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Synthesis and photovoltaic properties of two-dimensional conjugated polythiophene derivatives presenting conjugated triphenylamine/thiophene moieties

Hsing-Ju Wang^a, Yuan-Peng Chen^a, Yung-Chung Chen^b, Chih-Ping Chen^c, Rong-Ho Lee^{a,*}, Li-Hsin Chan^d, Ru-Jong Jeng^{e,**}

^a Department of Chemical Engineering, National Chung Hsing University, 250, Kuo Kuang Rd., Taichung 402, Taiwan

^b Institute of Chemistry, Academia Sinica, Taipei 115, Taiwan

^c Material and Chemical Laboratories, Industrial Technology Research Institute, Chutung 310, Taiwan

^d Department of Applied Materials and Optoelectronic Engineering, National Chi Nan University, Puli, Taiwan

^e Institute of Polymer Science and Engineering, National Taiwan University, Taipei 106, Taiwan

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ABSTRACT

In this study we synthesized three two-dimensional (2-D) polythiophene derivatives (PTs), namely PTBPTPA, PTStTPA, and PTCNStTPA, featuring three different conjugated units—biphenyl (BP), stilbene (St), and cyanostilbene (CNSt), respectively—in the polymer backbones and presenting conjugated triphenylamine/thiophene (TPATh) moieties on the side chains. In addition, we also synthesized three conjugated BP-, St-, and CNSt-based main-chain-type conjugated polymers (PTBP, PTSt, and PTCNSt, respectively). Incorporating the St and CNSt moieties into the polymer backbones and appending TPATh units induced high degrees of intramolecular charge transfer within the conjugated frameworks of the polymers, thereby resulting in lower band gap energies and red-shifting of the maximal UV–Vis absorption wavelengths. Moreover, the energy levels of the highest occupied molecular orbitals of the BP-, St-, and CNSt-based main-chain-type and 2-D PTs were lower than that of P3HT, implying that they would be applicable for the preparation of polymer solar cells (PSC) with greater open-circuit voltages. The photovoltaic performances of PSCs fabricated from blends of the 2-D PTs and the fullerene derivative PC₆₁BM were superior to those of PSCs based on the main-chain-type polymer/PC₆₁BM blends.

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1. Introduction

Conjugated polymers consisting of an electronically delocalized backbone are significant technological materials used in optoelectronics [1–3]. Solar cells incorporating bulk heterojunctions (BHJs) based on low-band gap π -conjugated polymers have received much interest because of their promise for the development of solution-processable, highly flexible, large-area, low-cost, light-weight solar modules [4–6]. The photoactive layer in a typical BHJ cell is based on a blend of a conjugated polymer as the electron donor and a high-electron-affinity fullerene derivative—for example, [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) or [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM)—as the electron acceptor [4–6]. The photovoltaic (PV) performances of polymer solar cells (PSCs) have improved significantly in the past decade through optimization of the device structure, interfacial layer engineering, and processing conditions [7–10]. Although photo-energy conversion efficiencies (η) of greater than 7% have been achieved for PSCs based on blends of polythiophene derivatives and fullerene derivatives [11–16], the efficiencies of PSCs remain too low for commercial applications; several key factors must be resolved if a theoretical efficiency of 10% is to be realized [17].

Efficient photon-to-charge conversion in PSCs would require a conjugated polymer exhibiting a combination of suitable optical, electrochemical, and electronic properties. Generally, a high shortcircuit current (J_{SC}) and a large open-circuit voltage (V_{OC}) are both required if a PSC is to display a high photo-energy conversion efficiency (η). A conjugated polymer with a broad absorption band and low band gap will harvest more solar radiation—a favorable feature for a PSC exhibiting a high value of J_{SC} [18–20]. Moreover,



^{*} Corresponding author. Tel.: +886 4 22854308; fax: +886 4 22854734.

^{**} Corresponding author. Tel.: +886 2 33665884; fax: +886 2 33665237.

E-mail addresses: rhl@dragon.nchu.edu.tw (R.-H. Lee), rujong@ntu.edu.tw (R.-J. Jeng).

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high charge mobility is also required of the polymer to achieve high values of J_{SC} in PSCs [19–21]. Introducing strong electron-donating or -withdrawing moieties into the polymer backbone is an effective means of decreasing the band gap energy of the conjugated polymer. Unfortunately, the energy level of the highest occupied molecular orbital (HOMO) of the polymer would increase upon decreasing the band gap energy. In a typical PSC cell, the value of V_{OC} will correlate proportionally to the difference in energy between the HOMO of the electron-donating conjugated polymer and the lowest unoccupied molecular orbital (LUMO) of the electron-accepting fullerene derivative [22]. Therefore, the value of V_{OC} of a PSC would decrease upon decreasing the band gap energy of the polymer [23].

In recent years, several groups of chemists have proposed the use of two-dimensional (2-D) conjugated polymers, namely conjugated polymers presenting electron-donating and -withdrawing pendent groups, for PSC applications [20,24-35]. 2-D conjugated polymers sometimes exhibit two absorption bands in the UV and visible regions, therefore harvesting a greater amount of solar light [20,25,35]; indeed, high values of J_{SC} have been obtained for PSCs fabricated from such 2-D conjugated polymers. Li et al. have reported 2-D polythiophene derivatives (2-D PTs) presenting electron-donating triphenylamine (TPA) moieties as side chain units [34]. The presence of the TPA moieties twists the main chain out of planar π -conjugation and decreases the effective conjugation length of the polymer backbone. The HOMO energy levels of such TPA-containing 2-D PTs were lower than that of poly(3hexylthiophene) (P3HT). Accordingly, higher values of V_{OC} were observed for the corresponding PSCs. Nevertheless, the enhanced band gap energies of these TPA-containing 2-D PTs did not favor the harvesting of solar light [34].

Our objective in this present study was to develop a series of 2-D PTs featuring efficient conjugation lengths and deep HOMO energy levels for the preparation of PSCs exhibiting high values of J_{SC} and $V_{\rm OC}$. We synthesized three 2-D PTs, namely PTBPTPA, PTStTPA, and PTCNStTPA, featuring different conjugated units—biphenyl (BP), stilbene (St), and cyanostilbene (CNSt), respectively-in their polymer backbones and each presenting conjugated triphenylamine/thiophene (TPATh) pendent moieties. The conjugated polymer containing electron-donating moiety TPA has been widely studied for optoelectronic applications [36-39]. Although the HOMO energy levels of 2-D PTs incorporating electron-donating moieties are deeper than those of their parent PTs [34], the presence of bulky moieties would decrease the effective conjugation lengths of their polymer backbones [34]. We suspected that twisting of the main chain out of planar π -conjugation in the presence of bulky moieties could be suppressed though incorporation of rigid conjugation units (BP, St, CNSt) into the backbone. Thus, we expected PTBPTPA, PTStTPA, and PTCNStTPA to display a high degree of intramolecular charge transfer between the polymer backbones and the electron-donating pendent moieties. Consequently, the 2-D PTs PTBPTPA, PTStTPA, and PTCNStTPA should maintain deep HOMO energy levels and higher values of $V_{\rm OC}$; effective tuning of energy levels to modulate the absorbance profit would result in higher values of J_{SC}. For the sake of comparison, we also synthesized three main-chain-type conjugated polymers, namely PTBP, PTSt, and PTCNSt, based on BP, St, and CNSt units, respectively. We have used UV-Vis absorption spectroscopy and cyclic voltammetry (CV) to study the effects of the rigid conjugation segment (BP, St, CNSt) on the photophysical and electrochemical behavior, respectively, of the TPATh-containing 2-D PTs. We have also used atomic force microscopy (AFM) to study the morphologies of the TPATh-functionalized 2-D PT/PC₆₁BM and main-chain-type PT (PTBP, PTSt, PTCNSt)/PC₆₁BM blends. Herein, we also discuss the effect of the chemical structure on the morphologies and PV performances of PSCs based on these TPAThcontaining 2-D PT/PC₆₁BM blends.

2. Experimental details

2.1. Chemical materials

All reagents were purchased from Aldrich, Alfa, or TCI Chemical and used as received. Dichloromethane (DCM), tetrahydrofuran (THF), and toluene were freshly distilled over appropriate drying agents prior to use and then purged with N₂. The syntheses of 4,4'bis(trimethylstannyl)biphenyl (1), (*E*)-1,2-bis(4-bromophenyl) ethane (2), (*E*)-1,2-bis[4-(trimethylstannyl)phenyl]ethene (3), (*Z*)-2,3-bis(4-bromophenyl)acrylonitrile (4), and (*Z*)-2,3-bis[4-(4,4,5,5tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]acrylonitrile (5) are presented in Scheme 1. Compound (4-bromobenzyl)phosphonic acid diethyl ester, 2,5-dibromo-3-dodecanethiophene (6) and (*E*)-4-{5-[2-(2,5-dibromothiophen-3-yl)vinyl]thien-2-yl}-*N*,*N*-diphenylaniline (7) were synthesized according to previously described procedures [35,40]. Detailed procedures for the syntheses of the conjugated copolymers PTBP, PTBPTPA, PTSt, PTStTPA, PTCNSt, and PTCNStTPA are displayed in Scheme 2.

2.1.1. 4,4'-Bis(trimethylstannyl)biphenyl (1)

A solution of 4,4'-dibromophenyl (3.12 g, 10.0 mmol) in dry THF (60 mL) was stirred at -78 °C under N₂ for 10 min and then *n*-BuLi (2.5 M in hexane, 10.0 mL, 25.0 mmol) was added dropwise. The mixture was maintained at -78 °C with continued stirring for a further 3 h, at which point a solution of trimethyltin chloride (4.23 g, 25.0 mmol) in THF (10 mL) was added dropwise. After warming to room temperature and stirring for 8 h, MeOH was added to quench the reaction. The solution was partitioned between DCM and water; the organic phase was collected, dried (MgSO₄), filtered, and evaporated to dryness. The residue was recrystallized (MeCN) to provide a white solid (3.17 g, 66%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 0.27 (s, 18 H), 7.53 (d, *J* = 7.4 Hz, 4 H). EIMS (*m*/*z*): calcd for C₁₈H₂₆Sn₂: C, 45.06; H, 5.42. Found: C, 45.41; H, 5.65.

2.1.2. (E)-1,2-Bis(4-bromophenyl)ethane (2)

A mixture of (4-bromobenzyl)phosphonic acid diethyl ester (2.71 g, 11.0 mmol) and potassium *tert*-butoxide (3.37 g, 30.0 mmol) in THF (20 mL) was stirred in an ice-water bath for several minutes and then 4-bromobenzaldehyde (1.85 g, 10.0 mmol) was added. The solution was maintained at 0 °C and stirred continuously for a further 5 h. Then, the reaction was quenched through the addition of ice water. The mixture was partitioned between DCM and water and then the organic phase was collected, dried (MgSO₄), filtered, and evaporated to dryness. The residue was recrystallized (MeOH/THF) to provide a white solid (2.43 g, 72%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.09 (s, *J* = 7.4 Hz, 2 H), 7.24 (d, *J* = 7.4 Hz, 4 H), 7.45 (d, 4 H). EIMS (*m*/*z*): calcd for C₁₄H₁₀Br₂, 338.3; found: 338.1. Anal. Calcd for C₁₄H₁₀Br₂: C, 44.20; H 2.96. Found: C, 44.32; H, 2.975.

2.1.3. (E)-1,2-Bis[4-(trimethylstannyl)phenyl]ethene (3)

A solution of **2** (2.77 g, 10.0 mmol) in dry THF (60 mL) was stirred at -78 °C under a N₂ atmosphere and then *n*-BuLi (2.5 M in hexane, 10 mL, 25 mmol) was added dropwise. The mixture was maintained at -78 °C with continued stirring for a further 3 h, at which point a solution of trimethyltin chloride (4.23 g, 25.0 mmol) in THF (10 mL) was added dropwise. After warming to room temperature and stirring for 8 h, water was added to quench the reaction. The mixture was partitioned between DCM and water; the organic phase was dried (MgSO₄), filtered, and evaporated to dryness. The



Scheme 1. Synthesis of the conjugation units BP, St, and CNSt.

residue was recrystallized (MeCN) to provide a white solid (2.98 g, 59%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 0.28 (s, 18 H), 7.09 (s, 2 H), 7.46 (d, *J* = 8 Hz, 4 H), 7.52 (d, *J* = 8 Hz, 4 H). MS (*m*/*z*): calcd for C₂₀H₂₈Sn₂, 505.86; found, 506.0. Anal. Calcd for C₂₀H₂₈Sn₂: C, 47.49; H, 5.58. Found: C, 47.57; H, 5.75.

2.1.4. (Z)-2,3-Bis(4-bromophenyl)acrylonitrile (4)

4-Bromobenzaldehyde (1.85 g, 10 mmol) was added to an icewater-cooled mixture of 4-bromophenylacetonitrile (2.35 g, 12.0 mmol) and K₂CO₃ (0.560 g, 5.00 mmol) in THF (30 mL). After 5 h, the reaction was quenched through the addition of ice water and the mixture partitioned between DCM and water. The organic phase was dried (MgSO₄), filtered, and evaporated to dryness. The residue was purified chromatographically (SiO₂; EtOAc/hexanes, 1:10) to provide a white solid (2.69 g, 74%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.43 (s, 1 H), 7.55–7.60 (m, 6 H), 7.60–7.71 (m, 2 H). MS (*m*/*z*): calcd for C₁₅H₉NBr₂, 362.8; found, 362.9. Anal. Calcd for C₁₅H₉NBr₂: C, 49.60; H, 2.48; N, 3.86. Found: C, 49.95; H, 2.52; N, 3.89.

2.1.5. (Z)-2,3-Bis[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenyl]acrylonitrile (**5**)

A mixture of **4** (3.63 g, 10.0 mmol), KOBu^{*t*} (4.91 g, 50.0 mmol), and bis(pinacolate)diboron (6.35 g, 25.0 mmol) in a dry 1,4-dioxane (50 mL) was deoxygenated with N₂ for 30 min. Pd(PPh₃)₂Cl₂ (0.140 g, 0.200 mmol) was added to the mixture, which was then stirred and heated under reflux for 24 h. After cooling to room temperature, the mixture was partitioned between EtOAc and water. The organic phase was dried (MgSO₄), filtered, and evaporated to dryness. The residue was purified chromatographically (SiO₂; EtOAc/hexanes, 1:10) to provide a white solid (3.02 g, 66%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 1.34 (s, 24 H), 7.59 (s, 1 H), 7.65 (d, *J* = 8 Hz, 2 H), 7.86 (d, *J* = 7 Hz, 6 H). MS (*m*/*z*): calcd for

C₂₇H₃₃B₂NO₄, 457.18; found, 457.3. Anal. Calcd for C₂₇H₃₃B₂NO₄: C, 70.86; H, 7.22; N, 3.06. Found: C, 70.93; H, 7.25; N, 3.12.

2.1.6. PTBP

A solution of **1** (0.72 g, 1.5 mmol) and **6** (0.62 g, 1.5 mmol) in dry toluene (20 mL) was purged with N₂ and subjected to three freeze/ pump/thaw cycles to remove traces of O₂. Pd(PPh3)4 (30 mg, 1 mol %) was added to the mixture, which was then stirred and heated under reflux for 48 h. After cooling to room temperature, the mixture was poured into MeOH (100 mL) and the precipitated material was filtered through a Soxhlet thimble. Soxhlet extractions were performed sequentially with MeOH, hexane, acetone, and CHCl₃. The polymer was recovered through rotary evaporation of the CHCl₃ fraction. Drying under vacuum for 24 h provided an orange-red solid (44%). Gel permeation chromatography (GPC; THF): weight-average molecular weight (M_w) , 13.9 kg mol⁻¹; polydispersity index (PDI), 2.03. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 0.86 (t, 3 H), 1.26 (br, 18 H), 1.57-1.62 (m, 2 H), 2.55-2.75 (t, 2 H), 7.12 (s, 1 H), 7.28–7.71 (br, 8 H). Anal. Calcd for C₂₈H₃₄S: C, 83.57; H, 8.45; S, 7.96. Found: C, 83.62; H, 8.38; S, 7.87.

2.1.7. PTSt

Using the same procedure as that described for the synthesis of PTBP, the reaction of **3** (0.77 g, 1.5 mmol) and **6** (0.62 g, 1.5 mmol) provided a yellowish solid (0.22 g, 51%). GPC (THF): M_{W} , 10.5 kg mol⁻¹; PDI, 2.18. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 0.80 (t, 3 H), 1.18 (br, 18 H), 1.56–1.61 (m, 2 H), 2.30–2.62 (t, 2 H), 7.09–7.20 (br, 3 H), 7.25–7.65 (br, 8 H). Anal. Calcd for C₃₀H₃₆S: C, 84.10; H, 8.41; S, 7.47. Found: C, 83.92; H, 8.58; S, 7.39.

2.1.8. PTBPTPA

Using the same procedure as that described for the synthesis of PTBP, the reaction of **1** (0.72 g, 1.5 mmol), **6** (0.31 g, 0.75 mmol), and



Scheme 2. Synthesis of the main-chain-type and 2-D PTs.

7 (0.45 g, 0.75 mmol) provided a dark-red solid (0.45 g, 61%). GPC (THF): M_{w} 13.4 kg mol⁻¹; PDI, 2.22. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 0.85 (br, 3 H), 1.24 (br, 18 H), 1.57 (br, 2 H), 2.55–2.75 (m, 2 H), 7.03–7.83 (br, 31 H). Anal. Calcd for (C₂₈H₃₄S)_{1.24}(C₄₀H₂₇NS₂)₁: C, 82.74; H, 6.38; N, 1.28; S, 9.57. Found: C, 82.88; H, 6.47; N, 1.17; S, 9.15.

2.1.9. PTStTPA

Using the same procedure as that described for the synthesis of PTBP, the reaction of **3** (0.77 g, 1.5 mmol), **6** (0.31 g, 0.75 mmol), and **7** (0.45 g, 0.75 mmol) in dry toluene (20 mL) provided a red solid (0.42 g, 53%). GPC (THF): M_{W^2} 13.54 kg mol⁻¹; PDI, 2.02. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 0.85 (br, 3 H), 1.26 (br, 18 H), 1.62–1.65 (m, 2 H), 2.55–2.75 (t, 2 H), 7.00–7.88 (br, 33 H). Anal. Calcd for (C₃₀H₃₆S)_{1.85}(C₄₂H₂₉NS₂)₁: C, 83.40; H, 6.81; N, 0.99; S, 8.78. Found: C, 83.35; H, 6.77; N, 1.02; S, 8.68.

2.1.10. PTCNSt

A stirred mixture of **5** (0.69 g, 1.5 mmol), **6** (0.61, 1.5 mmol), Pd(PPh₃)₄ (0.03 g, 1 mol %), 2 M K₂CO_{3(aq)} (5 mL), and anhydrous

toluene (30 mL) was deoxygenated with N₂ for 1 h. The mixture was heated at 90 °C and stirred under a N₂ atmosphere for 48 h. After cooling to room temperature, the mixture was poured into MeOH (100 mL) and the precipitated material then filtered into a Soxhlet thimble. Soxhlet extractions were performed sequentially with MeOH, hexane, acetone, and CHCl₃. The polymer was recovered from the CHCl₃ fraction through rotary evaporation. Drying under vacuum for 24 h provided a black-red solid (0.30 g, 43%). GPC (THF): M_w , 12.34 kg mol⁻¹; PDI, 2.27. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 0.87 (t, 3 H), 1.26 (br, 18 H), 1.56–1.61 (m, 2 H), 2.55–2.75 (t, 2 H), 7.15 (s, 1H), 7.40–7.80 (br, 8 H), 7.94 (s, 1 H). Anal. Calcd for C₃₁H₃₅NS: C, 82.10; H, 7.73; N, 3.09; S, 7.05. Found: C, 82.32; H, 7.58; N, 3.12; S, 6.89.

2.1.11. PTCNStTPA

Using the same procedure as that described for the synthesis of PTCNSt, the reaction of **5** (0.69 g, 1.5 mmol), **6** (0.31 g, 0.75 mmol), and **7** (0.45 g, 0.75 mmol) provided an orange-red solid (0.38 g, 51%). GPC (THF): $M_{\rm W}$, 10.09 kg mol⁻¹; PDI, 1.29. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 0.85 (br, 3H), 1.26 (br, 18 H), 1.56–1.62 (m, 2 H), 2.55–2.75 (t, 2H), 6.95–8.12 (br, 33 H). Anal. Calcd for (C₃₁H₃₅NS)_{1.27}(C₄₃H₂₈N₂S₂)₁: C, 81.60; H, 5.95; N, 3.77; S, 8.65. Found: C, 81.98; H, 6.23; N, 2.93; S, 8.08.

2.2. Characterization

¹H NMR (400 MHz) and ¹³C NMR (150 MHz) spectra were recorded using a Varian Unity Inova Spectrometer. The average molecular weights of the polymers were measured using the GPC method. GPC was performed using a Waters chromatography system (717 plus Autosampler), two Waters Styragel linear columns, polystyrene as the standard, and THF as the eluent. The glass transition temperatures (T_g) and thermal decomposition temperatures (T_d ; at which a 5% weight loss occurred) of the copolymers were determined through differential scanning calorimetry (TA Instruments, DSC-2010) and thermogravimetric analysis (TA Instruments, TGA-2050), respectively. Both thermal analyses were performed under a N2 atmosphere at scanning (both heating and cooling) rates of 10 °C min⁻¹. The temperatures at the intercept of the curves in the thermogram (endothermic, exothermic, or weight loss) and the leading baseline were taken as estimates of the onset values of T_g and T_d . Absorption spectra were measured using a Hitachi U3010 UV-Vis spectrometer. Fluorescence spectra were measured using a Varian Cary Eclipse luminescence spectrometer. Redox potentials of the polymers were determined through CV using a CHI 611D electrochemical analyzer (scanning rate: 50 mV s⁻¹) equipped with Pt electrodes and an Ag/ Ag⁺ (0.10 M AgNO₃ in MeCN) reference electrode in an anhydrous, N₂-saturated solution of 0.1 M Bu₄NClO₄ in MeCN. Bu₄NClO₄ (98%, TCI) was recrystallized three times from MeOH and water (1:1) and then dried at 100 °C under reduced pressure. A Pt plate coated with a thin polymer film was used as the working electrode; a Pt wire and an Ag/Ag⁺ electrode were used as the counter and reference electrodes, respectively. The electrochemical potential was calibrated against ferrocene/ferrocenium. The morphologies of the conjugated copolymer/PC₆₁BM blend films were studied using an atomic force microscope (AFM, Seiko SII SPA400) operated in the tapping mode, and a transmission electron microscope (TEM, JEOL JEM-1400).

2.3. Fabrication and characterization of PSCs

Glass substrates [Sanyo, Japan (8 $\Omega \square^{-1}$)] coated with indium tin oxide (ITO) were sequentially patterned lithographically, cleaned with detergent, ultrasonicated in acetone and isopropyl

alcohol, dried on a hot plate (120 °C, 5 min), and treated with oxygen plasma for 5 min. The hole-transporting material poly(3,4ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS; Clevios P-VP AI4083) was passed through a 0.45-µm filter prior to being deposited on the ITO-coated glass using the spin-coating method (3000 rpm). The sample was then dried at 150 °C for 30 min in a glove box. A solution of PC₆₁BM and a conjugated copolymer [weight ratio, 1:1: 15 mg mL⁻¹ in o-dichlorobenzene (o-DCB)] was stirred overnight and then filtered through a 0.2-µm polytetrafluoroethylene (PTFE) filter. A film of the photoactive layer (copolymer/PC₆₁BM composite) was formed above the PEDOT:PSS layer through spin-coating (1000 rpm, 30 s) of the mixture solution. The photoactive layers were thermally treated at 80 °C for 1 h or 140 °C for 10 min. The film thicknesses of the photoactive layer in PSCs were determined (AFM) to be approximately 110 nm. The LiF (1 nm)/Al (100 nm) cathode was thermally deposited onto the photoactive thin film in a high-vacuum chamber. The active area of the PSC was 4 mm². After deposition of the Al electrode, the PSC was encapsulated using UV-curing glue (Nagase, Japan). Current density-voltage (I-V) curves of the PSCs were recorded using a programmable electrometer, equipped with current and voltage sources (Keithley 2400), under illumination (100 mW cm^{-2}) with solar light from a Peccell AM 1.5G solar simulator. The illumination intensity was calibrated using a standard Si photodiode detector equipped with a KG-5 filter. The output photocurrent was adjusted to match the photocurrent of the Si reference cell to obtain a power density of 100 mW cm⁻².

3. Results and discussion

3.1. Characterization of polymers

We used ¹H NMR spectroscopy to determine the chemical structures of the conjugated polymers. ¹H NMR spectra of the mainchain type and 2-D PTs are shown in Figure S1-1-S1-6 (see supporting information). Chemical shifts in the range 6.9-8.2 ppm represented the signals of the protons in the vinylene, phenyl, and thiophene groups. The signals of the protons in the dodecyl chains were observed at chemical shifts ranging from 0.8 to 2.8 ppm. For the 2-D PTs PTBPTPA, PTStTPA, and PTCNStTPA, the repeat unit ratio (m/n) was modulated by controlling the feed ratio of the conjugation unit (BP, St, CNSt), 6, and 7. The actual values of m/n were determined from the relative integral areas of the peaks at 6.9–8.2 ppm (protons in the vinylene, phenyl, and thiophene groups) and 0.8–2.8 ppm (protons in the dodecyl chains) in the ¹H NMR spectra of the copolymers. The repeat unit ratios (m/n) of the conjugated copolymers PTBPTPA, PTStTPA, and PTCNStTPA were approximately 1.24:1, 1.85:1, and 1.27:1, respectively (Table 1). The repeat unit ratios (m/n) were close to 1:1 for the copolymers PTBPTPA and PTCNCtTPA, but approximated 2:1 for the copolymer PTStTPA. We attribute the higher *m*:*n* ratio of PTStTPA to the poor solubility of the St/TPATh segment [41] inhibiting the propagation of the polymer chains; the good solubility of the St/3dodecanethiophene segment had the opposite effect. A higher content of St/TPATh segments would lead to precipitation at the initial stages of polymerization, resulting in the polymer being removed during the purification procedure. Therefore, we obtained PTStTPA with a higher m/n ratio. Using GPC with THF as the eluent and polystyrenes as internal standards, we determined the values of M_w and PDI (M_w/M_n) of the conjugated polymers to be 10.09–13.90 (kg mol⁻¹) and 1.19–2.27, respectively (Table 1). All of the conjugated copolymers, expect for PTSt, were soluble in common organic solvents, including DCM, THF, toluene, and *o*-DCB. The relatively poor solubility of PTSt was due to the high planarity of its St groups [42].

The operational stability of an optoelectronic device is directly related to the thermal stability of its conjugated polymers. Thus, high values of T_g and T_d are desirable for a conjugated polymer to be applied in PSCs. We obtained the values of T_g and T_d of the conjugated copolymers through thermal analyses using DSC and TGA (Table 1). The values of T_d of the conjugated copolymers were in the range 373-422 °C. The char yields at 800 °C of the conjugated copolymers were in the range 22-54%. Higher residues were observed for the 2-D PTs as compared to that of the main-chain type PTs. Generally, the incorporation of bulky TPATh pendent units into the polymer backbone improved the thermal decomposition properties of the conjugated copolymers. As a result, the values of T_d for PTBPTPA and PTStTPA were higher than those of PTBP and PTSt. Notably, however, the value of T_d of PTCNStTPA was lower than that of PTCNSt, presumably because of the relatively low molecular weight of PTCNStTPA. In addition, the presence of cvano groups resulted in the values of T_d of PTCNSt and PTCNStTPA being lower than those of the other copolymers. We determined all of the transition temperatures from the second round of DSC heating scans. DSC analysis revealed superior values of T_g (ca. 100–153 °C) for our copolymers, making them suitable for PSC applications [43,44]. Only one endotherm glass transition was observed for each conjugated copolymer, implying that the dodecyl chain-containing and TPATh segments were distributed homogeneously. The presence of rigid TPATh pendent units with high polarity hindered the molecular motion of the polymer backbone; therefore, the values of T_{g} for PTBPTPA and PTCNStTPA were higher than those for PTBP and PTCNSt [45]. Notably, however, PTStTPA exhibited a lower value of T_{g} than that of the PTSt. For PTStTPA, the incorporation of a low content of TPATh units did not favor a high value of T_g. Conversely, the presence of TPATh pendent units enhanced the free volume between the polymer backbones. Therefore, the value of T_{g} for PTStTPA was lower than that of PTSt. In addition, the high polarity of the cyano moieties enhanced the interactions between the polymer chains, resulting in the values of Tg of PTCNSt and PTCNStTPA being higher than those of PTBP and PTBPTPA, respectively [46]. Furthermore, unlike the high planarity of St units in the polymer backbone, the presence of cyano groups resulted in steric hindrance and twisting of the CNSt units, resulting in poorer packing of the polymer backbones [47]. Therefore, the value of T_g of PTCNSt was lower than that of PTSt. On the other hand, PTCNStTPA

Table 1

| Molecular weights and thermal properties of the main-chain-type and 2-D F | ΥTS. |
|---|------|
|---|------|

| Polymer | M_w (kg mol ⁻¹) | PDI | Repeat unit ratio (<i>m</i> : <i>n</i>) ^a | <i>T</i> _d (°C) | Char yields at 800 °C (%) | T_g (°C) |
|-----------|-------------------------------|------|--|----------------------------|---------------------------|------------|
| PTBP | 13.90 | 2.03 | 1:0 | 403 | 49 | 100 |
| PTSt | 10.50 | 2.18 | 1:0 | 414 | 25 | 153 |
| PTCNSt | 12.34 | 2.27 | 1:0 | 406 | 22 | 126 |
| PTBPTPA | 13.41 | 2.22 | 1.24:1 | 421 | 54 | 130 |
| PTStTPA | 13.54 | 2.02 | 1.85:1 | 422 | 42 | 125 |
| PTCNStTPA | 10.09 | 1.29 | 1.27:1 | 373 | 39 | 141 |

^a Calculated from the ¹H NMR spectra of the polymers.



Fig. 1. Normalized UV–Vis absorption spectra of the main-chain-type and 2-D PTs ((a) in *o*-DCB solution and (b) as solid film).

exhibited a higher value of T_g relative to that of PTStTPA, due to the lower TPATh content of PTStTPA. Thus, the thermal stability of each conjugated copolymer was affected by the planarity and polarity of its conjugated units (BP, St, CNSt) and the bulk of its pendent groups.

3.2. Optical properties of the conjugated copolymers

Fig. 1 presents the normalized UV-Vis absorption spectra of the copolymers in o-DCB solutions and as solid films. Table 2 summarizes the photophysical properties of the copolymers. The absorptions of the conjugated copolymers in solution and as films ranged from 300 to 600 nm. The absorptions were attributed to the π - π * transitions of the conjugated main chains. In solution, the maximal absorption wavelengths for the conjugated polymers PTBP and PTSt appeared near 376 and 407 nm, respectively. This red-shifting of the absorption band for PTSt relative to PTBP implies that the St units in PTSt had a longer conjugation length and better coplanarity and π -electron delocalization along the polymer backbone than did the BP units in PTBP. The poor coplanarity of the BP units in the polymer backbone of PTBP was due to steric repulsion between the ortho hydrogen atoms of the two neighboring phenyl groups [48]. Consequently, the maximal absorption wavelength of PTSt was greater than that of PTBP. Moreover, introducing the electrondeficient cyano groups into the polymer backbone enhanced the intramolecular charge transfer capacity of the polymer chains. As a result, the maximal absorption wavelength of PTCNSt was greater Table 2

Optical and electrochemical properties of the main-chain-type and 2-D PTs.

| Polymer | λ ^{abs} (nm) ^a | λ ^{abs} (nm) ^b | λ ^{abs} onset (nm) ^c | E_g^{opt} $(eV)^d$ | E ^{ox} (V) | HOMO (eV) | LUMO (eV) |
|-----------|---------------------------------------|---------------------------------------|--|-------------------------|------------------------|--------------|--------------|
| PTBP | 376 | 387 | 468 | 2.65 | 1.00 | -5.61 | -2.96 |
| PTSt | 407 | 409 | 502 | 2.47 | 0.80 | -5.41 | -2.94 |
| PTCNSt | 431 | 447 | 539 | 2.30 | 1.00 | -5.61 | -3.31 |
| PTBPTPA | 391 | 395 | 506 | 2.45 | 0.74 | -5.35 | -2.90 |
| PTStTPA | 407 | 414 | 525 | 2.36 | 0.76 | -5.37 | -3.01 |
| PTCNStTPA | 434 | 443 | 563 | 2.20 | 0.55 | -5.16 | -2.96 |

^a Maximal absorption wavelength of the polymer in solution.

^b Maximal absorption wavelength of the polymer as a thin film.

^c Onset of UV–Vis absorption of the polymer as a thin film.

 d Calculated from the onset absorption ($\lambda_{onset})$ of the polymer thin film: $E_{g}^{opt}=1240/\lambda_{onset}.$

than those of PTBP and PTSt. We also observed the influences of the coplanarity of the St unit and the polarity of the cyano groups on the effective conjugated lengths of the conjugated copolymers incorporating the TPATh pendent moieties. The maximal absorption wavelength and full width at half-maximum of PTCNStTPA were greater than those of PTBPTPA and PTStTPA. Furthermore, the red-shifts and full widths at half-maximum of the absorption bands of the copolymers in the solid films were greater than those in solution, presumably because of noncovalent interactions (e.g., π – π stacking) between the polymer chains.

We determined the band gap energies (E_g^{opt}) of the conjugated polymers in their thin film state from the onset wavelengths of their absorption bands. As listed in Table 2, the values of E_{σ}^{opt} for PTBP, PTSt, PTCNSt, PTBPTPA, PTStTPA, and PTCNStTPA were 2.65, 2.47, 2.30, 2.45, 2.36, and 2.20 eV, respectively. Because its phenyl rings rotate freely, the BP units provided low conjugation lengths, thereby minimizing electron transfer in its polymer backbones. Conversely, the extended planar structure of the St units ensured effective conjugation in its polymer backbones [42]. Notably, the introduction of cyano units as electron-withdrawing groups in the polymer backbones enhanced the intramolecular charge transfer capacity of the conjugated polymers [49,50]. The value of E_{σ}^{opt} for PTBP was higher than that of PTCNSt. In addition, the incorporation of electron-donating pendent units induced a higher degree of intramolecular charge transfer within the conjugated framework of the polymers, thereby decreasing the band gap energy of the conjugated polymers [51,52]. Consequently, the values of E_g^{opt} of PTBPTPA, PTStTPA, and PTCNStTPA were lower than those of PTBP, PTSt, and PTCNSt, respectively. In general, a higher-intensity of UV–Vis absorption and a lower value of E_g^{opt} are favorable for a conjugated polymer to harvest solar light. A strong absorption intensity and a broad absorption band should improve the absorption efficiency of the photoactive layer, thereby enhancing the photocurrent generated in a PSC. Apart from that, the E_g^{opt} values of PTBPTPA, PTStTPA, and PTCNStTPA incorporated with conjugated unit (TBP, St, CNSt) are larger than that of the TPATh moiety-containing thiophene-derivatized copolymers [35]. This is due to the fact that the conjugated units (TBP, St, CNSt) exhibit a larger energy gap than that of the thiophene unit.

Fig. 2 presents normalized UV–Vis absorption spectra of PTStTPA/PC₆₁BM blend films. The absorption band of the conjugated polymer ranged from 350 to 700 nm, while that of $PC_{61}BM$ ranged from 300 to 375 nm [53]. A red-shift of the absorption bands was observed for the PTStTPA/PC₆₁BM blend films as compared to that of the PTStTPA film. This implies that the dilution of the small molecules $PC_{61}BM$ resulted in the decreased main chains aggregation of PTStTPA. Consequently, the effective conjugation length of PTStTPA was enhanced by the blending of $PC_{61}BM$ [35]. Moreover, the absorption intensity of the conjugated polymer decreased upon increasing the $PC_{61}BM$ content in the PTStTPA/PC₆₁BM blend films.



Fig. 2. Normalized UV-Vis absorption spectra of PTStTPA/PC₆₁BM blend films.

For the other conjugated polymer/PC₆₁BM blend films, the decreases in absorption intensity upon increasing the $PC_{61}BM$ content were similar to those of the PTStTPA/PC₆₁BM blend films. From the point of view of photon absorption, it would be preferable to employ less $PC_{61}BM$ in the photoactive layer; a high proportion of $PC_{61}BM$ limits optical absorption in the composite layer because its absorption is quite inefficient in the visible region. We observed similar absorption behavior for the blend films based on the other conjugated polymers and $PC_{61}BM$.

Fig. 3 displays photoluminescence (PL) spectra of the copolymers in solution and as thin films. The maximal PL wavelengths (λ_{max}^{em}) increased upon increasing the effective conjugation length of the conjugated polymers. The values of λ_{max}^{em} of the polymers containing St units (PTSt, PTStTPA) were greater than those of the BPcontaining polymers (PTBP, PTBPTPA). Moreover, the presence of cyano groups resulted in the values of λ_{max}^{em} of PTCNSt and PTCNStTPA being greater than those of PTSt and PTStTPA, respectively. The 2-D PTs incorporating TPATh pendent moieties (PTBPTPA, PTStTPA, PTCNStTPA) exhibited greater values of λ_{max}^{em} than did the main-chain polymers (PTBP, PTSt, PTCNSt). In addition, we observed bathochromic shifts of the maximum emission wavelengths and broadening of the emission peaks for the copolymers as solid films, relative to those in solution, due to $\pi - \pi$ stacking and interchain aggregation in the polymer films. Notably, however, a hypsochromic shift appeared for the maximum emission wavelength of the thin film of PTCNStTPA ($\lambda_{max}^{em} = 599 \text{ nm}$) relative to that in solution (in *o*-DCB; $\lambda_{max}^{em} = 623 \text{ nm}$). On the contrary, the maximal emission wavelength of PTCNStTPA as thin film state ($\lambda_{max}^{em} = 599$ nm) presented a bathochromic shift relative to that in toluene ($\lambda_{max}^{em} = 587$ nm). An apparent solvent-induced solvatochromism was observed in a highly polar solvent, o-DCB. Similar fluorescence properties of bipolar conjugated polymers in relation to the polarity of the solvent have been investigated in the literature [54,55].

Next, we investigated the PL spectra of the conjugated polymer/ PC₆₁BM blend films. The PL emissions were almost completely quenched upon the addition of PC₆₁BM (w/w, 1:1) to all of the copolymer blend films (see Supporting Information, Fig S2). These highly efficient PL quenching phenomena suggest that the excitons generated by the absorbed photons dissociated completely to free charge carriers (electrons, holes). Thus, effective charge transfer existed from the conjugated copolymer to the electron acceptor PC₆₁BM—a basic requirement for preparing a PSC exhibiting satisfactory PV performance [56].



Fig. 3. PL spectra of the main-chain-type and 2-D PTs ((a) in o-DCB solution and (b) as solid film).

3.3. Electrochemical properties of the conjugated copolymers

We employed CV to investigate the electrochemical behavior of the conjugated polymers and to estimate their HOMO and LUMO energy levels. Fig. 4 presents CV traces of the conjugated polymer films in MeCN, recorded at a scanning rate of 50 mV s⁻¹ Table 2 summarizes the electrochemical properties of the copolymers. The oxidation potentials of PTBPTPA, PTStTPA, and PTCNStTPA were 0.74, 0.76, and 0.55 V, respectively; those of PTBP, PTSt, and PTCNSt were 1.00, 0.80, and 1.00 V, respectively. Thus, the values of $E_{1/2}^{ox}$ of the 2-D PTs (PTBPTPA, PTStTPA, PTCNStTPA) were lower than those of the main-chain polymers (PTBP, PTSt, PTCNSt). We attribute the relatively lower values of $E_{1/2}^{ox}$ of the 2-D PTs containing TPATh moieties to the increased effective conjugation length resulting from the presence of those TPATh moieties [57]. Moreover, the value of $E_{1/2}^{ox}$ of PTSt was lower than that of PTBP. The presence of the St unit enhanced the effective conjugation length of the polymer backbone and decreased the oxidation potential of the conjugated polymer. Conversely, the presence of a cyano group on the St unit decreased the oxidation capacity of the polymer backbone and enhanced the oxidation potential of the polymer. As a result, the value of $E_{1/2}^{ox}$ of PTCNSt was higher than that of PTSt.



Fig. 4. Electrochemical properties of the main-chain-type and 2-D PTs.

Notably, PTCNStTPA exhibited two quasi-reversible oxidation peaks in the positive potential region. The first oxidation potential, near 0.55 V, was presumably due to oxidation of the electron-donating TPATh pendent unit. Moreover, the potential of the oxidation peak of the TPATh pendent moieties was lower than those of PTBPTPA and PTStTPA, presumably because of strong intratransfer polymers molecular electron in possessing a donor- π -acceptor structure [58]. We suspect that the second oxidation potential, near 0.89 V, was due to the non-planarity of the CNSt units in the PTCNStTPA main chain, thereby minimizing the electronic communication of the polymer backbone. As a result, the oxidation of the CNSt unit occurred at higher potential [47]. The oxidation-onset potentials for the main-chain-type and 2-D PTs incorporating the BP, St, and CNSt units were greater than those of P3HT [34], suggesting that their air stabilities were greater than that of P3HT. From the values of $E_{1/2}^{ox}$, we calculated the HOMO energy levels of the conjugated copolymers using the equation

HOMO =
$$-e \left(E_{1/2}^{ox} - E_{1/2}^{ox}, \text{ ferrocene} + 4.8 \right) (eV)$$

Here, 4.80 eV is the energy level of ferrocene below the vacuum level; the value of $E_{1/2}^{\infty}$ of ferrocene/ferrocenium in the 0.1 M

Bu₄NClO₄/MeCN solution was 0.19 V. Hence, the corresponding HOMO energy levels were -5.61 eV for PTBP, -5.41 eV for PTST, -5.61 eV for PTCNST, -5.35 eV for PTBPTPA, -5.37 eV for PTStTPA, and -5.16 eV for PTCNSTPA. Because no reversible *n*-doping process was observable in the CV spectrum, we estimated the LUMO energy levels from the HOMO energy levels and the values of E_g^{opt} from the UV–Vis absorption spectra, using the equation

$$LUMO = (HOMO + E_g^{opt})(eV)$$

Accordingly, the LUMO energy levels were -2.96 eV for PTBP, -2.94 eV for PTST, -3.31 eV for PTCNST, -2.90 eV for PTBPTPA, -3.01 eV for PTStTPA, and -2.96 eV for PTCNStTPA. Typically, the introduction of electron-withdrawing cyano groups decreases the value of E_g^{opt} by lowering the LUMO energy level, while the introduction of electron-donating TPATh groups decreases the value of E_g^{opt} by increasing the HOMO energy level. According to donor/acceptor orbital hybridization of a bipolar conjugated polymer, the HOMO of the donor segment will interact with the LUMO of the acceptor segment to yield a lower value of E_{α}^{opt} [59,60]. The HOMO energy levels of the main-chain-type polymers and TPATh-containing 2-D PTs based on BP, St, and CNSt units were lower than that of P3HT (ca. -4.7 to -4.9 eV) [29,30]. In general, the HOMO energy level of a p-type conjugated polymer is an important parameter affecting the performance of a BHJ cells. High open circuit voltages (V_{OC}) are typically obtained for PSCs fabricated from conjugated polymers with low HOMO energy levels. Here, the HOMO energy levels of PTBPTPA, PTStTPA, and PTCNStTPA were slightly higher than those of PTBP, PTSt, and PTCNSt, respectively. The introduction of the TPATh moieties did not twist the main chains out of planar π -conjugation and did not curtail the effective conjugation length of the polymer backbones. Conversely, the electron-donating ability of the TPATh moiety resulted in good conjugation and intramolecular charge transfer with the BP, St, and CNSt units. Therefore, the HOMO energy level increased slightly after the incorporation of the TPATh moieties. Nevertheless, for the BP-, St-, and CNSt-based conjugated polymers, low HOMO energy levels were maintained after attachment of the TPATh pendent moieties. This effect of the incorporated TPATh moieties on the backbones of the conjugated polymers is quite different from the results published previously in the literature [34]. Li et al. reported that the effective conjugation length of PTs was curtailed after the incorporation of bulky triphenylaminecontaining side chains, due to twisting of the main chains out of planar π -conjugation [34]; consequently, the HOMO energy level was lowered after grafting the bulky pendent groups onto the PT [34]. On the other hand, lower HOMO levels were observed for the 2-D PTs (PTBPTPA, PTStTPA, and PTCNStTPA) as compared to those of the TPATh moiety-containing thiophene-derivatized copolymers [35].

3.4. Morphologies of conjugated polymer/PC₆₁BM blend films

The performance of a PSC is strongly dependant on the morphology of the conjugated polymer/fullerene-derivative composite film [61]. To avoid recombination of excitons, the P/N heterojunction phase must be controlled under nanoscale distribution, due to the diffusion range of the charge carrier being approximately 3–10 nm [62,63]. We used AFM microscopy to investigate the compatibility and morphology of the conjugated polymer/PC₆₁BM composite films. Fig. 5 displays topographic and phase images of the PTBP/PC₆₁BM, PTSt/PC₆₁BM, and PTCNSt/PC₆₁BM blend films (1:1, w/w) after they had been annealed at 80 °C for 1 h Table 3 summarizes the roughnesses of these



Fig. 5. Topographic (a, c, e) and phase (b, d, f) images of PTBP/PC₆₁BM (a, b), PTSt/PC₆₁BM (c, d), and PTCNSt/PC₆₁BM (e, f) blend films (1:1, w/w) that had been annealed at 80 °C for 1 h.

composite films. For the PTBP/PC₆₁BM blend film, we observed a phase-separated interpenetrating network with sizable $PC_{61}BM$ domains. A certain degree of phase separation is critical for efficient formation of free carriers, which might provide optimal PV

| Table 3 | |
|---|--|
| PV performances of PSCs based on conjugated polymer/PC ₆₁ BM blends. | |

| PSC | Polymer/PC ₆₁ BM (1:1, w/w) | RMS (nm) ^a | V _{OC} (V) | J _{SC} (mA cm ⁻²) | FF | η (%) |
|---------|---|--------------------------|------------------------|---|------|-------|
| PSC I | PTBP/PC ₆₁ BM | 2.37 | 0.68 | 0.69 | 0.26 | 0.12 |
| PSC II | PTSt/PC61BM | 2.49 | 0.83 | 0.04 | 0.12 | 0.01 |
| PSC III | PTCNSt/PC61BM | 5.51 | 0.83 | 0.17 | 0.28 | 0.04 |
| PSC IV | PTBPTPA/PC61BM | 0.79 | 0.86 | 1.38 | 0.32 | 0.38 |
| PSC V | PTStTPA/PC61BM | 1.69 | 0.86 | 0.90 | 0.31 | 0.24 |
| PSC VI | PTCNStTPA/PC61BM | 0.88 | 0.65 | 1.99 | 0.27 | 0.36 |
| PSC VII | PTStTPA/PC61BMb | 3.02 | 0.83 | 1.73 | 0.33 | 0.49 |

 a RMS: the root-mean-square (RMS) value of polymer/PC_{61}BM blend film measured by AFM.

^b The photo-active layer was annealed under 140 °C for 10 min.

properties for the resulting PSC. For the PTSt/PC₆₁BM blend film, the poor solubility of PTSt resulted in serious separation of the PTSt and PC₆₁BM phases. For the PTCNSt/PC₆₁BM blend film, we observed good miscibility of the PTCNSt and PC₆₁BM units. We did, however, observe nanoparticles (<100 nm) on the surface of PTCNSt/PC61BM blend film, presumably because of the presence of non-soluble polymer material [64,65]. Fig. 6 displays topographic and phase images of the PTBPTPA/PC₆₁BM, PTStTPA/PC₆₁BM, and PTCNStTPA/ PC₆₁BM blend films (1:1, w/w) after they had been annealed at 80 °C for 1 h. The PC₆₁BM molecules were distributed in a homogeneous manner in the composite films based on the 2-D PTs (PTBPTPA, PTStTPA, PTCNStTPA), suggesting that the presence of the TPATh pendent moieties enhanced the miscibility of the conjugated polymer and PC₆₁BM. The bulky side chains also provided sufficient free volume for the PC₆₁BM units to intercalate into the polymer chains, enhancing the compatibility of the polymer and fullerene derivative. Nevertheless, several nanoparticles were present on the surface of the PTStTPA/PC₆₁BM blend film, presumably because of the relatively poor solubility of PTStTPA. In



Fig. 6. Topographic (a, c, e) and phase (b, d, f) images of PTBPTPA/PC₆₁BM (a, b), PTStTPA/PC₆₁BM (c, d), and PTCNStTPA/PC₆₁BM (e, f) blend films (1:1, w/w) that had been annealed at 80 °C for 1 h.

addition, the surface roughnesses of the 2-D PT-based blend films were lower than those of the blend films based on main-chain-type polymers. Because the incorporation of the TPATh moieties enhanced the miscibility of the conjugated polymer and $PC_{61}BM$, the 2-D PT-based blend films exhibited lower surface roughnesses.

3.5. PV properties of PSCs based on conjugated polymer/PC₆₁BM blend films

We fabricated PSCs incorporating films of the conjugated polymer/PC₆₁BM (1:1, w/w) blends prepared from *o*-DCB solutions (15 mg mL⁻¹) using an optimized spin-coating procedure. The photoactive layers based on the conjugated polymer/PC₆₁BM blends were thermally treated at 80 °C for 1 h Fig. 7 displays the photocurrent density–voltage plots of the PSCs. Table 3 summarizes the PV properties of these PSCs, including their open-circuit voltages (V_{OC}), short-circuit current densities (J_{SC}), fill factors (FFs), and photo-energy conversion efficiencies (η). The values of J_{SC} and η of the PTBP/PC₆₁BM blend-based PSC I were much greater than those of the PTSt/PC₆₁BM and PTCNSt/PC₆₁BM blend-based PSCs (PSC II and PSC III, respectively). We attribute the poorer PV performances of PSC II and PSC III to the phase separation and low quality of the photoactive layer. Phase separation, which results in current leakage in PSCs, decreased the values of J_{SC} and FF for PSC II and PSC III [66]. Therefore, the values of η for the PSCs based on the PTSt/PC₆₁BM and PTCNSt/PC₆₁BM blends were lower than that of the PTBP/PC₆₁BM blend-based PSC. Conversely, the values of V_{OC} of PSC II and PSC III were slightly larger than that of PSC I. Although the value of V_{OC} is determined primarily by the difference between the LUMO energy level of the electron acceptor (in this case, PC₆₁BM) and the HOMO energy level of the electron donor (the conjugated polymer), it is also affected by the morphology of the photoactive layer [67] (Fig. 8).

Notably, the PV performances of the PSCs based on the 2-D PT (PTBPTPA, PTStTPA, PTCNStTPA)/PC₆₁BM blends (PSCs IV–VI) were much better than those of the PSCs based on the main-chain-type



Fig. 7. Photocurrent density–voltage plots of PSCs fabricated from the conjugated polymer/PC₆₁BM blends (1:1, w/w) that had been annealed at 80 °C for 1 h or 140 °C for 10 min.

conjugated polymer (PTBP, PTSt, and PTCNSt)/PC₆₁BM blends (PSCs I–III). Several factors are responsible for this behavior, including the effective conjugation length and hole mobility of the conjugated polymer and the morphology of the photoactive layer. The presence of electron-donating TPATh pendent units enhanced the effective conjugation length and hole mobility of the conjugated polymer, thereby improving the solar light absorption capacity and hole mobility in the photoactive layer of the corresponding PSC [35]. Moreover, the compatibility of the conjugated polymer and PC₆₁BM improved upon appending the TPATh moieties to the polymer backbone. Their presence also had a positive effect on the charge separation and transporting capacity in the photoactive layer. Accordingly, the J_{SC} and η of the PSCs based on the TPAThpresenting 2-D PTs were much better than those of the PSCs based on the main-chain-type conjugated polymers. Moreover, higher values of V_{OC} were observed for the TPATh-containing 2-D PTs based PSCs IV and PSC V as compared to those of the mainchain-type PTs based PSCs I and II, despite the fact that the HOMO levels of PTBPTPA and PTStTPA were higher than those of PTBP and PTSt. We attribute the lower values of V_{OC} of PSCs I and II to the poorer thin film quality PTBP and PTSt [67]. Notably, the PV performance of PSC V was poorer than that of PSC IV, even through the conjugation length in PTStTPA was larger than that in PTBPTPA; we suspect that the film quality of the PTStTPA/PC₆₁BM blend was poorer than that of the PTBPTPA/PC₆₁BM blend. Moreover, the value of Isc for PSC VI was higher than that for PSC IV, presumably because of the enhanced effective intramolecular charge transfer and light-harvesting capacity of the PTCNStTPA/PC61BM blendbased PSC. In contrast, however, the PTCNStTPA/PC61BM-based PSC VI provided a value of *n* that was lower than that of PSC IV because of its lower values of V_{OC} and FF. We attribute the lower value of V_{OC} of PSC VI to the higher HOMO energy level of PTCNStTPA. Incorporating electron-withdrawing cyano groups not only enhanced the effective intramolecular charge transfer of the polymer backbone but also decreased the hole mobility in PTCNStTPA [23]. Accordingly, PSC VI provided a lower FF.

In addition, the thermal annealing effect on the PV performance of the 2-D PT/PC61BM blend film based PSC was also studied. The photo-active layer of PTStTPA/PC₆₁BM blend film (w/w = 1:1) based PSC VII was thermally annealed above the T_g of the copolymer (140 °C for 10 min). The photocurrent density-voltage plot of PSC VII is shown in Fig. 7. The PV properties of PSC VII are summarized in Table 3. The values of J_{SC} and η of the PSC VII were much greater than those of the PSC V. The enhancement of PV performance of PTStTPA/PC₆₁BM blend based PSC was further investigated by the observation of morphological change of the photo-active layer annealed at 140 °C for 10 min. AFM images of the PTStTPA/PC₆₁BM blend film indicate that a phase-separated interpenetrating network with sizable PC₆₁BM domains was formed after annealing. A certain degree of phase separation might provide better charge separation for the resulting PSC. TEM images of the PTStTPA/ PC₆₁BM blend film after thermal annealed at 80 °C for 1 h or 140 °C for 10 min are shown in Fig. 9. It was found that the PC₆₁BM unit was uniformly distributed in blend film after being annealed at 80 °C for 1 h (Fig. 9(a)). Moreover, the morphology of phase separation became obvious for the blend film annealed at 140 °C for 10 min (Fig. 9(b)). The change in morphology resulted in a large interfacial area for efficient charge generation [68]. Therefore, the photo-current density and photo-conversion efficiency of the PTStTPA/PC₆₁BM blend film based PSC were enhanced significantly after the photo-active layer was thermal annealed at 140 °C for 10 min.



Fig. 8. Topographic (a) and phase (b) images of PTStTPA/PC₆₁BM (1:1, w/w) that had been annealed at 140 °C for 10 min.



Fig. 9. TEM images of PTStTPA/PC_{61}BM (1:1, w/w) ((a) annealed at 80 $^\circ C$ for 1 h (b) annealed at 140 $^\circ C$ for 10 min).

On the other hand, the PV performances of PSCs fabricated from 2-D PTs (PTBPTPA, PTStTPA, and PTCNStTPA) incorporated with the conjugated unit (TBP, St, CNSt) are different from those of PSCs based on TPATh moiety-containing thiophene-derivatized copolymers [35]. Higher values of J_{SC} and η were observed for the thiopene-derivatized copolymer based PSCs. This was attributed to the lower absorption band-gap of the copolymers. Conversely, higher values of V_{OC} were observed for the PTBPTPA, PTStTPA, and PTCNStTPA based PSCs, which was corresponding to the lower HOMO levels of conjugated unit (TBP, St, CNSt) incorporated 2-D PTs.

4. Conclusions

A series of low-band gap, conjugated polymers featuring BP, St, and CNSt units in the polymer backbone in the absence or presence of conjugated TPATh moieties as pendent units were prepared for PSC applications. Incorporating the St and CNSt moieties into the polymer backbone and appending TPATh units induced a high degree of intramolecular charge transfer within the conjugated framework of the polymers, thereby decreasing the band gap energies and red-shifting the maximal UV-Vis absorption wavelengths of the conjugated polymers. CV indicated that the HOMO energy levels of the BP-, St-, and CNSt-based main-chain-type and 2-D PTs were lower than that of P3HT, making them attractive materials for the preparation of PSCs exhibiting higher values of V_{OC}. The low solubility of PTSt and PTCNSt led to phase separation between the polymer and $PC_{61}BM$ in their composite films. As a result, PSCs based on the PTSt/PC₆₁BM and PTCNSt/PC₆₁BM blend films displayed poor PV performance. Notably, the presence of TPATh pendent units enhanced the effective conjugation length and hole mobility of the 2-D PTs, thereby improving the solar light absorption capacity and hole mobility in the photoactive layer of the corresponding PSC. Moreover, the compatibility of the conjugated polymer and PC₆₁BM improved upon appending the TPATh moieties to the polymer backbone. Accordingly, the PV performances of the PSCs based on the TPATh-presenting 2-D PTs were much better than those of the PSCs based on the main-chain-type conjugated polymers.

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Appendix A. Supplementary material

Supplementary material associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.polymer. 2012.07.010.

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