Polythiophenes comprising conjugated pendants toward long-term air-stable inverted polymer solar cells with high open circuit voltages

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A series of polythiophenes (PTs) functionalized with bulky conjugated side chains comprising tert-butyl substituted carbazole (tCz) as an electron donor pendant and bisbenzothiazolylvinyl (DBT) as an electron acceptor pendant were synthesized via Stille copolymerization for polymer solar cell (PSC) applications. We use the descriptors PTtCz, PT(tCz)0.9(DBT)0.1, PT(tCz)0.64(DBT)0.36, PT(tCz)0.45(DBT)0.55, and PTDBT to identify each of these conjugated polymers, with the names denoting the compositions of the bulky pendants. The tunable energy levels of the PTs were accomplished by incorporating both tCz as a donor pendant and DBT as an acceptor pendant, while retaining the low-lying HOMO levels (−5.26 to −5.39 eV). Furthermore, lower bandgaps were observed for the DBT-derived PTs because of stronger donor–π–acceptor characteristics and more efficient intramolecular charge transfer.

Conventional PSCs were fabricated by spin-coating the blend of each PT and the fullerene derivative (PC71BM). The conventional PSC devices exhibited high open circuit voltages \( (V_{oc}) \) of around 0.79–0.91 V. The power conversion efficiency \( (PCE) \) of the PSCs based on PTtCz : PC71BM (w/w = 1 : 2.5) reached 2.48% with a \( V_{oc} \) of 0.91 V, short circuit current \( (J_{sc}) \) of 6.58 (mA cm\(^{-2}\)) and fill factor \( (FF) \) of 41% under the illumination of AM1.5, 100 mW cm\(^{-2}\). Furthermore, a PTtCz/PC71BM-based inverted PSC with ZnO and MoO\(_3\) as an electron extraction layer and a hole extraction layer respectively was capable of retaining ca. 80% of its original efficiency after storage under ambient conditions (without encapsulation) for 1032 h, according to the ISOS-D-1 shelf protocol. The highly durable inverted PSC accompanied by a large \( V_{oc} \) value was achieved for the PT-type polymers.

Introduction

Wet-processing is the main advantage of polymer solar cells (PSC). In this process, the active layer can be manufactured using fast roll-to-roll based methods at a cost that has the potential to be competitive, pending further development.\(^1,^2\) On the basis of the concept of the bulk heterojunction (BHJ) structure, PSCs made by blending poly(3-hexylthiophene) (P3HT) as a donor and fullerene derivative [6,6]-phenyl-C\(_{61}\)/71-structure, PSCs made by blending poly(3-hexylthiophene) with high open circuit voltages \( (V_{oc}) \) of value of about 0.6 V and narrow absorption spectra in the UV-visible region which limited the photocurrent generation of its related BHJ solar cell.\(^3,^4\) In general, the \( V_{oc} \) of a PSC is proportional to the difference between the HOMO of the electron-sufficient polymer and the lowest unoccupied molecular orbital (LUMO) of the electron-deficient fullerene. Lower HOMO levels of the polymers would provide a higher \( V_{oc} \) according to the theoretical prediction. Additionally, conjugated polymers with higher ionization potentials are capable of minimizing the p-doping level under ambient \( O_2 \) and increasing the environmental stability.\(^6,^7\)

Much of the improvement in PSCs can be attributed to the design of novel conjugated polymers with (i) strong and broad visible absorption with high charge carrier mobility to increase the short-circuit current density \( (J_{sc}) \) and (ii) low-lying HOMO levels to achieve large \( V_{oc} \) values. The absorption properties and the energy levels can be modulated by introducing conjugated side chains onto the conjugated polymers.\(^8,^9\) Li and coworkers first studied a PT with conjugated pendants attached that exhibited a broad absorption band in the UV and visible regions, and was capable of harvesting a great amount of solar light.\(^10\) Subsequently, the investigations on PTs comprising
conjugated pendants as side-chains have attracted a great deal of interest.14–19 Our previous studies on conjugated polymers presenting bulky conjugated electron donor moieties as side-chains revealed that the sterically induced twisting of the polymer backbone was responsible for achieving a low-lying HOMO level and enhancing the oxidative stability of conjugated polymers as compared to the parent P3HT.20,21 Larger Voc values of the conjugated PTs functionalized with bulky pendants have been observed in conventional PSCs.15,22–24 Nevertheless, the bulky substituents increase the degree of twisting from planarity in the backbone, resulting in a decreased intramolecular charge transfer and larger optical bandgaps (Eg). To address this issue, the incorporation of electron acceptor pendants on PTs was studied by Wei and coworkers.25–27 The results showed that a lower Eg was obtained due to the presence of the efficient intramolecular charge transfer from the PT backbone to the conjugated acceptor side chain induced by the electron-accepting imidazole moiety.

To systematically investigate the variation of photophysical properties and energy levels via the strategy of developing PTs with covalently attached both electron donor and acceptor pendants, we first synthesized PTs functionalized with various contents of tert-butyl substituted carbazole (tCz) as an electron donor pendant22,28 and dibenzothiazole-ethylvinyl (DBT) as an electron acceptor pendant.27,28 The synthesis, properties and PSC performances of the novel PTs comprising 2-ethylhexyl-substituted quaterthiophene (T) as the conjugated unit in the PT backbone along with different composition ratios of tCz and DBT as bipolar pendant groups were reported in this study (Scheme 1).

According to the literature,29 the optical and electronic properties of the polymers can be easily manipulated through the attachment of electron-withdrawing groups while taking the variation of the acceptor strengths into account. Therefore, one would anticipate further energy level adjustment when the acceptor moiety DBT is incorporated. Depending on the copolymer composition of PTs comprising conjugated pendants, samples such as PTtCz, PT(tCz)0.64(DBT)0.36, PT(tCz)0.45(DBT)0.55, and PTDBT were synthesized and investigated (Scheme 1). To validate the dual-adjustment of the lower-lying HOMO levels and narrow Eg values, UV-vis absorption spectroscopy and cyclic voltammetry (CV) were employed to study the effect of bipolar pendants on the photophysical and electrochemical properties of the PT-based copolymers. We fabricated conventional PSCs by spin-coating the solutions of PT-based copolymers/PC71BM blends, and then the dried films were sandwiched between a transparent anode ITO and cathodes (Ca/Al). The PV performance of these PSCs was studied in terms of the influence of the conjugated pendant groups. Additionally, in order to investigate the important issue of air stability, the PTtCz based inverted devices without encapsulation were tested under ambient conditions for 1032 h, under the ISOS-D-1 shelf measurement.30,31

### Experimental

#### Chemicals

Trimethylstannyl chloride, n-bromosuccinimide, 2-formylthiophene, phosphorous oxychloride, 2,2′-methylene bisbenzothiazole, n-butyl lithium (2.5 M in hexane) and other reagents and chemicals were purchased from Aldrich, Alfa and TCI Chemical Co., and used as received. Dichloromethane (DCM), tetrahydrofuran (THF), dimethylformamide (DMF), toluene, and o-dichlorobenzene (o-DCB) were freshly distilled over appropriate drying agents prior to use, while being purged with nitrogen. The tert-butyl-substituted carbazole-containing moiety (tCz) and 2,2′-methylenebisbenzothiazole substituted moiety (DBT) were synthesized according to Scheme 2. Syntheses of a series of PTs-based donor-acceptor random copolymers via Stille polymerization with various tCz/DBT feed ratios are illustrated in Scheme 3. Compounds 2-(4-ethylhexyl-5-trimethylsilanyltiophen-2-yl)-4,4,5,5-tetramethyl-[1,2,3]dioxaborole (1), diethyl[2,5-dibromothiophen-3-yl]methylphosphonate (2), 5-(4-(3,6-di-tert-9-carbazolyl)phenylthiophene)-2-carbaldehyde (5) and 5,5′- dibromo-3,3′-diethylthiophene-2,2′; 5′,2′; 5′,2″-quater-thiophene were synthesized according to the literature.22,32

#### Synthesis of compound (3)

A mixture of compound (2) (0.58 g, 1.5 mmol), compound (1) (1.21 g, 3.3 mmol), and Pd(PPh3)4 (0.037 g, 0.03 mmol) was dissolved in a degassed mixture of toluene (12 mL) and 2 M K2CO3 (aq.), toluene, reflux, 8 h; (ii) NBS, AcOH, DCM, 0 °C, 1 h; (iii) CH3ONa, DMF, 0 °C, 2 h; (iv) 2-carboxaldehyde, potassium tert-butoxide, THF,0 °C, 1 h; (v) DMF, phosphoryl chloride, dichloroethane, from 0 °C to reflux, 8 h; (vi) 2,2′-methylenebisbenzothiazole, i2, K2CO3, DMF, 60 °C, 6 h.

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**Scheme 1** Synthesis of the conjugated pendants tCz and DBT (i) Pd(PPh3)4, 2M K2CO3 (aq.), toluene, reflux, 8 h; (ii) NBS, AcOH, DCM, 0 °C, 1 h; (iii) CH3ONa, DMF, 0 °C, 2 h; (iv) 2-carboxaldehyde, potassium tert-butoxide, THF,0 °C, 1 h; (v) DMF, phosphoryl chloride, dichloroethane, from 0 °C to reflux, 8 h; (vi) 2,2′-methylenebisbenzothiazole, i2, K2CO3, DMF, 60 °C, 6 h.

**Scheme 2** Syntheses of the conjugated pendants tCz and DBT (i) Pd(PPh3)4, 2M K2CO3 (aq.), toluene, reflux, 8 h; (ii) NBS, AcOH, DCM, 0 °C, 1 h; (iii) CH3ONa, DMF, 0 °C, 2 h; (iv) 2-carboxaldehyde, potassium tert-butoxide, THF,0 °C, 1 h; (v) DMF, phosphoryl chloride, dichloroethane, from 0 °C to reflux, 8 h; (vi) 2,2′-methylenebisbenzothiazole, i2, K2CO3, DMF, 60 °C, 6 h.
K₂CO₃(aq) (12 mL). The solution was stirred at reflux temperature for 48 h, and then poured into methanol (100 mL). The crude product was partitioned between EA and water, and the organic phase was dried (MgSO₄), filtered, and evaporated to dryness. The residue was purified using silica gel chromatography (EA : hexane = 1 : 1) to give a yellow liquid (0.72 g, yield = 63%). ¹H NMR (δ/ppm, CDCl₃): 0.28 (s, 18H), 0.84 (m, 18H), 1.22 (m, 16H), 1.55 (m, 2H), 2.58 (m, 4H), 3.25 (d, J = 6.4 Hz, 2H), 4.02 (m, 4H), 6.76 (d, J = 4.95 Hz, 1H), 7.05 (s, 1H), 7.15 (m, 2H).

Synthesis of compound (4)
Compound (3) (6.22 g, 10 mmol) was dissolved in dry THF (7 mL) and cooled to 0 °C with methanol. The solution was then added dropwise to the compound (3) solution over 15 minutes. A solution of 2-carbadehydethiophene (1.68 g, 15 mmol) in dry methanol (10 mL) was then added to the mixture. After 2 h, the reaction was quenched with methanol. Further purification was performed using silica gel chromatography (hexane as eluent) to give a yellow oil (4.95 g, yield = 67%). ¹H NMR (δ/ppm, 400 MHz, CDCl₃): 0.87 (m, 12H), 1.27 (m, 16H), 1.58 (m, 2H), 2.43 (m, 4H), 3.18 (d, J = 5.2 Hz, 2H), 4.02 (m, 4H), 6.80 (s, 1H), 6.84 (s, 1H), 7.08 (s, 1H).

Synthesis of compound DBT
A mixture of dibenzo[d]thiazol-2-ylmethane (3.11 g, 11 mmol), K₂CO₃ (0.04 g, 0.3 mmol), and I₂ (0.07 g, 0.3 mmol) in 20 mL DMF was stirred under room temperature for 15 minutes. A solution of 2-carbadehydethiophene (1.68 g, 15 mmol) in dry THF (7 mL) was then added to the mixture. After 2 h, the reaction was quenched with methanol. Further purification was performed using silica gel chromatography (hexane as eluent) to give a yellow solid (7.19 g, yield = 66%). ¹H NMR (δ/ppm, 400 MHz, CDCl₃): 0.88 (m, 12H), 1.29 (m, 16H), 1.44 (s, 18H), 1.59 (m, 2H), 2.48 (m, 4H), 6.85 (d, J = 1.2 Hz, 2H), 7.07 (m, 3H), 7.25 (d, J = 8.8 Hz, 1H), 7.28 (d, J = 7.6 Hz, 1H), 7.38 (d, J = 0.8 Hz, 2H), 7.44 (m, 2H), 7.54 (d, J = 9.2 Hz, 2H), 7.77 (d, J = 4 Hz, 2H), 8.12 (t, J = 1.6 Hz, 2H). ESIMS (m/z): calcd for C₇₀H₆₀Br₂NS₄: 1092.26. Found: 1092.4. Anal calcld for C₇₀H₆₀Br₂NS₄: C, 65.98; H, 6.37; N, 1.28. Found: C, 65.72; H, 6.44; N, 1.14%.

Synthesis of compound (6)
A mixture of compound (4) (7.81 g, 10 mmol) and K₂CO₃ (2.76 g, 20 mmol) in 30 mL dry THF was stirred under an ice water bath for 15 minutes. A solution of 2-carbadehydethiophene (1.68 g, 15 mmol) in dry THF (7 mL) was then added to the mixture. After 2 h, the reaction was quenched with methanol. Further purification was performed using silica gel chromatography (hexane as eluent) to give a yellow oil (4.95 g, yield = 67%). ¹H NMR (δ/ppm, 400 MHz, CDCl₃): 0.87 (m, 12H), 1.27 (m, 16H), 1.52 (m, 2H), 2.45 (m, 4H), 6.81 (d, J = 10 Hz, 1H), 6.98 (m, J = 8.4 Hz, 1H), 7.02 (s, 1H), 7.05 (s, 1H), 7.08 (d, J = 3.2 Hz, 1H), 7.14 (s, 1H), 7.19 (d, J = 5.2 Hz, 1H), 7.23 (d, J = 3.6 Hz, 1H).

Synthesis of compound (7)
POCl₃ (7.45 mL, 80 mmol) was added dropwise to freshly distilled DMF (3.09 mL, 40 mmol) at 0 °C under nitrogen atmosphere. Compound 6 (7.39 g, 10 mmol) dissolved in dichloroethane (50 mL) was added dropwise to the above-mentioned POCl₃/DMF complex at room temperature. The reaction mixture was stirred at 80 °C for 3 h. Subsequently, the reaction was cooled to 0 °C and 2 M NaOH aqueous solution was added to quench the reaction. The mixture was partitioned between EA–water, and the organic phase was dried (MgSO₄), filtered, and evaporated to dryness. The residue was purified using silica gel chromatography (EA : hexane = 1 : 1) to give a yellow oil (5.09 g, yield = 77%). ¹H NMR (δ/ppm, 400 MHz, CDCl₃): 0.86 (m, 12H), 1.27 (m, 16H), 1.59 (m, 2H), 2.45 (m, 4H), 6.81 (d, J = 10.4 Hz, 1H), 7.06 (s, 1H), 7.10 (s, 1H), 7.12 (d, J = 2.8 Hz, 1H), 7.23 (d, J = 2.4 Hz, 1H), 7.25 (d, J = 4.0 Hz, 1H), 7.63 (d, J = 5.6 Hz, 1H), 9.89 (s, 1H).

Synthesis of compound fCz
A mixture of compound fCz (7.81 g, 10 mmol) and CH₂ONa (1.78 g, 33 mmol) in 30 mL DMF was stirred under an ice water bath for several minutes. Compound 5 (4.66 g, 10 mmol) was then added to the solution. After 2 h, the reaction was quenched with methanol and a yellow powder was precipitated. Further purification was performed using silica gel chromatography (hexane as eluent) to give a yellow solid (7.19 g, yield = 66%). ¹H NMR (δ/ppm, 400 MHz, CDCl₃): 0.82 (m, 12H), 1.29 (m, 16H), 1.44 (s, 18H), 1.59 (m, 2H), 2.48 (m, 4H), 6.85 (d, J = 1.2 Hz, 2H), 7.07 (m, 3H), 7.25 (d, J = 8.8 Hz, 1H), 7.28 (d, J = 7.6 Hz, 1H), 7.38 (d, J = 0.8 Hz, 2H), 7.44 (m, 2H), 7.54 (d, J = 9.2 Hz, 2H), 7.77 (d, J = 4 Hz, 2H), 8.12 (t, J = 1.6 Hz, 2H). ESIMS (m/z): calcd for C₇₀H₆₀Br₂NS₄: 1092.26. Found: 1092.4. Anal calcld for C₇₀H₆₀Br₂NS₄: C, 65.98; H, 6.37; N, 1.28. Found: C, 65.72; H, 6.44; N, 1.14%.

Synthesis of compound (6)
Synthesis of compound T

A solution of 5,5″-dibromo-3,3″-diethylhexyl-2,2′; 5′,2″; 5″,2‴-quaterthiophene (7.12 g, 10 mmol) in dry THF (150 mL) was stirred at −78 °C under a N₂ atmosphere and then n-BuLi (2.5 M in hexane, 8.40 mL, 21 mmol) was added dropwise to the solution. The solution mixture was maintained at −78 °C with stirring for 1 h, at which point trimethyltin chloride (4.98 g, 25 mmol) in dry THF (5 mL) was added dropwise. The mixture was warmed to room temperature and stirred for 8 h. Subsequently, HCl (1 N) was added to quench the reaction. The resulting mixture was partitioned between EA and water, and the organic phase was dried (MgSO₄), filtered, and evaporated to dryness. The residue was purified using silica gel chromatography (hexane, with 1% TEA) to give a greenish oil (7.13 g, 78%). Gel permeation chromatography (GPC; THF): weight-average molecular weight (Mₚ), 28 875 g mol⁻¹; PDI, 2.93. ¹H-NMR (δ/ppm, 400 MHz, CDCl₃): 0.88 (br, 84H), 1.27–1.30 (br, 64H), 1.46–1.70 (br, 8H), 2.72 (br, 16H), 6.95–7.46 (br, 33H), 7.57 (br, 2H), 7.80 (br, 3H), 7.91 (br, 1H), 8.01 (br, 1H), 8.14 (br, 4H), 8.20 (br, 1H).

Synthesis of PT(Cz)ₐ₀.₆₄(DBT)₀.₃₅

Using the same procedure as that described for the synthesis of PT(Cz), the reaction of fCz (0.40 g, 0.37 mmol), DBT (1.16 g, 1.13 mmol), and T (1.32 g, 1.5 mmol) gave a dark-red solid (65%). GPC: Mₚ, 29 616 g mol⁻¹; PDI, 3.49. ¹H-NMR (δ/ppm, 400 MHz, CDCl₃): 0.89 (br, 84H), 1.30–1.34 (br, 64H), 1.57–1.62 (br, 8H), 2.47–2.80 (br, 16H), 6.90–7.31 (br, 18H), 7.77 (br, 1H), 7.88 (br, 1H), 7.98 (br, 1H), 8.17 (br, 1H).

Characterization of copolymers

¹H-NMR (400 MHz) spectra were recorded using a Varian Unity Inova spectrometer. The average molecular weights of the polymers were measured by means of GPC on a Waters chromatography system (717 plus Autosampler) equipped with two Waters Styragel linear columns. Polystyrene standards were used, with THF as the eluent. The glass transition temperature (Tₘ) and thermal decomposition temperature (Tₐ₀, the temperature at which weight loss reaches 5%) of the copolymers were determined by means of differential scanning calorimetry (TA Instruments, DSC-2010) and thermogravimetric analysis (TA Instruments, TGA-2050), respectively. Both analyses were performed under N₂ atmosphere at a scanning rate of 20 °C min⁻¹. The absorption spectra were measured using a Hitachi U3101 UV-Vis spectrometer. Fluorescence spectra were measured using a Varian Cary Eclipse luminescence spectrometer. Dilute o-DCB solutions of the PTs were filtered through a 0.45 μm filter to remove insoluble materials before spectral measurements. Redox potentials of the polymers were determined with a CHI 611D electrochemical analyser (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 ethyl acetate and then dried at 60 °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. CV curves were calibrated using ferrocene as the standard, whose HOMO level is set at −4.8 eV with respect to zero vacuum level. The Eₘᵋᵣₚₜ of ferrocene/ferrocenium⁺ is 0.36 V in Bu₄NClO₄/MeCN solution (0.1 M). The HOMO energy levels were obtained from the equation: HOMO = −e(Eₘᵋᵣₚₜ − Eₘᵋᵣₚₜ, ferrocene + 4.8) (eV). The
LUMO levels of the polymer were obtained from the equation:

\[ \text{LUMO} = -e\left(\varepsilon_{\text{onset}}^{\text{red}} - \varepsilon_{\text{onset,ferrocene}}^{\text{red}} + 4.8\right) \text{(eV).} \]

Fabrication and characterization of PSCs

All the conventional PSCs in this study were based on a structure like the indium tin oxide (ITO)-coated glass/ hole-transporting material (HTM)/ photoactive layer/Ca (30 nm)/Al (100 nm) structure, in which the photoactive layer consisted of an interpenetrating network of PTs/PC71BM. The ITO substrates (obtained from Sanyo, Japan) were first patterned by lithography, cleaned with detergent, and ultrasonicated in acetone and isopropyl alcohol, dried on a hot plate at 120 °C for 5 min, and finally treated with oxygen plasma for 5 min. PC71BM was purchased from Nano-C and used as received. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, Baytron P-VP AI4083) was filtered through a 0.45 μm filter and spin-coated (1200 rpm, 30 s) onto the PEDOT:PSS layer to prepare the PT/PC71BM composite films. The ITO substrates (obtained from Nagase, Japan) were then placed in a glove box. A solution mixture of PTs-based donor-acceptor random copolymers and PC71BM (10 mg mL⁻¹ in o-DCB) was stirred overnight, then filtered through a 0.2 μm poly(tetrafluoroethylene) (PTFE) filter and spin-coated (1200 rpm, 30 s) onto the PEDOT:PSS layer to prepare the PT/PC71BM composite film-based photo-active layer. The optimal thickness of the active layers obtained under these conditions was ca. 60 nm. Subsequently, the device was completed by depositing ca. (30 nm) and Al (100 nm) under <10⁻⁶ mm-Hg pressure, respectively. The active area of the conventional device was 5 mm². Finally, the cell was encapsulated using UV-curing glue (obtained from Nagase, Japan). During the encapsulation process, the UV-glue was dispensed onto the edge of a piece of glass in the air. The UV-glue coated glass was transferred to the glove box for covering the PSC device. The device was then sealed by pressing the UV-glue coated glass on top of the device, and the device underwent UV curing (254 nm) for 2 min. Upon device encapsulation, the I–V curves of the PSC devices were measured in an ambient atmosphere at 25 °C using a computer-controlled Keithley 2400 source measurement unit (SMU) equipped with a Peccell solar simulator under AM 1.5G illumination (100 mW cm⁻²). 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. An inverted device of PT/Cz/PC71BM-based film with the structure of ITO/ZnO/PT/Cz:PC71BM/MoO3/Ag, in which ITO acted as the cathode and Ag as the anode, was prepared using the following procedure. A ZnO precursor solution was spin-cast on top of the pre-cleaned ITO-glass substrate. The films were annealed at 150 °C for 1 h in air. The ZnO film thickness was approximately 30 nm, as determined by a profilometer. The ZnO-coated substrates were then placed in a glove box. A photoactive layer, PT/Cz:PC71BM, was fabricated according to the condition for preparing the conventional device. Subsequently, a thin MoO3 layer with a thickness of approximately 7 nm was vacuum-deposited on the top of the photoactive layer with an evaporation rate of 0.1 Å s⁻¹. In addition, the top electrode Ag (50 nm) was thermally-deposited through a shade mask with an effective device area of 3 mm². The use of metal oxides on both sides of the PT/Cz:PC71BM layer would prevent the diffusion of moisture into the active layer. Under ambient atmosphere, the measurements of long-term photovoltaic characteristics of the PT/Cz-derived inverted devices without encapsulation were performed in the same manner as those of the conventional devices as described above.

Results and discussion

Characterization of conjugated polymers

The molar ratios (m/n, Fig. 1) of the PTs were manipulated by controlling the feed ratios of the Cz/DBT conjugation units. In addition, the actual values of m/n were determined from the relative integral areas attributed to the peaks of tCz (7.48–7.50 ppm) and DBT (7.77–7.98 ppm and 8.17 ppm) by 1H NMR spectra. The characteristic signals of Cz and DBT moieties are shown in Fig. 1 and indicated as blue and red arrows, respectively. The copolymer compositions were determined and named according to the actual ratios as indicated by PT/Cz, PTz/DBT. The blue and red arrows indicate the characteristic signals of the tCz and DBT moieties, respectively.
PT(\text{Cz})_{0.9}(\text{DBT})_{0.1},\ PT(\text{Cz})_{0.84}(\text{DBT})_{0.36},\ PT(\text{Cz})_{0.45}(\text{DBT})_{0.55},\ \text{and\ PTDBT.}\ It\ is\ important\ to\ note\ that\ a\ higher\ actual\ m/n\ ratio\ was\ obtained\ despite\ the\ equal\ \text{Cz}/\text{DBT}\ feed\ ratio\ during\ polymerization,\ for\ example\ in\ the\ case\ of\ PT(\text{Cz})_{0.64}(\text{DBT})_{0.36}.\ This\ might\ be\ due\ to\ the\ fact\ that\ the\ relatively\ poor\ solubility\ of\ the\ \text{DBT}\ bulky\ segment\ would\ inhibit\ the\ propagation\ of\ the\ polymer\ chains.\ Furthermore,\ a\ higher\ content\ of\ \text{DBT}-containing\ segments\ would\ also\ lead\ to\ precipitation\ at\ the\ initial\ stages\ of\ polymerization,\ resulting\ in\ better\ propagation\ of\ the\ \text{Cz}-containing\ segment.\ All\ of\ the\ conjugated\ copolymers\ were\ soluble\ in\ common\ organic\ solvents,\ including\ chloroform,\ THF,\ and\ o-DCB.\ In\ general,\ conjugated\ polymers\ exhibit\ poor\ solubility\ due\ to\ strong\ \pi-\pi\ interaction\ between\ planar\ polymer\ backbones.\ Moreover,\ the\ presence\ of\ the\ branched\ 2-ethylhexyl\ side-chains\ is\ effective\ in\ improving\ the\ solubility\ of\ conjugated\ copolymers.\ Using\ GPC\ with\ THF\ as\ the\ eluent\ and\ calibrating\ by\ a\ polystyrene\ standard,\ we\ determined\ the\ weight-average\ molecular\ weights\ \(M_{w}\)\ and\ PDIs\ of\ the\ conjugated\ PTs.\ The\ values\ of\ \(M_{w}\)\ and\ PDIs\ of\ PT(\text{Cz}),\ PT(\text{Cz})_{0.9}(\text{DBT})_{0.1},\ PT(\text{Cz})_{0.64}(\text{DBT})_{0.36},\ PT(\text{Cz})_{0.45}(\text{DBT})_{0.55},\ \text{and\ PTDBT\ were\ (21,421,\ 2.35),\ (41,531,\ 3.49),\ (34,235,\ 3.23),\ (28,875,\ 2.93),\ and\ (29,616,\ 2.29),\ respectively.\}

PTs functionalized with conjugated \text{Cz/DBT} were manifested. Herein, the \text{Cz} and \text{DBT} moieties as pendants in PTs were a feasible strategy to adjust the electron-donating and electron-withdrawing characteristic and more efficient intramolecular charge transfer. As shown in Fig. 2(b), the absorption bands of the PTs as thin films were located between 350 and 650 nm. More red shift of the maximum absorption wavelengths and absorption edges was observed for these polymers as solid films than those in o-DCB. Bandgap energies \(E_{g}\) of the conjugated PTs were determined from the onset wavelengths of their absorption bands. As shown in Table 1, the values of \(E_{g}\) were in the following order: PT(\text{Cz}) (1.97) > PT(\text{Cz})_{0.9}(\text{DBT})_{0.1} (1.96) > PT(\text{Cz})_{0.64}(\text{DBT})_{0.36} (1.90) = PT(\text{Cz})_{0.45}(\text{DBT})_{0.55} (1.90) > PTDBT (1.87) (eV). The \(E_{g}\) decreased with an increasing molar ratio of \text{DBT} in the PTs. In solution, these polymers exhibited absorption edges ranging from 550 to 580 nm which underwent a 50–70 nm red shift in the solid state. Interestingly, the PTDBT film revealed a broad and strong absorption band in the region from 350 to 650 nm, covering the UV and visible regions. This is because the incorporation of the electron-deficient \text{DBT} group results in a smaller \(E_{g}\) of the polymer. With increasing the \text{DBT} contents of the PTs, the stronger donor–\pi–acceptor characteristic and more efficient intramolecular charge transfer between the polymer backbones to conjugated pendants were manifested. Herein, the absorbance edge was extended from 570 to 650 nm for the PTs when the \text{DBT} content was increased to a certain extent. This indicates that using geometric donor–\pi–acceptor conjugated moieties as pendants in PTs is a feasible strategy to adjust the \(E_{g}\) of conjugated polymers. In other words, the photophysical properties can be tailored for the pursuit of better photovoltaic performance via the variation of the molar ratios of conjugated pendants.

**Optical properties of the conjugated polymers**

The normalized UV-vis absorption spectra of the PTs in o-DCB solution and as solid films are shown in Fig. 2. Table 1 summarizes the photophysical properties of the copolymers. As shown in Fig. 2(a), the absorption bands of the PTs in o-DCB ranged from 325 to 600 nm, and each polymer exhibited a single broad absorption band. In general, PTs functionalized with conjugated pendants exhibit two maximum absorption peaks, one in the visible region attributed to the \pi–\pi* transition of the conjugated polymer main chains, and the other in the UV region attributed to the conjugated side chains.\(^{16,35}\) In this study, the PTs functionalized with conjugated \text{Cz/DBT} moieties showed only a single broad absorption peak. This indicates that a high degree of intramolecular conjugation was present within the conjugated frameworks of the polymers when in solution. Due to the electron withdrawing characteristic of the DBT moiety, the maximum absorption band located in the longer wavelength region would generally take place.\(^{27,28}\) Further red-shift of the maximum absorption wavelengths (Table 1) for the copolymer with increasing \text{DBT} content could be due to the stronger donor–\pi–acceptor characteristic and more efficient intramolecular charge transfer.
Electrochemical properties of the conjugated polymers

Since the PV performance of PSCs is closely related to the energy levels of the conjugated polymer, we determined the onset oxidation/reduction potentials of the PTs in air by employing cyclic voltammetry to calculate the HOMO/LUMO energy levels. This onset is defined by the intersection of the extrapolated baseline with the tangent to the inflection point. In Fig. 3, the onset oxidation potentials \( E_{\text{onset}} \) of PT-Cz, PT(tCz)_{0.39}(DBT)_{0.1}, PT(tCz)_{0.64}(DBT)_{0.36}, PT(tCz)_{0.64}(DBT)_{0.55}, and PT-DBT were 0.95, 0.87, 0.85, 0.84, and 0.82 V, respectively. The HOMO energy levels were calculated and listed in the order as follows: PT-Cz, (−3.59) < PT(tCz)_{0.39}(DBT)_{0.1}, (−3.51) < PT(tCz)_{0.64}(DBT)_{0.36}, (−5.29) < PT(tCz)_{0.45}(DBT)_{0.55}, (−5.28) < PT-DBT, (−5.26) (V) (Table 1). These numbers are in an ideal range to ensure better air-stability and larger attainable Voc in the device. The HOMO energy levels were calculated and listed in the order as following: PT-Cz, (−3.13) > PT(tCz)_{0.39}(DBT)_{0.1}, (−3.14) > PT(tCz)_{0.64}(DBT)_{0.36}, (−3.18) > PT(tCz)_{0.45}(DBT)_{0.55}, (−3.21) > PT-DBT, (−3.32) (eV). The electrochemical bandgap energies \( E^0_{\text{ec}} \) were calculated from the differences between the LUMO and HOMO energy levels (Table 1). The variations of electrochemical bandgap energies exhibited the same trend with those of the optical \( E_{\text{opt}} \)s. The lower \( E^0_{\text{ec}} \) values for the PTs with an increasing content of DBT are attributed to the stronger donor–π–acceptor characteristic. The \( E^0_{\text{ec}} \) values of the studied PTs were 0.1–0.3 eV larger than the \( E^0_{\text{opt}} \)s, which is probably due to the presence of the exciton binding energy of conjugated polymers. The HOMO levels of PTs were shifted to low-lying values by ca. 0.48–0.35 eV when compared to that of P3HT. It is known that attachment of the tert-butyl groups on the electrochemically active sites of aromatic amines leads to better electrochemical stability. Additionally, the dihedral angles formed between the 9-position substituted carbazole and benzene plane were approximately 60° along with two bulky tert-butyl group substituents, which inhibit the close π–π aggregation effectively between the polymer main chains. On the other hand, two vicinal benzothiazolyl substituents of donor–acceptor-substituted fluorine fluorophores are nearly perpendicular to each other from X-ray structure analysis. The rigid benzothiazolyl substituents prevent the fluorine molecules from π–π interaction. In this study, the most critical factor in tailoring the oxidation potentials was the incorporation of bulky conjugated pendants capable of twisting adjacent thiophene rings through steric interactions, thereby reducing the π orbital overlapping of PTs backbones and resulting in the deeper HOMO energy levels. This phenomenon was more pronounced in the tCz-derived polymers. Deeper HOMO energy levels were observed while the tCz content was increased. In contrast, a weak acceptor DBT group does not significantly affect the oxidation potentials. However, the attachment of the electron withdrawing group (DBT) onto the polymer backbone also had a positive effect in obtaining lower HOMO energy levels, as compared to the parent P3HT. PTs with an increasing content of DBT were still able to retain satisfactory anti-oxidation stability as compared to the oxygen energy level (−5.2 eV with respect to vacuum). As mentioned previously, the LUMO energy level is strongly influenced by the acceptor moiety. Apparently, the LUMO energy levels decreased with an increasing DBT content of PTs in a significant manner. Indeed,
the tunable energy levels of PTs were accomplished by incorporating both Cz as donor pendants and DBT as acceptor pendants. This approach revealed a molecular design avenue to narrow the bandgap energies while retaining the low-lying HOMO levels.

**PV properties of PSCs based on PT/PC_{71}BM films**

PSCs were fabricated based on the ITO/PEDOT:PSS (30 nm)/PTs:PC_{71}BM/Ca (30 nm)/Al (100 nm) structure. The optimum PTs/PC_{71}BM blend ratios were found to be 1 : 2.5 (w/w) and 1 : 3.5 (w/w) for PT/Cz-based and other PT-based photoactive films, respectively. Fig. 4 displays the J-V curves of each PTs/PC_{71}BM-based PSC, whereas the essential photovoltaic parameters (V_{oc}, J_{sc}, FF and PCE) are listed in Table 2. The devices based on PTs/PC_{71}BM all exhibited higher V_{oc} values (0.91–0.79 V), when compared with that of PTBTT/PC_{71}BM (0.65 V). These high values of V_{oc} for the PT devices are consistent with their deeper HOMO energy levels. The V_{oc} value was decreased with increasing the DBT content in PTs, which is also consistent with the CV result. As expected, an excellent V_{oc} (0.91 V) value was observed for PT/Cz due to its deep HOMO energy level (−5.39 eV). Among these PT-based photoactive layers, the PT/Cz-based sample exhibited the best PCE (2.48%) because of its higher J_{sc} and largest V_{oc} when compared with other samples in this study. One would have expected to further increase the PCE by introducing a DBT unit into the system. However, the PCE of PTDBT device was significantly limited by its low J_{sc} and V_{oc} despite the fact that the UV-vis absorption spectrum of PTDBT was more red-shifted than that of PT/Cz. The results obtained in the PCE performances prompted us to further investigate the relevance of the charge transport properties of the PTs, which will be addressed in a later section. The lower photocurrent density might result from charge transport-related recombination losses. Additionally, the PCE of PT(Cz)_{0.3}(DBT)_{0.7}/PC_{71}BM (0.89%) was the lowest among these PT-based PSCs. The presence of low molecular-weight fractions in the system (a rather broader PDI value 3.49) for PT(Cz)_{0.3}(DBT)_{0.7} would normally lead to a reduced performance in photovoltaic parameters. It has been demonstrated that the broad molecular weight distributions of PTs are responsible for this dramatic decrease in performance, particularly those with low molecular weight fractions. This phenomenon is caused by distinctly reduced charge carrier (hole) mobility in the donor phase of the devices built from the lower molecular-weight fractions of the PT samples.

**Morphology of the thin films of PT/PC_{71}BM blends**

The performance of a PSC is strongly dependent on the morphology of the conjugated polymer/fullerene derivative composite film. To generate more effective free carriers from bonding excitations and to avoid the recombination of excitons and free carriers, the P/N heterojunction phase must be controlled at the nanoscale level with an interpenetrating network. This is because the diffusion range of the exciton is approximately 10–20 nm. AFM was utilized to investigate the compatibility and morphology of the PT/PC_{71}BM composite films prepared in the same manner as those prepared in the device fabrication (Fig. 5, topographic (a) and phase (b) images). In each case, we observed a phase-separated interpenetrating network with sizable PC_{71}BM domains. The surface roughnesses of the PT/PC_{71}BM films were in the range of 0.21–0.32 nm. The overall small root mean square (RMS) values are probably due to the random conformation of the PTs and the presence of the steric bulky pendants in these PTs. These two factors prohibit the ordered packing of the polymer chains in the solid state. The bulky pendants in the PTs provide sufficient free volume for the PC_{71}BM units to intercalate into the polymer chains. This could permit better compatibility between PC_{71}BM and the polymer chains. In Fig. 5(b), a certain degree of phase separation was observed, which is favorable for efficient formation of free carriers to provide optimal PV properties of PSCs. These results indicate that the compatibility and surface morphology of the PTs/PC_{71}BM films were influenced by the geometric structure of the pendants, but not by the presence of the electron donor or acceptor moieties.

**Space charge limited current hole mobility**

In addition to the morphology, we suspect that the variation of hole mobility might play an important role in influencing the device performance. To evaluate the contribution of polymer mobility, we employed hole-only devices using a high-work-function material, palladium (Pd), as the cathode to block the

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**Table 2** Photovoltaic performances of the PTs/PC_{71}BM-based conventional PSCs

<table>
<thead>
<tr>
<th>PTs</th>
<th>V_{oc} (V)</th>
<th>J_{sc} (mA cm^{-2})</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PT/Cz</td>
<td>0.91</td>
<td>6.58</td>
<td>0.41</td>
<td>2.48</td>
</tr>
<tr>
<td>PT(Cz)<em>{0.3}(DBT)</em>{0.7}</td>
<td>0.82</td>
<td>3.54</td>
<td>0.31</td>
<td>0.89</td>
</tr>
<tr>
<td>PT(Cz)<em>{0.64}(DBT)</em>{0.36}</td>
<td>0.85</td>
<td>5.52</td>
<td>0.35</td>
<td>1.65</td>
</tr>
<tr>
<td>PT(Cz)<em>{0.45}(DBT)</em>{0.55}</td>
<td>0.80</td>
<td>4.93</td>
<td>0.35</td>
<td>1.39</td>
</tr>
<tr>
<td>PDDBT</td>
<td>0.79</td>
<td>5.05</td>
<td>0.33</td>
<td>1.31</td>
</tr>
</tbody>
</table>

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*PTs/PC_{71}BM = 1 : 2.5.*
Where \( \varepsilon_r \) is the dielectric constant of the polymer, \( \varepsilon_0 \) is the permittivity of free space, \( \mu_0 \) is the hole mobility, \( V \) is the voltage applied to the device, and \( L \) is the blend film thickness. The experimental dark-current densities of the PTs devices were measured in the hole-only devices. The applied voltage was corrected for the built-in voltage (\( V_{bb} \)), which was estimated from the difference between the work function and the HOMO energy level of PTs. Based on the slopes from the plots of \( J^{0.5} \) with respect to \( V \) for the corresponding devices, we calculated the field-independent mobilities of the PTtCz, PT(tCz)\(_{0.9\,\text{DBT}\,0.1} \), PT(tCz)\(_{0.64\,\text{DBT}\,0.36}\), and PT(tCz)\(_{0.45\,\text{DBT}\,0.55}\) derived devices to be \( 1.35 \times 10^{-5} \), \( 9.19 \times 10^{-6} \), \( 9.23 \times 10^{-6} \), and \( 4.11 \times 10^{-6} \) (cm\(^2\) V\(^{-1}\) s\(^{-1}\)), respectively. With increasing the tCz content in the PTs, higher hole mobility values were observed, which is consistent with the PCE performance mentioned earlier. This is attributed to the electron-donating character and more efficient \( \pi-\pi^* \) charge transfer of the carbazole moiety, which has been widely used as a hole transport material for organic electronics.\(^{26}\) The increase in hole mobility exerts more influence on the \( J_{sc} \) value of the PTs-derived PSCs than the absorption characteristics. On the contrary, the losing hole mobility and lowering \( J_{sc} \) values were consistent for the PTs with increasing DBT content. The SCLC measurements are in good agreement with the PCE performances. With increasing the DBT content in the PTs, the presence of lower hole mobilities would lead to unbalanced charge transport and hole accumulation. The hole accumulation partially acted as the recombination centers of electron–hole pairs. Subsequently the photocurrent collection efficiency of the respective electrode was restricted.

**Air stability of the PTtCz-derived inverted device**

Our interests in understanding the air stability of our rationally designed low HOMO materials led us to evaluate their PCE degradation with time under ambient conditions. Due to the better environmental stability of the inverted cells,\(^{49-52}\) we further studied the durability of the PTtCz/PC\(_{71}\)BM-based film based on an inverted structure of ITO/ZnO/PTtCz/PC\(_{71}\)BM/MoO\(_3\)/Ag, as shown in Fig. 6(a). The long-term current density-potential characteristics of the PTtCz-derived inverted devices without encapsulation under ambient condition is shown in Table 3. The evaluated photovoltaic characteristics of the PTtCz/PC\(_{71}\)BM-based devices, as a function of elapsed time, are shown in Fig. 6(b). For each set of points in the plot, the average performance parameters of the devices were measured, and the standard deviation was recorded over an extended period of testing, further testifying the uniformity and robustness of the devices. As expected, the low-lying HOMO level of PTtCz (\(-5.39\) eV), which is relatively stable against oxidation in ambient conditions allowed the device to retain ca. 80% of its original efficiency over a period of 1032 h (ISOS-D-1 shelf).\(^{30,31}\) Preliminary results indicate that this new synthetic material exhibited good stability in ambient conditions (defined as 25 °C/RH 50% in general) using an air-stable inverted architecture. Nevertheless, factors such as heat and humidity would affect the OPV performance in long-term practical applications.\(^{39}\) Therefore, further long-term stability investigations are currently underway to understand the performance of inverted devices under outdoor conditions (ISOS-O-1 shelf).\(^{31}\)

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**Fig. 5** AFM tapping mode topographic (a) and phase (b) images of fabricated photoactive PTs/PC\(_{71}\)BM-based blend thin films (1-PTtCz, 2-PT(tCz)\(_{0.9\,\text{DBT}\,0.1} \), 3-PT(tCz)\(_{0.64\,\text{DBT}\,0.36}\), 4-PT(tCz)\(_{0.45\,\text{DBT}\,0.55}\), and 5-PTDBT).
Fig. 6 (a) Architecture of the PT/Cz:PC71BM-based inverted PSC. (b) Summary plots for the long-term photovoltaic performances in ambient condition without encapsulation of the PT/Cz:PC71BM-based inverted PSC.

Table 3 Long-term photovoltaic performances of the PT/Cz:PC71BM-based inverted PSC in ambient conditions without encapsulation

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF</th>
<th>PCE (%)</th>
<th>Efficiency decay (%)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.86</td>
<td>8.43</td>
<td>0.36</td>
<td>2.58</td>
<td>—</td>
</tr>
<tr>
<td>430</td>
<td>0.85</td>
<td>7.67</td>
<td>0.35</td>
<td>2.26</td>
<td>12</td>
</tr>
<tr>
<td>600</td>
<td>0.85</td>
<td>8.30</td>
<td>0.36</td>
<td>2.55</td>
<td>1</td>
</tr>
<tr>
<td>768</td>
<td>0.76</td>
<td>8.13</td>
<td>0.38</td>
<td>1.98</td>
<td>23</td>
</tr>
<tr>
<td>936</td>
<td>0.76</td>
<td>7.68</td>
<td>0.34</td>
<td>2.01</td>
<td>22</td>
</tr>
<tr>
<td>1032</td>
<td>0.77</td>
<td>7.56</td>
<td>0.35</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Based on its original conversion efficiency (0 h).

Conclusion

In conclusion, we synthesized a series of PT-based random copolymers functionalized with different composition ratios of Cz and DBT as bipolar pendant groups via Stille copolymerization. The dual-adjusted strategy towards narrow (1.97 to 1.80 eV) and lower-lying HOMO levels (−5.39 to −5.26 eV) of PTs were accomplished by incorporating both electron donor- and acceptor-DBT pendants onto PTs. As expected, each PTs/PC71BM PSC exhibited significantly high $V_{oc}$ values (0.91 to 0.79 V) in the conventional device fabrication. The PSC based on PT/Cz:PC71BM (w/w = 1 : 2.5) reached a PCE of 2.48% under the illumination of AM 1.5, 100 mW cm$^{-2}$, along with a $V_{oc}$ of 0.91 V, a $J_{sc}$ of 6.58 mA cm$^{-2}$, and a FF of 41%. An inverted PSC without encapsulation based on PT/Cz:PC71BM as a photoactive layer, was capable of retaining ca. 80% of its original efficiency for 1032 h, according to the ISOS-D-1 shelf protocol. The excellent $V_{oc}$ value for a long-term air stable inverted PSC based on a PT-type polymer using PCBM as an acceptor was achieved in this study.

Acknowledgements

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Notes and references


