

Structural Tuning of Low Band Gap Intermolecular Push/Pull Side-chain Polymers for Organic Photovoltaic Applications*

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Abstract A series of novel low band gap donor-acceptor (D-A) type organic co-polymers (**BT-F-TPA**, **BT-CZ-TPA** and **BT-SI-TPA**) consisting of electron-deficient acceptor blocks both in main chains (**M1**) and at the pendant (**M2**) were polymerized with different electron rich donor (**M3–M5**) blocks, *i.e.*, 9,9-dihexyl-9H-fluorene, *N*-alkyl-2,7-carbazole, and 2,6-dithiinosilole, respectively, *via* Suzuki method. These polymers exhibited relatively low band gaps (1.65–1.88 eV) and broad absorption ranges (680–740 nm). Bulk heterojunction (BHJ) solar cells incorporating these polymers as electron donors, blended with [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) or [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) as electron-acceptors in different weight ratios were fabricated and tested under 100 mW/cm² of AM 1.5 with white-light illumination. The photovoltaic device containing donor **BT-SI-TPA** and acceptor PC₇₁BM in 1:2 weight ratio showed the best power conversion efficiency (PCE) value of 1.88%, with open circuit voltage (V_{oc}) = 0.75 V, short circuit current density (J_{sc}) = 7.60 mA/cm², and fill factor (FF) = 33.0%.

Keywords Polymer solar cells; Low band gap; Conducting polymers; Charge transfer; Donor-acceptor; Bulk heterojunction solar cell

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INTRODUCTION

Over the past decade, the development of organic solar cells based on polymers has attracted intense research interests due to their unique advantages of low cost, light weight, and compatibility of making flexible and large area devices^[1–3]. Bulk heterojunction (BHJ) structure is considered as one of the most promising candidates for next generation of large area, low-cost solar cell, which can be processed by solution-processing techniques^[4]. Recent advances in the structural tuning through functional groups of D-A moiety in polymer networks proved to be an effective way to reduce the band gap of the polymers^[5–41]. Furthermore the energy offset between the highest occupied molecular orbital level (HOMO) and the lowest unoccupied molecular orbital levels (LUMO) played a key role for their net open circuit voltage (V_{oc}) and driving force for excitation dissociation^[17–19]. In addition the increase in PCE values to 11%^[5] and the large-area fabrication techniques through roll-to-roll model^[6] have increased the interest of research community; however for the future commercialization, the efficiency and lifetime must be improved further at lower cost. Typical donor units which originate from

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electron-donating compounds such as benzo[1,2-b:4,5-b']dithiophene, cyclopenta[2,1-b:3,4-b']dithiophene, dithieno[3,2-b:2',3'-d]silole, 2,7-carbazole, triphenylamine derivatives, dithieno[3,2-b:2',3'-d]pyrrole, 9,9-dialkyl-9H-fluorene *etc.* have been copolymerized with strong acceptors such as 2,1,3-benzothiadiazole (BTZ) and its derivatives^[29–39] including ours^[40, 41] designed architectures comprising electron-acceptor groups at the pendant and electron-donors in the main-chain or vice versa, which had the unique advantages of allowing charge separation through sequential transfers of electrons from the main-chains to the side-chains and then to PC₆₁/71BM to achieve high performances. In addition to the applications of these existing donors, it remains still a great challenge to explore D-A copolymers with different architectures of donor and acceptors to gain further understanding of the structure-property relationships to improve the performances of such polymers. Moreover the utilizations of electron-deficient conjugated building blocks both in main chain and pendent along with those electron-rich conjugated building blocks would further endorse the optimization of the intrinsic properties as *p*-type semiconductors in organic solar cells.

In this paper, we report the synthesis and characterization of three novel low band gap acceptor-donor-acceptor (A-D-A) type conjugated polymers (**BT-F-TPA**, **BT-CZ-TPA** and **BT-SI-TPA**) where two acceptor units, (1) benzothiadiazole with two symmetric hexylthiophene units (**M1**) and (2) triphenylamine derivative (**M2**) bearing electron-withdrawing cyano- and dicyano-vinyl pendants were co-polymerized with three different electron-rich donor blocks, 9,9-dihexyl-9H-fluorene (**M3**), *N*-alkyl-2,7-carbazole (**M4**) and 2,6-dithinosilole (**M5**) respectively *via* Suzuki/Stille polymerization (see Fig. 1 and Scheme 1). These highly electron-rich donor

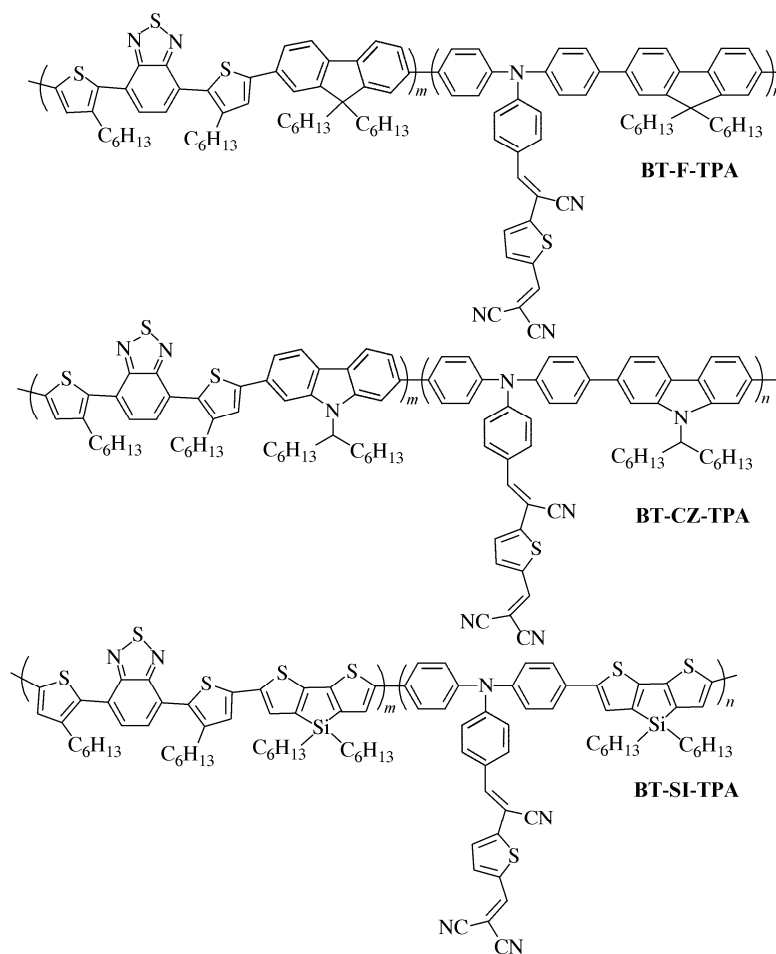
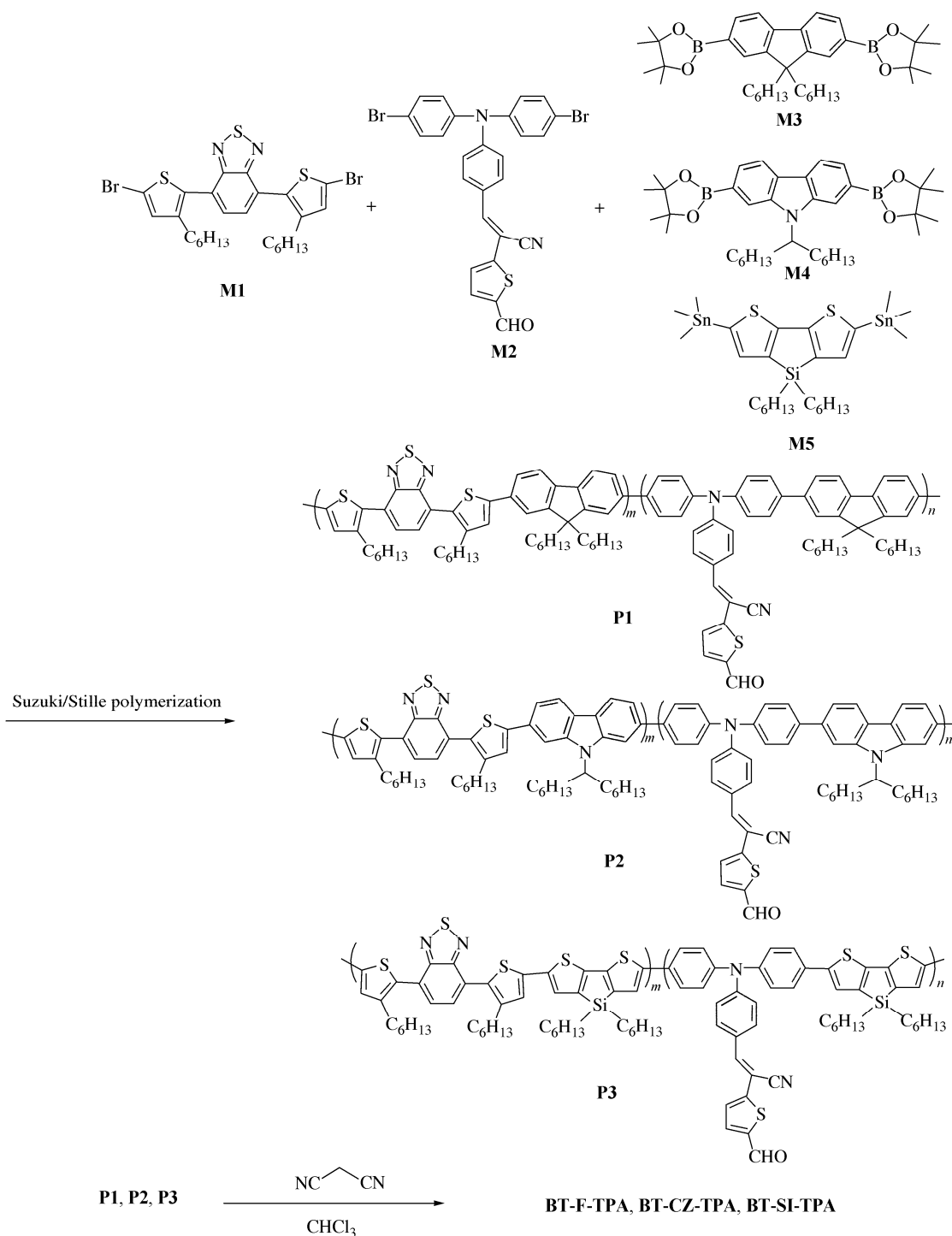


Fig. 1 Structure of co-polymers (**BT-F-TPA**, **BT-CZ-TPA** and **BT-SI-TPA**)



Scheme 1 Synthetic routes of co-polymers (**BT-F-TPA**, **BT-CZ-TPA** and **BT-SI-TPA**)

groups (**M3–M5**), including triphenylamine derivative (**M2**) both in the main-chain and pendant of copolymers endowed with tuned HOMO and LUMO levels and led to high values of V_{oc} and short circuit current density (J_{sc}) respectively. Furthermore the electron deficient benzothiadiazole and dicyanovinyl in the main chain and pendant respectively enriched its intermolecular charge transfer characteristics. This led to strong and broad absorption

spectra to obtain superior harvesting of sunlight from solar-terrestrial radiation. In addition, solution processed BHJ polymer solar cell (PSC) devices composed of an active layer of electron-donor polymers blended with electron-acceptor PC₆₁BM or PC₇₁BM were developed and their photovoltaic properties were investigated as well.

EXPERIMENTAL

Materials

All the used chemicals in this work were purchased from Aldrich, ACROS, TCI, Strem, Fluka, and Lancaster Chemical Co. Tetrahydrofuran (THF) and dichloromethane were distilled over sodium/benzophenone and calcium hydride respectively. Tetra-*n*-butyl ammonium hexafluorophosphate (TBAPF₆) was recrystallized twice from absolute ethanol and further dried for two days under vacuum. The other chemicals were used without further purification. Chromatography was performed with Merck silica gel (mesh 70–230) and basic aluminum oxide, deactivated with water and ethanol.

Measurements and Characterization

Varian Unity 300 MHz spectrometer was used to measure ¹H- and ¹³C-NMR spectra. Elemental analyses were performed on a HERAEUS CHN-OS RAPID elemental analyzer. Thermogravimetric analyses (TGA) were conducted on a Perkin Elmer Pyris 1 analyzer at a heating rate of 10 K/min under nitrogen (100 mL/min) atmosphere. Gel permeation chromatographic (GPC) analysis was performed with a Water 1515 separations module using polystyrene as a standard and THF as an eluent (flow rate: 1 mL/min, concentration: 1 mg/mL in THF). Optical absorption studies were carried out at 300 K using a dual beam UV-Vis spectrophotometer, Shimadzu UV-1800 in dilute THF solutions (10^{−6} mol/L). Solid films of UV-Vis spectra measurements were spin-coated on a glass substrate from THF solutions with a concentration of 10 mg/mL. Cyclic voltammetry (CV) measurements were performed at room temperature using a BAS 100 electrochemical analyzer with a standard three-electrode electrochemical cell in a 0.1 mol/L tetra-*n*-butyl ammonium hexafluorophosphate (TBAPF₆) solution (in acetonitrile) at room temperature with a scanning rate of 100 mV/s. During the CV measurements, the solutions were purged with nitrogen for 30 s. In each case, a carbon working electrode coated with a thin layer of polymers, a platinum wire as the counter electrode, and a silver wire as the quasi-reference electrode were used, and Ag/AgCl (3 mol/L KCl) electrode served as a reference electrode for all potentials quoted herein. The redox couple of ferrocene/ferrocenium ion (Fc/Fc⁺) was used as an external standard. The corresponding HOMO and LUMO levels were calculated using $E_{\text{ox,onset}}$ and $E_{\text{red,onset}}$ for experiments in solid films of polymers, which were performed by drop-casting films with similar thickness from THF solutions (*ca.* 5 mg/mL). Atomic force microscopy (AFM) images of the thin films (on glass substrates) were obtained using a Digital Instruments NS 3a controller and a D3100 stage.

Fabrication of Polymer Solar Cells

The PSCs in this study were composed of an active layer of blended polymers (polymer:PC_{61/71}BM) in solid films, which was sandwiched between a transparent indium tin oxide (ITO) anode and a metal cathode. Prior to the device fabrication, ITO-coated glass substrates (1.5 cm × 1.5 cm) were ultrasonically cleaned in detergent, deionized water, acetone, and isopropyl alcohol. After routine solvent cleaning, the substrates were treated with UV ozone for 15 min. Then a modified ITO surface was obtained by spin-coating a layer of poly(ethylene dioxythiophene):polystyrenesulfonate (PEDOT:PSS) (~30 nm). After baking at 130 °C for 1 h, the substrates were transferred to a nitrogen-filled glove-box. Then, on the top of PEDOT:PSS layer, the active layer was prepared by spin-coating the blended solutions of polymer:PC₆₁BM (with 1:1, *W:W*) and **BT-SI-TPA**:PC₇₁BM (with 1:1, 1:2, 1:3 and 1:4, *W:W*) subsequently. At spin rate *ca.* 1000 r/min for 60 s, thickness *ca.* 80 nm of the active layer was maintained. Initially, the blended solutions were prepared by dissolving both polymers and PC_{61/71}BM in 1,2-dichlorobenzene (20 mg/mL), followed by continuous stirring for 12 h at 50 °C. In the slow-growth approach, blended polymers in solid films were kept in the liquid phase after spin-coating in the high

boiling solvent. Finally, a calcium layer (30 nm) and a subsequent aluminum layer (100 nm) were thermally evaporated through a shadow mask at a pressure below 7.99×10^{-4} Pa. With an active area of the device 0.12 cm^2 , all PSC devices were prepared and measured under ambient conditions. The solar cell measurements were conducted inside a glove box under simulated AM 1.5 G irradiation (100 mW/cm^2) using a Xenon lamp based solar simulator (Thermal Oriel 1000W). The external quantum efficiency (EQE) spectra were obtained at short-circuit conditions. The light source was a 450 W Xe lamp (Oriel Instrument, model 6266) equipped with a water-based IR filter (Oriel Instrument, model 6123NS). The light output from the monochromator (Oriel Instrument, model 74100) was focused on the photovoltaic cell under test.

Fabrication of Hole- and Electron-only Devices

The hole- and electron-only devices were fabricated by blending films polymers:PC₆₁BM sandwiched between the transparent ITO anode and cathode. The devices were prepared following the same procedure as the fabrication of the BHJ devices except that in the hole-only devices, Ca was replaced by MoO₃ with work function (Φ) of 5.3 eV and in the electron-only devices, the PEDOT:PSS layer was replaced by Cs₂CO₃ with (Φ) of 2.9 eV. In the hole-only devices, MoO₃ was thermally evaporated to a thickness of 20 nm and then capped with 50 nm of Al on top of the active layer. In the electron-only devices, Cs₂CO₃ was thermally evaporated with a thickness of approximately 2 nm on top of the transparent ITO. For both devices, annealing of the active layer was performed at 130 °C for 20 min. The space-charge limited current (SCLC) method was used to evaluate the hole and electron mobilities of the polymer blend films of **BT-F-TPA/BT-CZ-TPA**:PC₆₁BM by fabricating the hole and electron-only devices. The electron and hole mobilities were determined precisely by fitting the plots of the dark current versus voltage (J - V) curves for single-carrier devices to the SCLC model. The dark current is given by:

$$J = 9 \epsilon_0 \epsilon_r \mu V^2 / (8L^3)$$

where $\epsilon_0 \epsilon_r$ is the permittivity of the polymer, μ is the carrier mobility, and L is the device thickness.

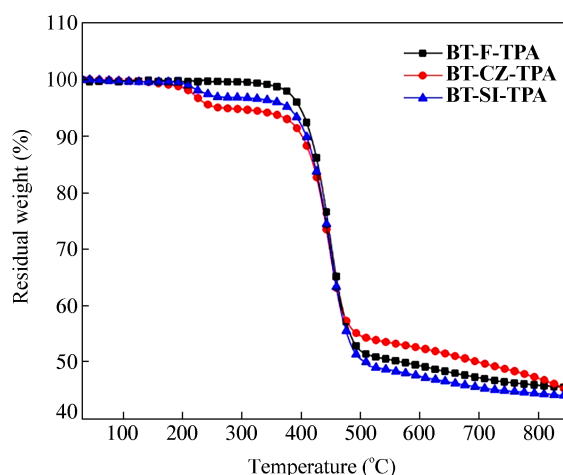
Synthesis of Monomers and Polymers

The general syntheses of monomers **M1–M5** were carried out by known literature procedure^[40–44] and the synthetic routes of polymers (**BT-F-TPA**, **BT-CZ-TPA** and **BT-SI-TPA**) and their structures are shown in Scheme 1 and Fig. 1, respectively. Monomers (**M1–M5**) were satisfactorily characterized by ¹H-NMR, ¹³C-NMR, MS spectroscopy, and elemental analyses. As shown in Scheme 1, polymer precursors **P1** and **P2** were prepared by the well-known Pd(0) catalyzed Suzuki polymerization of monomer **M1**, **M2** and diboronic esters of *N*-9,9-dihexyl-9H-fluorene (**M3**) and alkyl-2,7-carbazole respectively, and polymer precursor **P3** was synthesized by Pd(0) catalyzed Stille polymerization of **M1**, **M2** and **M5**. Furthermore, to increase the stability of polymers, end-capping reactions were carried out on all polymers. The obtained polymers were further purified by washing in Soxhlet apparatus using hexane and acetone, and later extracted by chloroform. The chloroform fraction was concentrated to 40–50 mL under reduced pressure, precipitated in methanol, filtered through 0.45 μm nylon filters, and finally dried under reduced pressure at room temperature. After purification and drying, all polymers were found as black solids with good yields. Condensations of aldehydes in polymer precursors **P1**, **P2** and **P3** with excess of malonitrile in chloroform solutions in the presence of pyridine afforded the corresponding polymers **BT-F-TPA**, **BT-CZ-TPA** and **BT-SI-TPA** in good yields. The molecular weights of polymers **BT-F-TPA**, **BT-CZ-TPA** and **BT-SI-TPA** were determined by gel permeation chromatography (GPC) against monodisperse polystyrene standards in THF and are summarized in Table 1. The number-average molecular weights (M_n) and the weight-average molecular weights (M_w) obtained in polymers (**BT-F-TPA**, **BT-CZ-TPA** and **BT-SI-TPA**) were in the range of 12.04–15.63 and 20.46–24.37 kg/mol, respectively and the polydispersity indices ($\text{PDI} = M_w/M_n$) found were in the range 1.55–1.62. The thermal properties of these polymers determined by thermogravimetric analysis (TGA) are summarized in Table 1 and obtained primary thermograms are shown in Fig. 2. The TGA thermograms of polymers **BT-F-TPA**, **BT-CZ-TPA** and **BT-SI-TPA** showed the decomposition temperatures (T_d with 5% weight loss) at 401, 365 and 376 °C, respectively.

Table 1 Molecular weights and thermal properties of polymers

Polymer	$M_n^a \times 10^{-3}$	$M_w^a \times 10^{-3}$	PDI ^a	T_d^b (°C)
BT-F-TPA	12.04	20.46	1.62	401
BT-CZ-TPA	15.63	24.37	1.55	365
BT-SI-TPA	13.26	21.14	1.59	376

^a Molecular weights and polydispersity were measured by GPC, using THF as an eluent, polystyrene as a standard. M_n , number-average molecular weight; M_w , weight-average molecular weight; ^b Temperature (°C) at 5% weight loss measured by TGA at a heating rate of 10 K/min under nitrogen

**Fig. 2** TGA thermograms of polymers (**BT-F-TPA**, **BT-CZ-TPA** and **BT-SI-TPA**)

4,7-Bis(5-bromo-4-hexyl-2-thienyl)-2,1,3-benzothiadiazole (**M1**)

Red solid (Yield: 94%). ¹H-NMR (300 MHz, CDCl₃, δ): 7.75 (s, 2H), 7.71 (s, 2H), 2.63 (t, J = 7.2 Hz, 4H), 1.67 (m, 4H), 1.33–1.40 (m, 12H), 0.89 (t, J = 7.1 Hz, 6H). ¹³C-NMR (75 MHz, CDCl₃, δ): 152.19, 143.01, 138.46, 128.03, 125.25, 124.80, 111.59, 31.62, 29.74, 29.67, 28.96, 22.64, 14.11. MS (FAB): m/z [M^+] 626, Calcd. m/z [M^+] 626.53. Element Anal. Calcd. for C₂₆H₃₀Br₂N₂S₃ (%): C, 49.84, H, 4.83, N, 4.47; Found: C, 49.62, H, 5.02, N, 4.62.

3-(4-(Bis(4-bromophenyl)amino)phenyl)-2-(5-formylthiophen-2-yl)acrylonitrile (**M2**)

Yellowish crystal (Yield: 64%). ¹H-NMR (300 MHz, CDCl₃, δ): 9.90 (s, 1H), 8.02 (d, J = 4.2 Hz, 1H), 7.97 (s, 1H), 7.89 (d, J = 8.7 Hz, 2H), 7.57–7.54 (m, 5H), 7.08 (d, J = 9 Hz, 4H), 7.02 (d, J = 8.7 Hz, 2H). ¹³C-NMR (75 MHz, CDCl₃, δ): 182.7, 150.2, 149.1, 145.2, 142.7, 142.5, 137.2, 133.1, 131.6, 127.4, 127.3, 127.0, 126.3, 121.4, 118.1, 116.9, 102.2. MS (FAB): m/z [M^+] 563, Calcd. m/z [M^+] 561.94. Element Anal. Calcd. for C₂₆H₁₆Br₂N₂OS (%): C, 55.34, H, 2.86, N, 4.96; Found: C, 55.41, H, 3.36, N, 4.92.

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene (**M3**)

White solid (Yield: 75%). ¹H-NMR (300 MHz, CDCl₃, δ): 7.70–7.81 (m, 6H), 1.39 (s, 24H), 1.01–1.11 (m, 12H), 0.72–0.76 (t, J = 6.9 Hz, 6H). ¹³C-NMR (75 MHz, CDCl₃, δ): 150.45, 143.89, 133.62, 128.89, 119.35, 83.69, 55.16, 40.07, 31.76, 29.91, 24.92, 23.57, 22.57, 14.05. MS (FAB): m/z [M^+] 586, Calcd. m/z [M^+] 586.44. Anal. Calcd. for C₃₇H₅₆B₂O₄ (%): C, 75.78, H, 9.62; Found: C, 75.81, H, 9.51.

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-(tridecan-7-yl)-9H-carbazole (**M4**)

White solid (Yield: 87%). ¹H-NMR (300 MHz, CDCl₃, δ): 8.61 (br, 1H), 8.41 (br, 1H), 8.19 (d, J = 7.8 Hz, 1H), 8.14 (t, J = 8.1 Hz, 2H), 8.09 (d, J = 7.7 Hz, 1H), 4.50 (m, 1H), 2.30 (m, 2H), 1.62 (m, 2H), 1.18 (br, 12H), 1.17 (br, 12H), 1.02 (br, 16H), 0.86 (t, J = 7.1 Hz, 6H). ¹³C-NMR (75 MHz, CDCl₃, δ): 142.81, 139.42, 127.59, 126.94, 125.77, 125.57, 125.44, 121.06, 120.67, 118.66, 118.62, 116.26, 116.22, 83.81, 83.79, 56.82, 34.20, 32.18, 29.60, 27.10, 25.09, 23.03, 14.39. MS (FAB): m/z [M^+] 601, Calcd. m/z [M^+] 601. Anal. Calcd. for C₃₇H₅₇B₂NO₄ (%): C, 73.88, H, 9.55, N, 2.33; Found: C, 73.79, H, 9.52, N, 2.51.

5,5'-Bis(trimethylstannyl)-3,3'-dihexylsilylene-2,2'-bithiophene (M5)

Yellow-brown residue was formed, which was used for the next step without further purification (Yield: 90%). ¹H-NMR (300 MHz, CDCl₃, δ): 7.10 (s, 2H), 1.28 (m, 16 H), 0.88 (m, 10H), 0.39 (s, 18H). ¹³C-NMR (75 MHz, CDCl₃, δ): 155.20, 143.30, 137.86, 125.03, 33.13, 31.65, 24.47, 22.83, 14.34, 12.20, 7.88. Anal. Calcd. for C₂₆H₄₆S₂SiSn₂ (%): C, 45.37, H, 6.74; Found: C, 45.46, H, 6.53.

Polymerization procedures for polymer precursors P1 and P2

Polymerization steps for **P1** and **P2** were carried out through the palladium(0)-catalyzed Suzuki coupling reactions. In a 50 mL flame dried two-neck round bottom flask, 1 equiv. of **M1**, 1 equiv. of **M2** and 1 equiv. of **M3/M4** and Pd(PPh₃)₄ (1.5 mol%) were dissolved in a mixture of toluene (monomer = 0.5 mol/L) and 2 mol/L Na₂CO₃ (3:1, *V:V*). The solution was first kept under a nitrogen atmosphere and vigorously stirred at 90–95 °C for 3 days. After completion of the reaction, an excess of bromobenzene was added to the reaction and after 1 h, excess of phenylboronic acid was added and the reaction refluxed overnight to complete the end-capping reaction. The polymer was purified by precipitation in methanol/water (10:1, *V:V*), filtered through 0.45 μm nylon filter and washed in Soxhlet apparatus using hexane, acetone and chloroform. The chloroform fraction was reduced to 40–50 mL under reduced pressure, precipitated in methanol/water (10:1, *V:V*, 500 mL), filtered through 0.45 μm nylon filters and finally air-dried overnight.

P1. Black solid (Yield: 71%). ¹H-NMR (CDCl₃, δ): 9.88 (s, 1H), 8.07–8.00 (m, 2H), 7.91–7.78 (m, 8H), 7.68–7.26 (m, 16H), 7.23–7.10 (m, 5H), 2.81–2.70 (m, 4H), 2.17–2.06 (m, 12H), 1.74 (m, 8H), 1.40–1.25 (m, 24H), 0.90 (m, 12H), 0.77 (m, 18H). GPC (THF, polystyrene standard): *M*_n = 11.88 kg/mol, *M*_w = 20.98 kg/mol, PDI = 1.76.

P2. Black solid (Yield: 74%). ¹H-NMR (CDCl₃, δ): 9.88 (s, 1H), 8.17–8.13 (m, 8H), 8.00–7.88 (m, 8H), 7.59–7.37 (m, 10H), 7.15–7.12 (m, 5H), 4.66 (m, 2H), 2.88 (m, 8H), 2.38 (m, 6H), 2.00 (m, 8H), 1.55 (m, 8H), 1.16 (m, 24H), 0.88 (m, 24H) (Fig. S1 in supporting information, SI). GPC (THF, polystyrene standard): *M*_n = 15.88 kg/mol, *M*_w = 24.48 kg/mol, PDI = 1.54.

P3. Polymerization steps for **P3** were carried out through the Stille reactions. In a 50 mL flame dried two-neck round bottom flask, 1 equiv. of **M1**, 1 equiv. of **M2** and 1 equiv. of **M5** followed by Pd(PPh₃)₄ (1 mol%) were dissolved in 8 mL of dry toluene and deoxygenated with nitrogen for 30 min. The reaction mixture was stirred at 110 °C for 3 days, and then an excess amount of 2-bromothiophene was added to end-cap the trimethylstannyl groups for 4 h. The reaction mixture was cooled to 40 °C and added slowly into a vigorously stirred mixture of methanol/acetone (3:1, *V:V*). The polymers were collected by filtration and re-precipitation from methanol. The crude polymers were further purified by washing with acetone and ethyl acetate (EA) for 2 days in a Soxhlet apparatus to remove oligomers and catalyst residues. The polymer formed was a black solid (Yield: 65%). ¹H-NMR (CDCl₃, δ): 9.87 (s, 1H), 7.98–7.84 (m, 8H), 7.77–7.69 (m, 7H), 7.43–7.06 (m, 8H), 2.88 (m, 8H), 1.76 (m, 24H), 1.35–1.25 (m, 28H), 0.86 (m, 18H). GPC (THF, polystyrene standard): *M*_n = 12.38 kg/mol, *M*_w = 22.14 kg/mol, PDI = 1.78.

General and synthetic procedures for polymers BT-F-TPA, BT-CZ-TPA and BT-SI-TPA

One equivalent of **P1/P2/P3** and 20 equiv. of malonitrile were dissolved in 20 mL of chloroform followed by some drops of pyridine. The mixture solution was stirred overnight at room temperature and then the resulting mixture was poured into methanol and the precipitate was filtered off and washed with water. The resulted black color polymer was purified by repeated precipitation from its THF solution to methanol.

BT-F-TPA. Black solid (Yield: 71%). ¹H-NMR (CDCl₃, δ): 8.17–8.01 (m, 2H), 7.86–7.41 (m, 10H), 7.23–7.09 (m, 15H), 7.04 (m, 5H), 2.74 (m, 4H), 2.26–2.13 (m, 12H), 1.68 (m, 8H), 1.52–1.25 (m, 24H), 0.88 (m, 12H), 0.74 (m, 18H). GPC (THF, polystyrene standard): *M*_n = 12.04 kg/mol, *M*_w = 20.46 kg/mol, PDI = 1.62.

BT-CZ-TPA. Black solid (Yield: 74%). ¹H-NMR (CDCl₃, δ): 8.09–8.05 (m, 8H), 7.85 (s, 1H), 7.80 (m, 8H), 7.57–7.27 (m, 10H), 7.12–7.01 (m, 5H), 4.72 (m, 2H), 2.48 (m, 6H), 2.24 (m, 8H), 1.88 (m, 6H), 1.51 (m, 10H), 1.09 (m, 24H), 0.82 (m, 24H) (Fig. S1 in SI). GPC (THF, polystyrene standard): *M*_n = 15.63 kg/mol, *M*_w = 24.37 kg/mol, PDI = 1.55.

BT-SI-TPA. (Yield: 84%). $^1\text{H-NMR}$ (CDCl_3 , δ): 8.01–7.82 (m, 8H), 7.44–7.21 (m, 8H), 7.18–7.02 (m, 8H), 2.79 (m, 8H), 1.64 (m, 24H), 1.28–1.11 (m, 28H), 0.81 (m, 18H). GPC (THF, polystyrene standard): $M_n = 13.26$ kg/mol, $M_w = 21.14$ kg/mol, PDI = 1.59.

RESULTS AND DISCUSSION

Optical Properties

In order to investigate the optical properties of donor-acceptor (D-A) polymers (**BT-F-TPA**, **BT-CZ-TPA** and **BT-SI-TPA**), UV-Vis spectroscopic studies were performed in THF solvent both for solution states and solid films. Figures 3(a) and 3(b) show the normalized UV-Vis absorption spectra of polymers in THF solutions (10^{-6} mol/L) and solid films, respectively, and the obtained data are tabulated in Table 2. In solution state polymers **BT-F-TPA**, **BT-CZ-TPA** and **BT-SI-TPA** showed two absorption peaks (see Fig. 3a), where one peak at 365 nm (**BT-F-TPA**), 363 nm (**BT-CZ-TPA**) and 369 nm (**BT-SI-TPA**) in each case was attributed to the π - π^* transition of their conjugated polymer backbones. The second absorption peak was observed at 496 nm (**BT-F-TPA**), 505 nm (**BT-CZ-TPA**) and 519 nm (**BT-SI-TPA**) respectively. The above two absorption peaks correspond to the intramolecular charge transfer (ICT) interactions between their polymer donors and acceptor segments^[40, 41]. Compared with other polymers, **BT-SI-TPA** had higher absorption maxima (λ_{max}) and broader absorption onset (λ_{onset}), which is attributed to combination of the electron rich thiophene and the electron-deficient silole in the main chain and thus produces a strong donor-acceptor (D-A)-type interaction in that system^[45, 46]. In comparison to solutions the UV-Vis absorption spectra of polymers in solid films were bathochromically shifted (14–29 nm), and this could be attributed to the interchain associations and aggregations in solid films^[42, 47]. Among these polymers (**BT-F-TPA**, **BT-CZ-TPA** and **BT-SI-TPA**), **BT-SI-TPA** showed the broadest absorption spectrum and tailed up to 700 nm, which was ascribed to a more extensive delocalization of electrons in the solid state^[48]. The optical band gaps found from λ_{onset} of polymers **BT-F-TPA**, **BT-CZ-TPA** and **BT-SI-TPA** were 1.82, 1.74 and 1.67 eV, respectively. The UV-Vis absorption spectra of the polymer:PC₆₁BM blend had been studied and are shown in Fig. 6. The polymer blend **BT-SI-TPA**:PCBM showed broader absorption spectra with best molar absorption coefficient at 400–700 nm in the active layer than **BT-F-TPA** and **BT-CZ-TPA**, thereby increasing the photon to current conversion efficiency. This result implies that, in order to get enhanced photovoltaic properties, it is an efficient way to tune optical properties of the D-A polymers by incorporating acceptors both in main chain and side-chain to absorb maximum photons from visible regions. Moreover, incorporation of fused aromatic donor segments to the polymer broadens the absorption spectra (as shown in Fig. 3b) so as to induce enhanced photovoltaic properties.

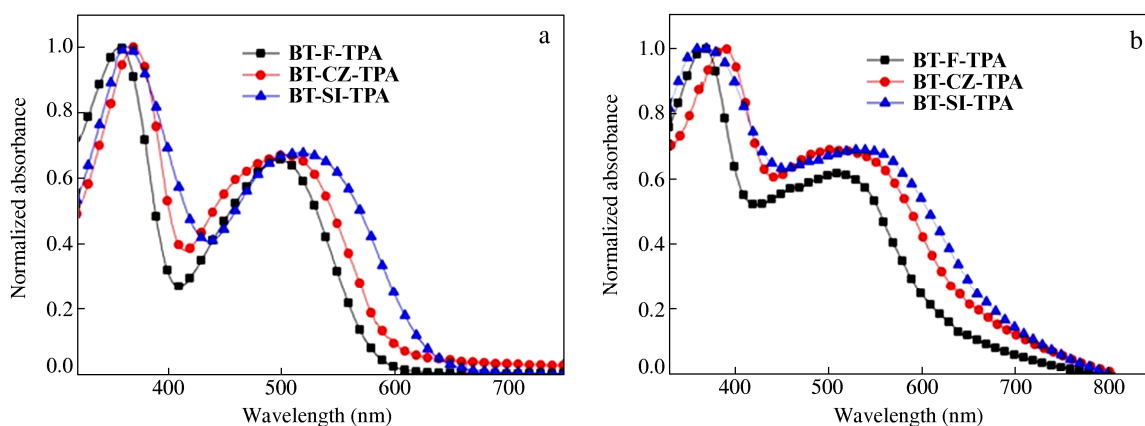


Fig. 3 Normalized UV-Vis spectra of polymers (**BT-F-TPA**, **BT-CZ-TPA** and **BT-SI-TPA**) in (a) dilute THF solutions (1×10^{-6} mol/L) and (b) solid films

Table 2 Optical properties of polymers

Polymer	$\lambda_{\text{abs, sol}}^{\text{a}}$ (nm)	$\lambda_{\text{abs, film}}^{\text{b}}$ (nm)	$\lambda_{\text{onset, film}}$ (nm)	$E_{\text{g}}^{\text{opt, film c}}$ (eV)
BT-F-TPA	365, 496	366, 510	680	1.82
BT-CZ-TPA	369, 505	388, 530	710	1.74
BT-SI-TPA	363, 519	368, 558	740	1.67

^a In THF dilute solutions; ^b Spin coated from THF solutions; ^c The optical band gaps were obtained from the equation $E_{\text{g}}^{\text{opt, film}} = 1240/\lambda_{\text{onset, film}}$.

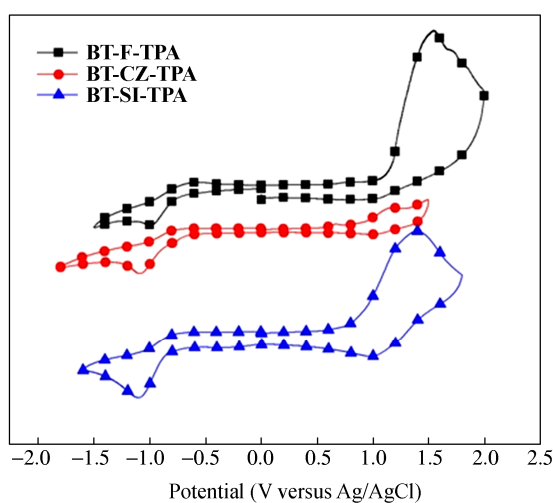
Electrochemical Properties

To probe deeply into the electronic structures, the HOMO and LUMO levels of polymers, CV measurements in solid films were conducted with Ag/AgCl as a reference electrode, calibrated by ferrocene ($E_{1/2(\text{ferrocene})} = 0.45$ mV versus Ag/AgCl). The HOMO and LUMO levels were estimated by the oxidation and reduction potentials from the reference energy level of ferrocene (4.8 eV below the vacuum level) according to the following equation: $\text{HOMO/LUMO} = [-(E_{\text{onset}} - 0.45) - 4.8]$ eV^[49, 50], and the results are summarized in Table 3. As shown in Fig. 4, all polymers (**BT-F-TPA**, **BT-CZ-TPA** and **BT-SI-TPA**) exhibited irreversible oxidation or *p*-doping/de-doping (oxidation/re-reduction) processes with onset oxidation potentials ($E_{\text{ox, onset}}$) 1.11, 0.90 and 0.84 V, respectively. Nevertheless, the *n*-doping/de-doping (reduction/re-oxidation) processes showed irreversible reduction potentials with onset reduction potentials ($E_{\text{red, onset}}$) of −0.77 V (**BT-F-TPA**), −0.85 V (**BT-CZ-TPA**), and −0.81 V (**BT-SI-TPA**), respectively. On the basis of their corresponding $E_{\text{ox, onset}}$ and $E_{\text{red, onset}}$ values, the HOMO/LUMO levels of **BT-F-TPA**, **BT-CZ-TPA** and **BT-SI-TPA** were −5.46/−3.58, −5.25/−3.50, −5.19/−3.54 eV, respectively. As HOMO levels of all the polymers were below the air oxidation threshold, good air stabilities is shown^[51]. The fluorene-containing polymer **BT-F-TPA** has deeper HOMO levels^[52], which later reflected as higher V_{oc} in photovoltaic devices^[15]. The electrochemical band gaps found (see Table 3) were in good agreement with an acceptable range of error to the obtained optical band gaps (see Table 2) and also in the desirable range for use in organic photovoltaic applications.

Table 3 Electrochemical properties of polymers

Polymer	$E_{\text{ox, onset}}^{\text{a}}$ (V)	$E_{\text{red, onset}}^{\text{a}}$ (V)	HOMO ^b (eV)	LUMO ^b (eV)	E_{g}^{cv} (eV)
BT-F-TPA	1.11	−0.77	−5.46	−3.58	1.88
BT-CZ-TPA	0.90	−0.85	−5.25	−3.50	1.75
BT-SI-TPA	0.84	−0.81	−5.19	−3.54	1.65

^a Onset oxidation and reduction potentials measured by cyclic voltammetry in solid films; ^b $\text{HOMO/LUMO} = [-(E_{\text{onset}} - 0.45) - 4.8]$ eV, where 0.45 V is the value for ferrocene versus Ag/Ag⁺ and 4.8 eV is the energy level of ferrocene below the vacuum.

**Fig. 4** Cyclic voltammograms of polymers (**BT-F-TPA**, **BT-CZ-TPA** and **BT-SI-TPA**)

Photovoltaic Properties

We explored the potential applications of D-A polymers (**BT-F-TPA**, **BT-CZ-TPA** and **BT-SI-TPA**) in PSCs by fabricating BHJ photovoltaic devices with a configuration of ITO/PEDOT:PSS (30 nm)/polymer:PC₆₁BM blend (~80 nm)/Ca (30 nm)/Al (100 nm). The polymer solutions for the active layer were prepared by blending polymers (**BT-F-TPA**, **BT-CZ-TPA** and **BT-SI-TPA**) and PC₆₁BM in a weight ratio of 1:1 initially, and the active layer compositions were modified later by various weight ratios of the best-performing molecule (**BT-SI-TPA**) blending with PC₆₁BM (owing to its broader absorption and higher absorption coefficient, relative to PC₆₁BM)^[53]. Table 4 lists the photovoltaic properties (V_{oc} , J_{sc} , FF and PCE) of the PSC devices based on **BT-F-TPA**, **BT-CZ-TPA** and **BT-SI-TPA** with PC₆₁BM at 1:1 weight ratio. As discussed earlier the V_{oc} values of polymers, which are dependent on the energy levels of the active layer components^[15], correlate well with the cyclovoltametric results, *i.e.*, polymers with lower HOMO values (−5.46 eV) have higher V_{oc} values and vice versa (see Fig. 5, Table 4). Thus polymer **BT-F-TPA** with the lowest HOMO value (−5.46 eV) had the highest V_{oc} (0.82 V) and polymer **BT-SI-TPA** with the highest HOMO value (−5.19 eV) had the lowest V_{oc} (0.74 V). The D-A polymer **BT-SI-TPA** blended with PC₆₁BM (1:1, *W:W*) provided a greater PCE (0.85%) with values of V_{oc} , J_{sc} , and FF of 0.74 V, 3.5 mA/cm², and 33%, respectively than that of the device incorporating **BT-F-TPA** (PCE = 0.43%, V_{oc} = 0.82 V, J_{sc} = 1.8 mA/cm², FF = 29%) and **BT-CZ-TPA** (PCE = 0.66%, V_{oc} = 0.76 V, J_{sc} = 2.9 mA/cm², FF = 30%). As shown in Fig. 3(b), the broader absorption of dithiansilole-containing polymer (**BT-SI-TPA**) had better light harvesting and helped to absorb a greater number of photons from solar spectrum, and thus showed a higher value of J_{sc} (3.5 mA/cm²) than that of **BT-F-TPA** (J_{sc} = 1.8 mA/cm²) and **BT-CZ-TPA** (J_{sc} = 2.9 mA/cm²). As shown in Fig. 6 and Table 4, the longest broadening of absorption spectra in polymer **BT-SI-TPA**:PC₆₁BM blend in 1:1 ratio and comparably higher hole and electron mobilities (μ_h and μ_e) in the same device (**BT-SI-TPA**:PC₆₁BM) developed higher photocurrent (3.5 mA/cm²), thereby contributing the

Table 4 Photovoltaic properties of polymer solar cell devices with a configuration of ITO/PEDOT:PSS/polymer:PC₆₁BM/Ca/Al ^a

Polymer:PC ₆₁ BM (1:1)	μ_e (cm ² /(V.s))	μ_h (cm ² /(V.s))	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
BT-F-TPA	3.3×10^{-8}	3.8×10^{-9}	0.82	1.8	29	0.43
BT-CZ-TPA	5.7×10^{-8}	6.6×10^{-9}	0.76	2.9	30	0.66
BT-SI-TPA	8.2×10^{-8}	9.7×10^{-9}	0.74	3.5	33	0.85

^a Measured under AM 1.5 irradiation, 100 mW/cm²

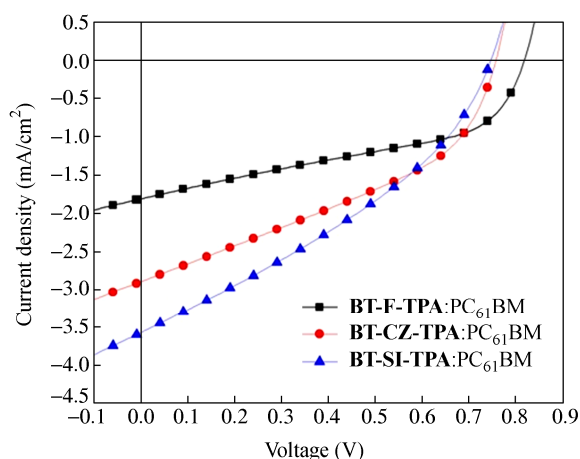


Fig. 5 Current-voltage (J - V) curves of polymer solar cells containing polymer blends of polymer:PC₆₁BM = 1:1 (*W:W*) under the illumination of AM 1.5 G, 100 mW/cm²

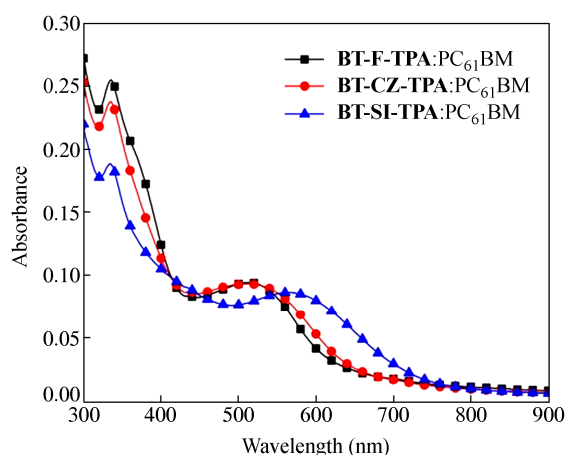


Fig. 6 Absorption spectra of polymer blends of polymer:PC₆₁BM = 1:1 (*W:W*) measured from solar cell devices by using the substrate of ITO/PEDOT as a reference

best PCE value among the polymers. Comparably poor PCE values could be attributed to the imbalance in hole and electron mobilities in devices which limited the net photocurrent^[54]. As shown in Fig. S2 (in SI) the poor crystallinity and surface morphology shown in AFM image of the polymer blend led to the poor phase separation which restricted the net charge transfer. It was observed that the highest J_{sc} value (3.5 mA/cm²) was induced in the device of **BT-SI-TPA**:PC₆₁BM (1:1, $W:W$) having the smoothest surface with a root-mean-square roughness (R_{rms}) of 1.6 nm, and J_{sc} values were reduced to 2.9 and 1.8 mA/cm² by increasing the roughness of **BT-CZ-TPA**:PC₆₁BM (R_{rms} = 1.9 nm) and **BT-F-TPA**:PC₆₁BM (R_{rms} = 2.8 nm), respectively. This is due to the fact that the smoother surface has a higher PCE value attributed to the better interfacial contacts of the polymer blend^[40]. In order to optimize the best performing PSC device, BHJ PSC devices was fabricated using **BT-SI-TPA** as a donor and PC₇₁BM as an acceptor (The PC₇₁BM was chosen as the acceptor because of its high absorption coefficient in the region from 440 nm to 530 nm, which could complement the absorption valley of the polymers.) in different weight ratios of 1:1, 1:2, 1:3 and 1:4. The J - V curve and corresponding photovoltaic properties, *i.e.*, V_{oc} , J_{sc} , FF and PCE values are shown in Fig. 7 and Table 5, respectively. The donor/acceptor blending ratio played a key role to determine the thin film characteristics and the excitation dissociation and thus the PCE values^[55]. As revealed in Table 5, The polymer blend **BT-SI-TPA**:PC₇₁BM with weight ratio 1:2 provided the optimal PCE value of 1.88% with V_{oc} = 0.75 V, J_{sc} = 7.60 mA/cm², FF = 33%. Increase in the PC₇₁BM ratio in the blended polymer reduced the J_{sc} value due to inefficient charge separation and transporting properties resulted the lower PCE values^[56]. Relatively low EQEs (see Fig. 8) in 1:1, 1:3 and 1:4 ratios compared to that in 1:2 ratio of **BT-SI-TPA**:PC₇₁BM offered relatively poor photocurrent response which is due to the suppression of the charge separation/transportation within the active layer. In general the device based on **BT-SI-TPA**:PC₇₁BM at 1:2 reached to higher PCE value (1.88%) which was attributed to the broader absorption spectra (λ_{onset} = 740 nm), lower band gap (1.67 V), broader and higher EQE of ~30% at ~550 nm respectively.

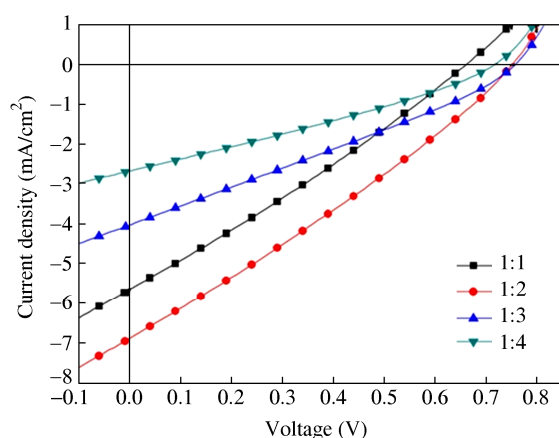


Fig. 7 Current-voltage (J - V) curves of polymer solar cells containing polymer blends **BT-SI-TPA**:PC₇₁BM in different weight ratios under the illumination of AM 1.5 G, 100 mW/cm²

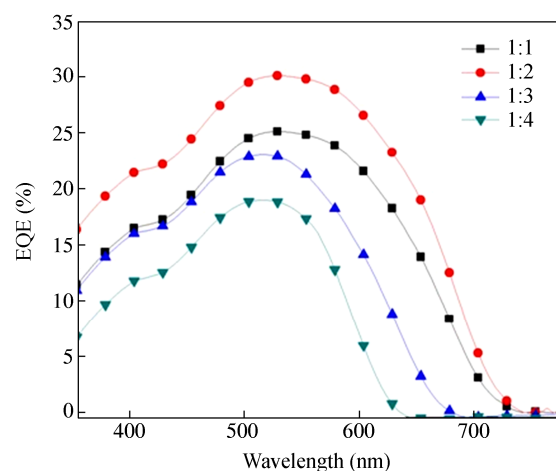


Fig. 8 External quantum efficiency (EQE) of polymer solar cells containing polymer blends **BT-SI-TPA**:PC₇₁BM in different weight ratios

Table 5 Photovoltaic properties of polymer solar cell devices with a configuration of ITO/PEDOT:PSS/**BT-SI-TPA**:PC₇₁BM/Ca/Al^a

BT-SI-TPA :PC ₇₁ BM	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
1:1	0.66	6.33	31	1.29
1:2	0.75	7.60	33	1.88
1:3	0.76	3.98	30	0.90
1:4	0.72	2.65	32	0.61

^a Measured under AM 1.5 irradiation, 100 mW/cm²

CONCLUSIONS

We synthesized low band gap D-A type side chain polymers (**BT-F-TPA**, **BT-CZ-TPA** and **BT-SI-TPA**) consisting of electron-deficient acceptor and electron rich donor blocks both in main chains and pendants by Suzuki/Stille polymerizations. With high solubility and adequate thermal stabilities these polymers exhibited relatively low band gaps (1.65–1.88 eV) and broad absorptions tailed up to 680–740 nm. Under 100 mW/cm² of AM 1.5 white-light illumination, we fabricated PSCs incorporating synthesized polymers as electron donors blended with electron-acceptor [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) or [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) in different weight ratios. The photovoltaic device containing donor **BT-SI-TPA** and acceptor PC₇₁BM in 1:2 weight ratio showed some promising photovoltaic characteristics with a PCE of 1.88%, $V_{oc} = 0.75$ V, $J_{sc} = 7.60$ mA/cm², and FF = 33.0%. To further optimize the optical and electrical properties, tunings of the pendent acceptor blocks with some strong electron deficient blocks are under progress.

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