than that of the binary-PSCs (PCE  $\approx 8.49\%,$  V<sub>oc</sub>  $\approx 0.76$  V, J<sub>sc</sub>  $\approx 16.43$  mA/cm², and  $FF \approx 68\%$ ) made from PTB7-Th:PC<sub>70</sub>BM (1:1.5 wt%) + 3 vol% DIO blend. Interestingly, all three parameters such as  $V_{oc}$ ,  $J_{sc}$ , and FF notably improved when P(BDTSi-DFBT) is added to the PTB7-Th:PC<sub>70</sub>BM blend.

XRD and SAXS analysis were performed for the polymer films prepared using a chloroform (5mg/0.5 mL) solution containing PTB7-Th, PTB7-Th:P(BDTSi-DFBT) (0.8:0.2 wt%) and P(BDTSi-DFBT) with the aim of studying the variation on the crystallinity of ternary blend film compared to their corresponding binary blend films. The corresponding XRD and SAXS (insert) spectra are shown in Fig. 7. The comparison suggests that P(BDTSi-DFBT) is highly crystalline compared to PTB7-Th. It is very clear that the intensities of the peaks (at  $2\theta \approx 24^\circ$ ,  $18^\circ$  and  $14^\circ$ ) are considerably increased for the film made using the PTB7-Th:P(BDTSi-DFBT) blend compared to the film made only from PTB7-Th. Also, a sharp characteristic peak at  $2\theta \approx 18^{\circ}$ , which comes from P(BDTSi-DFBT), is observed for the film made from the PTB7-Th:P(BDTSi-DFBT) blend. The SAXS spectra for the polymer films also exhibit a similar trend. High-intensity peaks for the film made from the PTB7-Th:P(BDTSi-DFBT) blend compared to the film made using only PTB7-Th were observed with XRD. Overall, the crystallinity of PTB7-Th is found to be notably improved with the addition of P(BDTSi-DFBT), which is expected to be favorable to acquire better photovoltaic performances.

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#### 16000 PTB7-Th PTB7-Th:P(BDTSi-DFBT) (0.8:0.2 wt%) 14000 P(BDTSi-DFBT) ntensity (a.u.) 12000 10000 8000 4 5 6 7 2θ (degree) 6000 4000 30 10 20 40 50 2θ (degree)

Fig. 7. Thin film XRD and SAXS spectra of PTB7-Th, PTB7-Th:P(BDTSi-DFBT) (0.8:0.2 wt%) and P(BDTSi-DFBT).

To get insight into the morphological modifications for films processed from ternary blends compared to that of the films made form binary blends, we examined the surface morphology of the films made from PTB7-Th:PC70BM (1:1.5 wt%) + 3 vol% DIO and PTB7-Th:P(BDTSi-DFBT):PC70BM

(08:0.2:1.5 wt%) + 3 vol% DIO blends using AFM and TEM The corresponding AFM and TEM images of these of these of these of these of the second sec in Fig. 8. The AFM images suggest that the morphology of the films processed with binary and ternary blends are very similar. No notable changes are observed on the AFM images. However, the surface roughness of the film processed with the ternary blend is slightly higher than that of the film prepared using a binary blend. Sometimes, higher roughness is favorable to get a better charge collection via an improved contact between the active layer and electrode.<sup>66,67</sup> According to the TEM images shown in Fig. 8, the nanoscale network between the ternary blend (PTB7-Th:P(BDTSi-DFBT):PC<sub>70</sub>BM) is found to be better than the network between their corresponding binary blend (PTB7-Th:PC<sub>70</sub>BM). As seen in the figure, the dark areas, which refer to PC70BM are somewhat visible for the film made using the PTB7-Th:PC70BM (1:1.5 wt%) + 3 vol% DIO blend, but the visibility of the dark areas are much lower for the film made from PTB7-Th:P(BDTSi-DFBT):PC70BM (08:0.2:1.5 wt%) + 3 vol% DIO blend. Overall, we think that the inclusion of crystalline P(BDTSi-DFBT) on PTB7-Th:PC70BM blend improves the morphology which is favorable for better charge transport. Consequently, the improved crystallinity and morphology of ternary blends offer enhanced photovoltaic performance compared to binary blends.



Fig. 8. Topology AFM and TEM images of the films made from PTB7-Th:PC70BM (1:1.5 wt%) + 3 vol% DIO and PTB7-Th:P(BDTSi-DFBT):PC70BM (0.8:0.2:1.5 wt%) + 3 vol% DIO blends.

#### 4. Conclusions

The Stille polymerization of the di-stannyl derivative of 4,8bis(triisopropylsilylethynyl)-benzo[1,2-b:4,5-b']dithiophene and di-bromo derivative of 5,6-difluoro-4,7-bis(4octylthiophen-2-yl)benzo[c][1,2,5]thiadiazole resulted in a new polymer P(BDTSi-DFBT). The estimated  $E_g$ , HOMO and LUMO levels of P(BDTSi-DFBT) are 1.74 eV, -5.45 eV and -3.71 eV, respectively. Several peaks appear in the XRD and SAXS spectra of P(BDTSi-DFBT) indicates that it is a crystalline polymer. The

binary-PSCs made with the P(BDTSi-DFBT):PC70BM (1:1.5

wt%)+3 vol% blend offered a *PCE* of 5.02% with a  $V_{oc}$  of 0.81 V, a  $J_{sc}$  of 11.68 mA/cm<sup>2</sup> and a *FF* of 53%. While, the ternary-PSCs made with a blend of PTB7-Th:P(BDTSi-DFBT):PC<sub>70</sub>BM (0.8:0.2:1.5 wt%) gave a maximum *PCE* of 10.05% with a  $V_{oc}$  of 0.79 V, a  $J_{sc}$  of 17.92 mA/cm<sup>2</sup>, and a *FF* of 71%. This study confirm that the crystallinity of benzodithiophene– benzothiadiazole copolymer is greatly improved by inserting the triisopropylsilylethynyl group on the 4 and 8-position of benzo[1,2-b:4,5-b']dithiophene unit. The high crystallinity of P(BDTSi-DFBT) was found to increase the surface roughness of the film made with P(BDTSi-DFBT):PC<sub>70</sub>BM blend via solution processing. Consequently, P(BDTSi-DFBT) exhibited moderate

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photovoltaic performance on binary-PSCs. However, the inclusion of crystalline P(BDTSi-DFBT) on the PTB7-Th:PC<sub>70</sub>BM blend was found to significantly improve the photovoltaic performance of the resulting ternary-PSCs.

#### **Conflicts of interest**

There are no conflicts to declare

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