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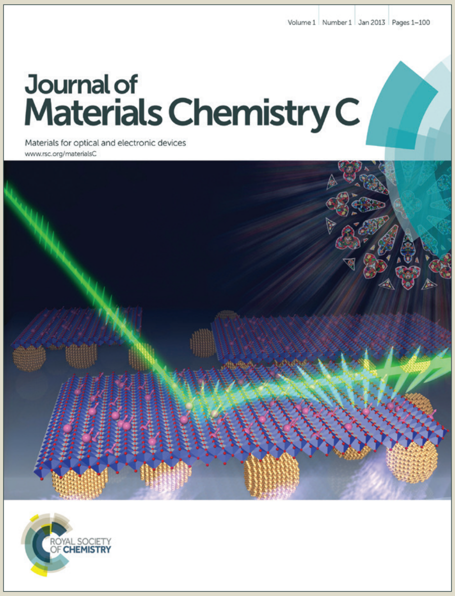

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ARTICLE TYPE

Property Modulation of Benzodithiophene-Based Polymers via the Incorporation of Covalently Bonded Novel 2,1,3-Benzothiadiazole-1,2,4-Oxadiazole Derivative in Their Main Chain for Polymer Solar Cells

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Two new electron accepting monomers (BBOB and BOB) containing serially connected two different electron deficient units such as 2,1,3-benzothiadiazole and 1,2,4-oxadiazole are prepared and copolymerized with electron rich benzodithiophene (BDT) derivative to afford polymers P(BDT-BBOB) and P(BDT-BOB), respectively. The optical band gaps of P(BDT-BBOB) and P(BDT-BOB) are calculated to be 2.32 eV and 1.99 eV, respectively, and their highest occupied molecular energy levels are determined to be −5.31 eV and −5.27 eV, respectively. Each of the newly synthesized polymers P(BDT-BBOB) and P(BDT-BOB) is used as an electron donor along with $PC_{61}BM$ as an electron acceptor in the preparation of polymer solar cells (PSCs). The PSCs made with the configuration of ITO/PEDOT:PSS/P(BDT-BBOB) or P(BDT-BOB):$PC_{61}BM$ (1:2 wt%)/LiF/Al gave a maximum power conversion efficiency (*PCE*) of 1.76% and 2.46%, respectively, and the respective device performance was further improved to 3.31% and 4.21%, respectively, by simply treating the photoactive layer of PSCs with isopropyl alcohol. Overall, the opto-electrical and photovoltaic properties of the two polymers are found to be quite dependent on the configuration of the covalently bonded 2,1,3-benzothiadiazole and 1,2,4-oxadiazole units incorporated in the polymer main chain.

1. Introduction

Recent progress of polymer solar cells (PSCs) demonstrates that they are promising renewable energy production technique due to their advantages such as flexible and light weight device fabrication at low cost via standard roll-to-roll (R2R) printing techniques.[1] The maximum solar to electrical energy conversion efficiency (*PCE*) of PSCs made from the blends of electron donating π−conjugated polymer and electron accepting fullerene derivative (example: $PC_{61}BM$, $PC_{71}BM$ or ICBM) improved in the range of 9−10.5% with the use of tandem structured PSCs[2–7] while the *PCE* was obtained in the range 7−9% for single layer PSCs.[8–13] Only one type polymer (either low or large band gap) is used in photoactive layer of single layer PSCs[8–13] while both large and low band gap polymers are used in tandem PSCs to utilize entire energy in the visible-NIR part of the solar spectra, and consequently, tandem PSCs gave higher *PCE* than single layer PSCs.[2–7] The theoretical studies suggest that the maximum *PCE* of single layer PSCs could reach up to 17% and tandem PSCs have capability for the maximum *PCE* of 24%.[14]

In this instance, it is essential to develop structurally novel polymers showing better opto-electrical and photovoltaic properties than the known polymers to boost the PSC performances further. The literatures reveal that the polymers incorporating electron deficient 2,1,3-benzothiadiazole (BT),[9] thieono[3,4-b]thiophene (TT),[10] thieno[3,4-c]pyrrole-4,6-dione (TPD),[11] and pyrrolo[3,4-c]pyrrole-1,4-dione (DKPP)[12,13] derivatives show excellent absorption, high carrier mobility and consequently high *PCE* in both single and tandem PSCs.[2–13] Among them, BT analogue is considered as a most promising acceptor unit and the polymers incorporating BT unit gave maximum *PCE* of 8.2% and 10.6%, respectively, in single layer and tandem PSCs.[6,9]

It is worth to notice that Dennler et. al. discussed well about the importance of tuning the HOMO and LUMO energy level of the alternating donor-acceptor (D-A) polymers via the modification of donor or acceptor unit in polymer main chain to maximize the device efficiency of single or tandem PSCs. They also clearly demonstrated that the *PCE* of the PSCs is related with the band gap and HOMO-LUMO energy levels of donor martial.[8] In this instance, many efforts have been shown to tune the photovoltaic properties of the polymers incorporating BT-based acceptor units via the incorporation/insertion of electron donating or accepting units on BT moiety.[15–28] In most of the studies, electron donating units[15–21] such as benzene, thiophene, thienothiophene and furan derivatives are covalently attached on

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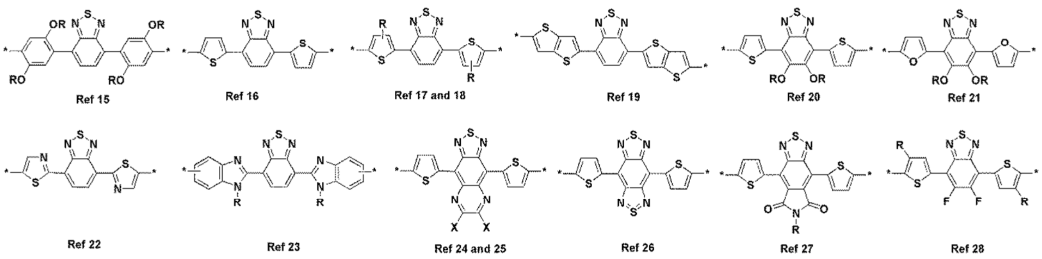
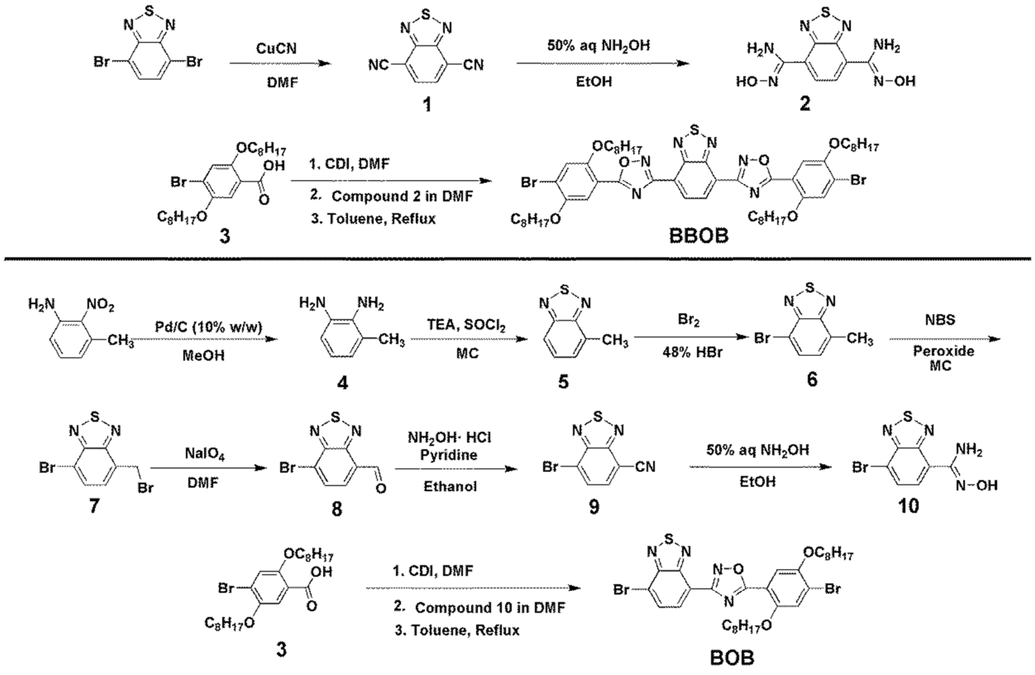


Fig. 1 Few examples of 2,1,3-benzothiadiazole (BT)-based acceptor units.

the both sides of BT unit or electron rich alkoxy[20,21] or electron attracting fluorides[8,28] are inserted on the back bone of BT unit with the aim of improving the absorption and carrier mobility and tuning the energy levels of BT-based polymers. In addition, electron accepting units such as thiazole[22] and benzimidazole[23] are also attached on the both sides of BT units or quinoxaline,[24,25] thiadiazole[26] and *N*-alkylpyrrolidine-2,5-dione rings[27] were fused on BT back bone with the aim of increasing the electron attracting ability of BT unit. Examples of BT-based acceptor units are presented in Fig. 1. Recently, we reported a series of 1,2,4-oxadiazole (Oxa) based polymers for PSC applications.[29] Polymers incorporating separated BT and Oxa units in polymer main chain were found to show broad absorption in between 300-900 nm.[29] However, polymers incorporating covalently bonded BT-Oxa unit have not been reported yet. We believe that the covalent attachment of high electron transporting Oxa unit on BT unit increases the electron deficiency as well as improves the electron mobility. Consequently, when the BT-Oxa unit is polymerized with electron rich units, broad absorbing polymers with high electron mobility are expected. In order to clearly understand the opto-electrical and photovoltaic properties of polymers incorporating covalently bonded BT-Oxa unit, we prepared two different electron deficient monomers namely BBOB (Oxa-BT-Oxa derivative) and BOB (BT-Oxa derivative). The strong electron deficient monomers such as BBOB and BOB were copolymerized with distannyl derivative of 4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b′]dithiophene (BDT) to give polymers P(BDT-BBOB) and P(BDT-BBOB), respectively. In this study, we report the synthesis, optical, electrochemical and photovoltaic properties of two new polymers P(BDT-BBOB) and P(BDT-BBOB) incorporating covalently bonded BT-Oxa unit in their main chain.



Scheme 1 Synthetic route to monomers BBOB and BOB.

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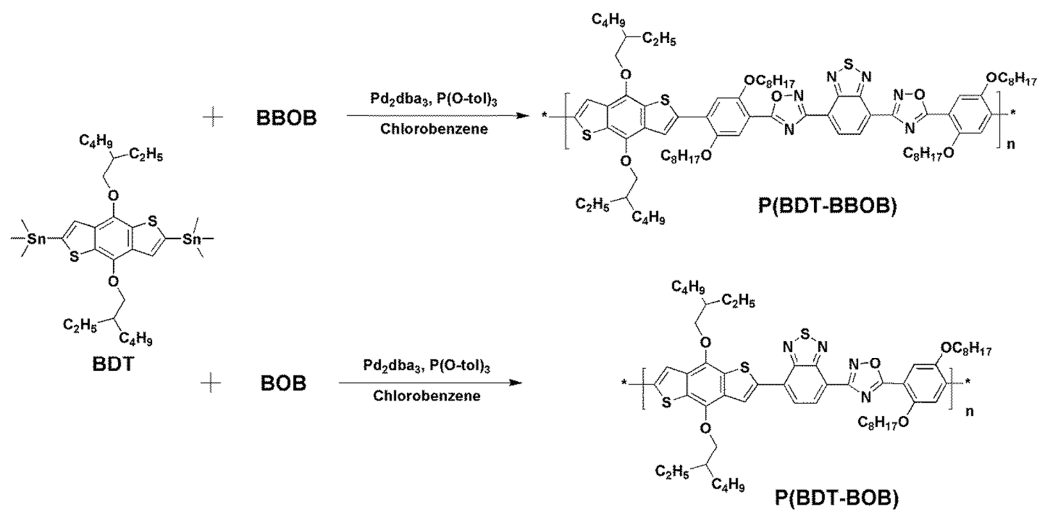

Scheme 2 Synthetic route to polymers P(BDT-BBOB) and P(BDT-BOB).

2. Experimental section

2.1 Materials and Instruments

The reagents were received from Aldrich or TCI chemicals and used without further purification. The common organic solvents were distilled and handled in a moisture-free atmosphere. The column purification of the compounds was performed on silica gel (Merck Kieselgel 60, 70-230 mesh ASTM). The compounds were characterized by using nuclear magnetic resonance (NMR) spectra performed on Varian Mercury Plus spectrometer (300 MHz and 75 MHz, respectively, for ^{1}H and ^{13}C) and high resolution mass spectra performed on Jeol JMS700 mass spectrometer. The molecular weights of the polymers were determined from Gel permeation chromatography (GPC) analyses by using Agilent 1200 Infinity Series separation module using polystyrene as a standard and chloroform as an eluent. Thermogravimetric analyses (TGA) were conducted with a TA instrument Q500 at a heating rate of 10 °C/min under nitrogen. The absorption spectra of the polymers were recorded on JASCO V-570 spectrophotometer at 25 ^{o}C in chloroform or as thin films on quartz. The cyclic voltammetry (CV) measurements were performed on CH Instruments Electrochemical Analyzer. Electrochemical measurements were performed with polymer cast platinum as a working electrode, Ag/AgCl as a reference electrode and platinum wire as a counter electrode in 0.1 M tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) acetonitrile solution. The impedance response of polymer:$PC_{61}BM$ blends was measured over the range of 1 Hz to 1MHz with oscillation amplitude of 15 mV (Bio-Logic VMP-3). The experimental data were simulated using commercial *Z*-view software to estimate the values for each component of the corresponding equivalent circuits.

2.2 Fabrication and characterization of PSCs

The device fabrication and characterization of PSCs are summarized below. Indium tin oxide (ITO)-coated glass substrates were cleaned stepwise by acetone, deionized water and isopropyl alcohol in an ultrasonic bath. Then 50 nm poly(ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) (Clevious P: isopropyl alcohol, 1:2 v/v %) buffer layer was spin-coated on the top of ITO substrate at 5000 rpm for 40 s and dried at 150 °C for 10 min under vacuum to remove the residual water. The active layer of polymer and $PC_{61}BM$ blend (1:1 wt%, 1:2 wt% and 1:3 wt%) was spin-coated at 800 rpm from dichlorobenzene (DCB) solution on the top of ITO/PEDOT:PSS substrate. The ITO/PEDOT:PSS/Polymer:$PC_{61}BM$ substrate was allowed to dry for 10 min in a glove box and then subjected to pre-annealing at 80 °C for 10 min. The thickness of the photoactive layer was found to be around 80 nm. Isopropyl alcohol (IPA) was spin-coated on the top of the ITO/PEDOT:PSS/Polymer:$PC_{61}BM$ substrate at 3000 rpm for 40 s for the devices subjected to solvent treatments and then ~ 0.7 nm thick layer of LiF was deposited on the substrate. Subsequently, 100 nm thick layer of Al was deposited through a shadow mask on the top of ITO/PEDOT:PSS/Polymer:$PC_{71}BM$/LiF substrate under high vacuum (1.2 x 10^{-6} torr). The top metal electrode area, comprising the active area of the solar cell, was found to be 0.36 cm^2. The *J-V* characteristics of the devices were measured using a Keithley 2400 source measure unit under a calibrated AM 1.5G solar simulator (Oriel® Sol3A™ Class AAA solar simulator, models 94043A) at 100 mW/cm^2. The intensity of sunlight illumination was calibrated using a standard Si photodiode detector with a KG-5 filter. The IPCE measurement system (Oriel IQE-200) was composed of a 250 W quartz-tungsten-halogen

(QTH) lamp as the light source, as well as a monochromator, optical chopper, lock-in amplifier, and calibrated silicon photodetector.

2.3 Synthesis of monomers

Benzo[c][1,2,5]thiadiazole-4,7-dicarbonitrile (1). To a stirred solution of 4,7-dibromobenzo[c][1,2,5]thiadiazole (7.35 g, 25 mmol) in *N,N*-dimethylformamide (DMF, 70 mL) was added copper cyanide (9.0 g, 100 mmol). The mixture was heated to 150 °C for 72 h and then it was cooled to room temperature (RT). The mixture was poured into 2 N HCl (200 mL) and extracted (2x100 mL) with ethyl acetate (EA). The combined organic layer was washed well with brine solution and then the organic layer was dried over anhydrous Na_2SO_4. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (silica gel, hexane:CH_2Cl_2, 20/80) to afford compound **1** as a colorless solid. Yield: 2.2 g (47%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.15 (s, 2H); ^{13}C NMR (75 MHz, CDCl3): δ (ppm) 152.6, 134.7, 114.1, 110.9; HRMS (EI$^+$, m/z) [M$^+$] Calcd for $C_8H_2N_4S$ 186.0000, found 186.0006.

(4Z,7Z)-N4',N7'-dihydroxybenzo[c][1,2,5]thiadiazole-4,7-dicarboxamidine (2). To a stirred solution of compound **1** (1.0 g, 5.40 mmol) in chloroform (10 mL) was added ethanol (60 mL) and 50% aqueous hydroxylamine solution (10 mL). Then, the whole mixture was heated to reflux for 3 h. The completion of the reaction was confirmed by TLC, and ethanol was removed by rotary evaporation. The crude product was washed with cold ethanol, diethyl ether and hexane. The solid was dried under vacuum to afford compound **2** as a yellow color solid. Yield: 1.1 g (81%). ^{1}H NMR (300 MHz, DMSO-d^6): δ (ppm) 10.00 (s, 2H), 7.99 (s, 2 H), 6.24 (s, 4 H).

4,7-Bis(5-(4-bromo-2,5-bis(octyloxy)phenyl)-1,2,4-oxadiazol-3-yl)benzo[c][1,2,5]thiadiazole (BBOB). To a stirred solution of compound **3** (0.50 g, 1.10 mmol), which was prepared by using the reported procedure,[30] in DMF (5 mL) was added 1,1'-carbonyldiimidazole (CDI, 0.19 g, 1.20 mmol) and stirred for 30 min. Then, (4Z,7Z)-*N*4',*N*7'-dihydroxybenzo[c][1,2,5]thiadiazole-4,7-dicarboxamidine (**2**) (0.13 g, 0.50 mmol) in DMF (10 mL) was added drop wise to the stirred solution. The solution was stirred for overnight and then poured into water. The aqueous layer was extracted (3x30 mL) with chloroform ($CHCl_3$). The combined organic layer was dried over anhydrous Na_2SO_4. The solvent was removed by rotary evaporation and the resulting sticky mass was dissolved in anhydrous toluene (30 mL). The solution was refluxed for 24 h and then toluene was removed by rotary evaporation. The crude product was purified by column chromatography (silica gel, CH_2Cl_2) to afford BBOB as a yellow color solid. Yield: 0.32 g (58%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.74 (s, 2H), 7.73 (s, 2 H), 7.32 (s, 2 H), 4.10 (q, 8H), 1.80-2.00 (m, 8H), 1.40-1.60 (m, 8H), 1.10-1.40 (m, 32H), 0.80-1.10 (m, 12H); ^{13}C NMR (75 MHz, CDCl3): δ (ppm) 175.0, 165.8, 152.9, 152.3, 150.0, 130.9, 122.9, 119.3, 115.2, 112.7, 70.5, 70.4, 32.1, 32.0, 29.6, 29.5, 29.4, 26.2, 22.9, 14.3; HRMS (EI$^+$, m/z) [M$^+$] Calcd for $C_{54}H_{74}Br_2N_6O_6S$ 1092.3757, found 1092.3750.

3-Methylbenzene-1,2-diamine (4). According to the reported procedure, the nitro group on 3-methyl-2-nitrobenzenamine was reduced to amino group by using $SnCl_2$ to afford compound **4**.[31] However, in this study, the nitro to amino group conversion was performed by using palladium/carbon. The modified procedure decreases the reaction time with high yield compared with the reported procedure. To a stirred solution of 3-methyl-2-nitrobenzenamine (5.0 g, 33.0 mmol) in methanol (200 mL) was added 0.75 g of palladium on carbon (10 wt. % loading, matrix carbon, dry support) and ammonium formate (15.5 g, 165 mmol). Then, the mixture was heated to 70 °C for 3 h. The completion of the reaction was confirmed by TLC and palladium on carbon was filtered out. The solvent was removed and the resulting solid material was dissolved in EA (100 mL). The organic solution was washed once with aqueous 2 N sodium hydroxide solution and the organic layer was dried over anhydrous Na_2SO_4. The solvent was removed by rotary evaporation and the product was dried under vacuum to afford compound **4** as a brown color solid. Yield: 3.94 g (98%). ^{1}H NMR (300 MHz, CDCl3): δ (ppm) 6.60-6.70 (m, 3H), 3.38 (s, 4H), 2.20 (s, 3H); ^{13}C NMR (75 MHz, CDCl3): δ (ppm) 134.1, 133.7, 123.6, 122.3, 119.4, 115.3, 17.71.

4-Methylbenzo[c][1,2,5]thiadiazole (5). The synthetic procedure for compound **5** was already reported,[31] but, in this study, we developed a slightly modified, more efficient and facile procedure. A stirred solution of compound **4** (3.7 g, 30.3 mmol) in dry CH_2Cl_2 (150 mL) was cooled to 0 °C in an ice bath for 15 min and then triethyl amine (17 mL, 121 mmol) was slowly added. And then, thionyl chloride (4.4 mL, 60.6 mmol) in dry CH_2Cl_2 (50 mL) was added drop wise at 0 °C. After the addition, the solution was allowed to stir for 1 h and then heated to 40 °C for 15 h. The reaction mixture was cooled to RT and poured into 2 N HCl (200 mL) and the organic layer was separated. The organic layer was dried over anhydrous Na_2SO_4. The crude product was purified by column chromatography (silica gel, hexane:EA, 80/20) to afford compound **5** as a brown color liquid. Yield: 4.2 g (92%). ^{1}H NMR (300 MHz, CDCl3): δ (ppm) 7.83 (1, 2H), 7.47 (t, 2 H), 7.33 (d, 1H), 2.74 (s, 3H); ^{13}C NMR (75 MHz, CDCl3): δ (ppm) 155.6, 155.2, 131.9, 129.8, 128.2, 119.2, 18.2.

4-Bromo-7-methylbenzo[c][1,2,5]thiadiazole (6). Compound **6** was prepared via the similar reported procedure.[31] Compound **5** (3.2 g, 21.3 mmol) and 48% HBr (80 mL) were stirred at RT. To this solution was added Br_2 (1.20 mL, 22 mmol) in 48% HBr (80 mL) drop by drop. Then, the mixture was heated to reflux for 16 h. The solution was cooled to RT and the mixture was poured into saturated sodium bisulfite solution. The mixture was stirred for 30 min and then extracted (2x100 mL) with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated by rotary evaporation. The crude product was purified by column chromatography (silica, hexane:EA, 90/10) to afford compound **6** as a colorless solid. Yield: 4.5 g (92%). ^{1}H NMR (300 MHz, CDCl3): δ (ppm) 7.72 (d, 1H), 7.22 (d, 1H), 2.70 (s, 3H); ^{13}C NMR (75 MHz, CDCl3): δ (ppm) 155.4, 153.4, 132.3, 131.5, 129.1, 111.4, 17.9.

4-Bromo-7-(bromomethyl)benzo[c][1,2,5]thiadiazole (7). Compound **7** was prepared via the similar reported procedure.[31] Compound **6** (4.0 g, 17.4 mmol), *N*-bromosuccinimide (*NBS*, 3.1 g, 17.5 mmol) and benzoyl peroxide (10 mg) were dissolved in CCl_4 (140 mL). The solution was heated to reflux and 33% HBr in acetic acid (1 mL) was added. After 3 h, the reaction mixture was poured into water (100 mL). The organic layer was separated and dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated by rotary evaporation. The crude product was purified by column chromatography (silica, hexane:EA, 90/10) to afford compound **7** as a colorless solid. Yield: 4.5 g (92%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.81 (d, 1H), 7.53 (d, 1H), 4.94 (s, 2H); ^{13}C NMR (75 MHz, CDCl3): δ (ppm) 155.4, 153.4, 132.3, 131.5, 128.8, 114.5, 27.9.

7-Bromobenzo[c][1,2,5]thiadiazole-4-carbaldehyde (8). Compound **8** was prepared via the slightly modified procedure.[32] Compound **7** (2.8 g, 9.1 mmol) and sodium periodate ($NaIO_4$) (0.42 g, 2.3 mmol) were taken in a round bottom flask and DMF (30 mL) was added. The reaction mixture was heated at 150 °C for 3h. Then again $NaIO_4$ (0.42 g, 2.3 mmol) was added to the solution and stirring was continued for 2 h at 150 °C. The reaction mixture was cooled and poured into water (100 mL) and then extracted with EA (2x50 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated by rotary evaporation. The crude product was purified by column chromatography (silica, hexane:EA, 90/10) to afford compound **8** as a yellow color solid. Yield: 1.2 g (54%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 10.73 (s, 1H), 8.11 (d, 1H), 8.06 (d, 1H); ^{13}C NMR (75 MHz, CDCl3): δ (ppm) 188.6, 154.5, 152.6, 132.4, 132.0, 127.1, 122.2.

7-Bromobenzo[c][1,2,5]thiadiazole-4-carbonitrile (9). Compound **9** was prepared via the similar reported procedure.[33] A stirred solution of compound **8** (1.0 g, 4.1 mmol) and hydroxylamine hydrochloride (0.57 g, 8.2 mmol) in DMSO (30 mL) was heated at 100 °C for 2 h. Then, the reaction mixture was cooled to RT and poured into water (100 mL). The mixture was stirred for 30 min and then allowed to settle down. The precipitates were filtrated off and washed well with MeOH and hexane. The solid was dried under vacuum to afford compound **9** as a colorless solid. Yield: 0.82 g (84%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.96 (d, 2H), 7.91 (d, 2 H); ^{13}C NMR (75 MHz, CDCl3): δ (ppm) 153.3, 152.6, 136.1, 131.6, 121.5, 115.0, 105.6.

(Z)-7-Bromo-N'-hydroxybenzo[c][1,2,5]thiadiazole-4-carboxamidine (10). To a stirred solution of compound **9** (0.7 g, 2.9 mmol) in ethanol (60 mL) was added 50% aqueous hydroxylamine solution (10 mL). The mixture was heated to reflux for 3 h. The completion of the reaction was confirmed by TLC, and ethanol was removed by rotary evaporation. The crude product was washed with diethyl ether and hexane. The solid was dried under vacuum to afford compound **10** as a yellow color solid. Yield: 0.65 g (82%). ^{1}H NMR (300 MHz, CD_3OD): δ (ppm) 7.97 (d, 2H), 7.86 (d, 2H), 3.25 (s, 1H).

4-Bromo-7-(5-(4-bromo-2,5-bis(octyloxy)phenyl)-1,2,4-oxadiazol-3-yl)benzo[c][1,2,5]thiadiazole (BOB). Under argon atmosphere, to the solution of compound **3** (0.64 g, 1.4 mmol) in DMF (10 mL) was added 1,1'-carbonyldiimidazole (CDI, 0.23 g, 1.4 mmol). The whole mixture was stirred for 30 min. Then, compound **10** (0.38 g, 1.4 mmol) in DMF (10 mL) was added drop wise to the stirred solution. The solution was stirred for overnight and then poured into water. The aqueous layer was extracted (3x30 mL) with chloroform ($CHCl_3$). The combined organic layer was dried over anhydrous Na_2SO_4. The solvent was removed by rotary evaporation and the resulting sticky mass was dissolved in anhydrous toluene (30 mL). The solution was refluxed for 24 h and then the toluene was removed by rotary evaporation. The crude product was purified by column chromatography (silica, hexane:EA, 80/20) to afford BOB as a yellow color solid. Yield: 0.53 g (55%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.46 (d, 1H), 8.00 (d, 1H), 7.69 (s, 1H), 7.30 (s, 1H), 4.08 (q, 4H), 1.80-2.00 (m, 4H), 1.40-1.60 (m, 4H), 1.20-1.40 (m, 16H), 0.90-1.00 (m, 6H); ^{13}C NMR (75 MHz, CDCl3): δ (ppm) 174.8, 165.7, 154.1, 152.9, 151.3, 150.0, 132.0, 131.7, 120.1, 119.3, 119.2, 118.2, 115.2, 112.7, 70.5, 70.4, 32.1, 32.0, 29.5, 29.4, 26.2, 22.9,14.3; HRMS (EI$^+$, m/z) [M$^+$] Calcd for $C_{30}H_{38}Br_2N_4O_3S$ 692.1031, found 692.1036.

Poly(4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophene-alt-4,7-bis(5-(2,5-bis(octyloxy)phenyl)-1,2,4-oxadiazol-3-yl)benzo[c][1,2,5]thiadiazole) (P(BDT-BBOB)): A solution of respective monomers such as BDT (0.23 g, 0.3 mmol) and BBOB (0.33 g, 0.3 mmol) in chlorobenzene (30 mL) was degassed well with argon for 45 min. Then, Pd_2dba_3 (0.14 g) and $P(o\text{-}tol)_3$ (0.30 g) were added. The stirred solution was heated to reflux under argon atmosphere for 48 h. Then, the solution was drop wise added to the vigorously stirred methanol (200 mL). The precipitate was recovered by filtration, and then extracted with methanol for 24 h and acetone for 24 h in a Soxhlet apparatus to afford pure polymer P(BDT-BBOB) as a light brown color solid. Yield: 0.37 g (90%). GPC (Chloroform): $M_n = 1.85 \times 10^4$ g/mol; $M_w = 1.28 \times 10^4$ g/mol; $PDI = 1.45$. Elemental analysis calcd for $(C_{80}H_{112}N_6O_8S_3)_n$: C, 69.53; H, 8.17; N, 6.08; S, 6.96. Found: C, 70.30; H, 7.86; N, 5.70; S, 7.01.

Poly(4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophene-alt-4-(5-(2,5-bis(octyloxy)phenyl)-1,2,4-oxadiazol-3-yl)benzo[c][1,2,5]thiadiazole) (P(BDT-BOB)): For the preparation of P(BDT-BOB), the synthetic procedure similar to that for the preparation of (P(BDT-BBOB) was used. In this reaction, monomers BDT (0.23 g, 0.3 mmol) and BOB (0.21 g, 0.3 mmol) were used for polymerization. Polymer (P(BDT-BOB) was obtained as a dark brown color solid. Yield: 0.26 g (90%). GPC (Chloroform): $M_n = 2.13 \times 10^4$ g/mol; $M_w = 1.30 \times 10^4$ g/mol; $PDI = 1.63$. Elemental analysis calcd for $(C_{56}H_{76}N_4O_5S_3)_n$: C, 68.53; H, 7.81; N, 5.71; S, 9.80. Found: C, 66.95; H, 7.93; N, 4.74; S, 9.16.

3. Results and discussion

3.1 Synthesis and structural characterization

The synthetic route for the monomers (BBOB and BOB) and polymers (P(BDT-BBOB) and P(BDT-BOB)) are outlined in Scheme 1 and Scheme 2, respectively. Benzo[c][1,2,5]thiadiazole-4,7-dicarbonitrile (**1**) was prepared by treating 4,7-dibromobenzo[c][1,2,5]thiadiazole with copper cyanide. Compound **1** was converted into compound **2** by treating with 50% aqueous hydroxyl amine solution. On the other hand, compound **3** was prepared by using the reported procedure.[30] The acid group on compound **3** was activated by treating with coupling agent (CDI) and then reaction with compound **2** followed by cyclization afforded monomer BBOB containing two Oxa and one BT units. Another monomer namely BOB was prepared form 3-methyl-2-nitrobenzenamine. In this route, the nitro group on 3-methyl-2-nitrobenzenamine was reduced to amino group with the use of Pd/C to give compound **4**. Compound **4** was treated with thionyl chloride and TEA in dichloromethane to afford compound **5**. The bromination of compound **5** with bromine afforded compound **6** and then compound **6** was treated with NBS to afford compound **7**.[31] The $NaIO_4$ oxidation[32] of compound **7** gave compound **8** and the formyl group of compound **8** was converted to the cyano group of compound **9** by treating with hydroxyl amine hydrochloride ($NH_2OH.HCl$).[33] Compound **10** and monomer BOB were prepared via the synthetic procedure used for the synthesis of compound **2** and BBOB, respectively. The ^1H and ^{13}C NMR spectra of BBOB and BOB are presented in Fig. 2.

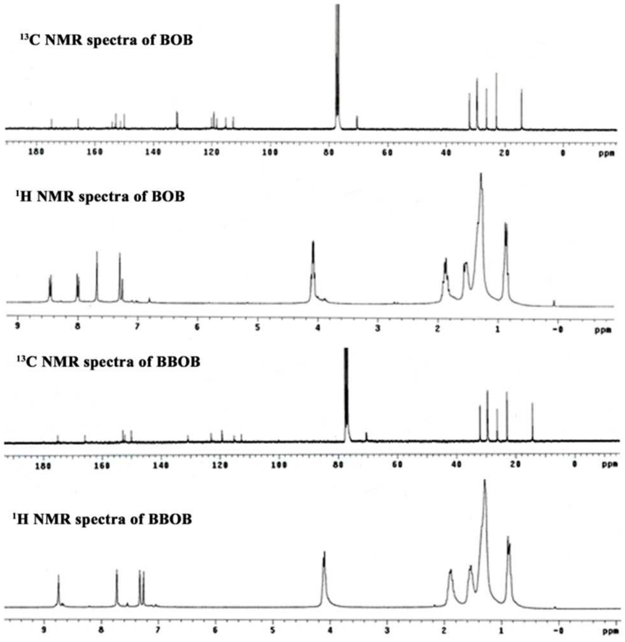

Fig. 2 The ^1H and ^{13}C NMR spectra of BBOB and BOB

The Stille polymerization between most promising electron rich BDT and new electron accepting BBOB and BOB afforded polymers P(BDT-BBOB) and P(BDT-BOB), respectively. Both polymers P(BDT-BBOB) and P(BDT-BOB) show good solubility in chloroform, chlorobenzene and dichlorobenzene and their weight average molecular weights (Mw) and polydispersities (PDI) determined by GPC analysis with chloroform as an eluent were 1.85×10^4, 2.13×10^4 and 1.45, 1.63, respectively. The 5% weight loss temperatures of P(BDT-BBOB) and P(BDT-BOB) were found to be 407 °C and 415 °C, respectively, from thermo gravimetric analysis (TGA). The good solubility and high thermal stability of P(BDT-BBOB) and P(BDT-BOB) allowed them to be utilized in PSCs. The molecular weights and 5% weight loss temperatures of P(BDT-BBOB) and P(BDT-BOB) are summarized in Table 1.

3.2 Optical properties

The absorption spectra of polymers P(BDT-BBOB) and P(BDT-BOB) measured in chloroform and as thin film on glass are presented in Fig. 3. Polymer P(BDT-BBOB) displayed absorption band in the range of 300–520 nm with two maximum absorption peaks at 399 and 454 nm in solution and 416 and 455 nm as film. On the other hand, polymer P(BDT-BOB) showed broad absorption band in between 300–600 nm with maximum absorption peaks at 431 and 509 nm both in solution and as film. The absorption bands of P(BDT-BBOB) are expected to be originated from the $\pi-\pi*$ transition while those of P(BDT-BOB) might be originated from the combined electronic transitions such as $\pi-\pi*$ transition and donor-acceptor internal charge transfer (ICT) transition between BDT and BT units. The presence of electron accepting Oxa units on the both sides of BT unit of P(BDT-BBOB) might restricts the ICT, but the covalent bond between the strong electron donating BDT and electron accepting BT units of P(BDT-BOB) might allow the ICT. Earlier reports confirmed that the incorporation of sterically hindered electron donor groups such as 3-octylthiophene, alkoxy benzene or electron accepting benzimidazole derivative on both sides of the BT restrict the ICT from donor to acceptor units when they were polymerized with electron rich units.[15,17,23,34] Those results suggest that the incorporation of Oxa units on the both sides of BT unit also diminish the ICT between D-A units. The absorption onset wavelength of P(BDT-BBOB) and P(BDT-BOB) was calculated to be 534 nm and 622 nm, respectively, from which the optical band gaps ($E_{g,\ opt}$) were determined to be 2.32 eV and 1.99 eV, respectively. The optical properties of polymers P(BDT-BBOB) and P(BDT-BOB) are summarized in Table 1.

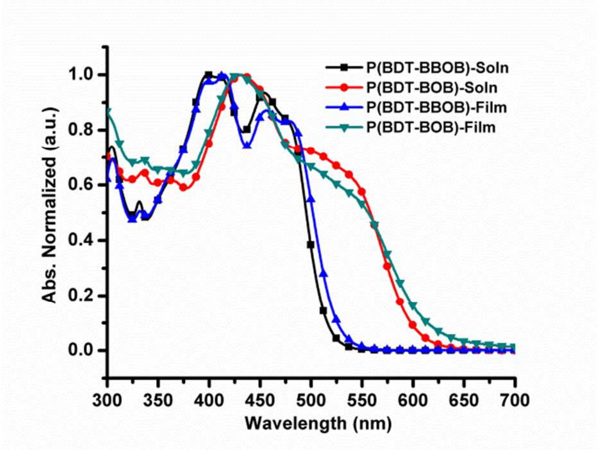

Fig. 3 Absorption spectra of polymers P(BDT-BBOB) and P(BDT-BOB) in chloroform and as thin film.

3.3 Electrochemical properties

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of P(BDT-BBOB) and P(BDT-BOB) were estimated form cyclic voltammetry (CV) analysis and the CV spectra of polymers are displayed in Fig. 4. The HOMO and LUMO energy levels of P(BDT-BBOB) and P(BDT-BOB) were calculated from the onset oxidation (E_{ox}) and onset reduction (E_{red}) potential values by using the following equations, $E_{\mathrm{HOMO}} = [-(E_{\mathrm{ox,\ onset\ vs.\ Ag/AgCl}} - E_{\mathrm{ferrocene\ vs.\ Ag/AgCl}}) - 4.8]$ eV and $E_{\mathrm{LUMO}} = [-(E_{\mathrm{red,\ onset\ vs.\ Ag/AgCl}} - E_{\mathrm{ferrocene\ vs.\ Ag/AgCl}}) - 4.8]$ eV. The $E_{\mathrm{ferrocene\ vs.\ Ag/AgCl}}$ is calculated from the oxidation potential of ferrocene standard to be 0.55 V. The $E_{\mathrm{ox,\ onset\ vs.\ Ag/AgCl}}$ and $E_{\mathrm{red,\ onset\ vs.\ Ag/AgCl}}$ values of P(BDT-BBOB) and P(BDT-BOB) were determined to be 1.06 V, 1.02 V and 1.35 V, 1.15 V, respectively. The HOMO/LUMO energy levels of P(BDT-BBOB) and P(BDT-BOB) were calculated to be –5.31 eV/–2.90 eV and –5.27 eV/–3.10 eV, respectively. The electrochemical band gap values were 2.41 eV and 2.17 eV, respectively. The electrochemical band gap ($E_{g,\ elect}$) values are

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Table 1 Polymerization Results and Thermal, Optical and Electrochemical Properties of P(BDTBBOB) and P(BDT-BOB).

Polymer	M_w[a] (g/mol)	PDI[a]	TGA[b] (°C)	λmax in solution (nm)[c]	λmax as film (nm)[d]	$E_{g,\ opt}$ (eV)[e]	HOMO (eV)[f]	LUMO (eV)[f]	$E_{g,\ elect}$ (eV)[g]
P(BDT-BBOB)	1.85×10^4	1.45	407	399, 454	416, 455	2.32	−5.31	−2.90	2.41
P(BDT-BOB)	2.13×10^4	1.63	415	431, 509	431, 509	1.99	−5.27	−3.10	2.17

[a] Weight average molecular weight (M_w) and polydispersity (PDI) of the polymers were determined by GPC using polystyrene standards. [b] 5 % weight loss temperature measured by TGA under N_2. [c] Measurements in chloroform solution. [d] Measurements in thin film were performed on the glass substrate. [e] Band gap estimated from the onset wavelength of the optical absorption in thin film. [f] The HOMO and LUMO levels were estimated from cyclic voltammetry analysis. [g] The electrochemical band gap values estimated form the HOMO and LUMO values.

found to be slightly higher than that of optical band gap values ($E_{g,\ opt}$). The deeper HOMO energy levels of P(BDT-BBOB) and P(BDT-BOB), and most importantly, the significant energy difference between the LUMO levels of newly synthesized polymers and $PC_{61}BM$ ensure that the polymers are suitable electron donor for PSCs application. The HOMO and LUMO energy levels of polymers P(BDT-BBOB) and P(BDT-BOB) are included in Table 1.

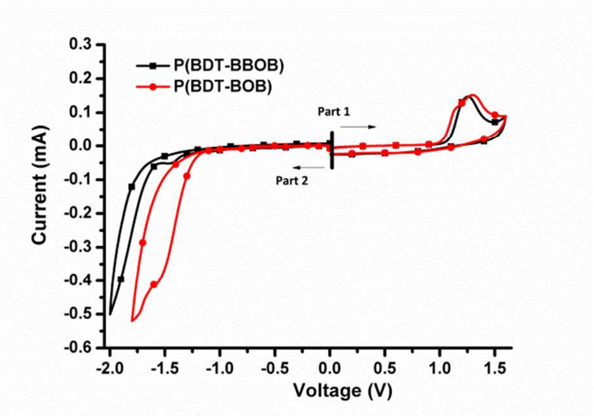

Fig. 4 Cyclic voltammograms of polymers P(BDT-BBOB) and P(BDT-BOB) films cast on platinum working electrode in 0.1 M TBATFB/acetonitrile at 100 mV/s, potential vs. Fe/Fe$^+$.

3.4 Photovoltaic properties

The PSCs were fabricated with the device structure of ITO/PEDOT:PSS/P(BDT-BBOB) or P(BDT-BOB):$PC_{61}BM$/LiF/Al. Among the devices prepared with three different donor:acceptor ratios of 1:1 wt%, 1:2 wt% and 1:3 wt% for each polymer P(BDT-BBOB) or P(BDT-BOB) as a donor and $PC_{61}BM$ as an acceptor, the highest power conversion efficiency (*PCE*) was obtained for the devices made from 1:2 wt% blends. The current density-voltage (*J–V*) curves of the PSCs were measured under the illumination of AM 1.5 G (100 mW/cm^2) and their corresponding *J–V* curves are shown in Fig. 5. The characteristic parameters of *J–V* curves of PSCs such as open circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (*FF*) and power conversion efficiency (*PCE*) are presented in Table 2. The device made from the blends of P(BDT-BBOB):$PC_{61}BM$ (1:2 wt%) and (BDT-BOB):$PC_{61}BM$ (1:2 wt%) gave the overall *PCE* of 1.76 % (V_{oc} of 0.69 V, a J_{sc} of 7.10 mA/cm^2, and a *FF* of 36%) and 2.46 % (V_{oc} of 0.71 V, a J_{sc} of 8.21 mA/cm^2, and a *FF* of 43%), respectively. Recently the post-solvent treatment on the photoactive layer of PSCs was reported to improve the photoactive performances of PSCs significantly.[35–37] We also tried the post-solvent treatment with various solvent such as acetone, methanol, ethanol and isopropyl alcohol (IPA) and the best result was obtained with IPA treatment. The *PCE* of the PSCs prepared from the blends of P(BDT-BBOB):$PC_{61}BM$ (1:2 wt%) and (BDT-BOB):$PC_{61}BM$ (1:2 wt%) was further improved to 3.31 % (V_{oc} of 0.70 V, a J_{sc} of 9.59 mA/cm^2, and a *FF* of 49%) and 4.21 % (V_{oc} of 0.70 V, a J_{sc} of 11.23 mA/cm^2, and a *FF* of 54%), respectively, with the IPA treatment on the active layer of PSCs.

The comparison of the device performances of P(BDT-BBOB) and P(BDT-BOB) suggests that the difference in the *PCE* is mainly originated from their different J_{sc} and *FF* values. Usually, the J_{sc} and *FF* of the PSCs are affected by absorption ability, series resistance (R_s), charge-transport properties, charge extraction and charge recombination.[36] Polymer P(BDT-BOB) displayed broad and red shifted absorption band in comparison with polymer P(BDT-BBOB), and consequently, the PSCs made from P(BDT-BOB) gave higher J_{sc} values than the PSCs made from P(BDT-BBOB). The lower *FF* value obtained for P(BDT-BBOB) indicates that the presence of the additional Oxa unit on the polymer main chain might reduce their hole mobility, because oxadiazoles have tendency to facilitate the electron transport more effectively than the hole transport,[38–40] and consequently, offered lower *FF* values compared with those of P(BDT-BOB). The higher series resistance (R_s) values (measured form dark *J–V* curves) of the PSCs made form P(BDT-BBOB):$PC_{61}BM$ blends compared with those of the PSCs made form P(BDT-BOB):$PC_{61}BM$ (1:2 wt%) agree with our arguments. In both cases, the series resistances of the PSCs were dramatically decreased after the IPA treatment as shown in Table 2, and consequently, higher J_{sc} and *FF* were obtained with IPA treatment.

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Table 2 PSCs Performance of Polymers P(BDT-BBOB) and P(BDT-BOB).

Polymer:$PC_{61}BM$ ratio	V_{oc} (V)[a]	J_{sc} (mA/cm^2)[b]	FF (%)[c]	PCE (%)[d]	R_s (Ω cm^2)[e]	Integrated J_{sc} (mA/cm^2)[f]
P(BDT-BBOB):$PC_{61}BM$ (1:1 wt%)	0.67±0.02	4.09±0.16	25.96±0.01	0.72±0.10	36	3.96±0.12
P(BDT- BBOB):$PC_{61}BM$ (1:2 wt%)	0.69±0.02	7.10±0.18	35.75±0.35	1.76±0.10	15	7.03±0.10
P(BDT- BBOB):$PC_{61}BM$ (1:3 wt%)	0.69±0.01	3.96±0.01	41.77±0.01	1.15±0.02	20	3.77±0.10
P(BDT- BBOB):$PC_{61}BM$ (1:2 wt%)+IPA	0.70±0.01	9.59±0.28	49.43±0.01	3.31±0.08	10	9.57±0.16
P(BDT-BOB):$PC_{61}BM$ (1:1 wt%)	0.70±0.01	4.44±0.26	33.33±0.02	1.04±0.03	31	4.31±0.17
P(BDT- BOB):$PC_{61}BM$ (1:2 wt%)	0.71±0.03	8.21±0.09	42.60±0.03	2.46±0.16	12	8.10±0.02
P(BDT- BOB):$PC_{61}BM$ (1:3 wt%)	0.70±0.01	5.07±0.05	45.43±0.02	1.62±0.05	14	5.00±0.10
P(BDT- BOB):$PC_{61}BM$ (1:2 wt%)+IPA	0.70±0.01	11.23±0.16	53.82±0.01	4.21±0.10	6	11.07±0.06

[a] Open-circuit voltage. [b] Short-circuit current density. [c] Fill factor. [d] Power conversion efficiency (Averages of 5 PSC devices are reported for each blend). [e] Series resistance. [f] estimated from IPCE curves.

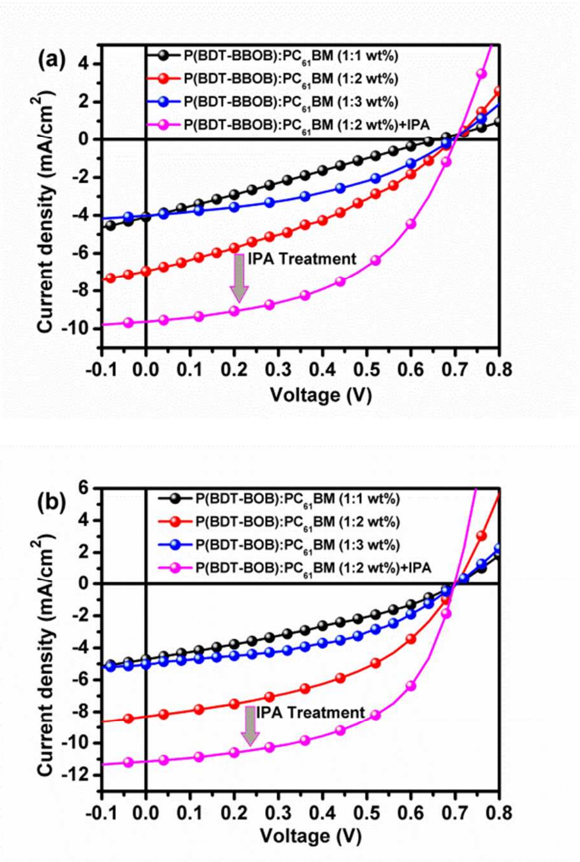

Fig. 5 *J–V* characteristics of PSCs prepared with the device structure of ITO/PEDOT:PSS/ P(BDT-BBOB) or P(BDT-BOB):$PC_{61}BM$/LiF/Al.

To make clearer our argument, we estimated the hole mobility of each polymers and polymer:$PC_{61}BM$ blends by the space charge limited current (SCLC) method. The device structure used in this study and the corresponding SCLC characteristics for the hole-only devices made with polymer or polymer:$PC_{61}BM$ blend as an active layers are presented in Fig. 6. The device made with P(BDT-BBOB) and P(BDT-BBOB):$PC_{61}BM$ blend displayed relatively lower hole mobility, $\mu \sim 6.11 \times 10^{-5}$ $cm^2V^{-1}s^{-1}$ and 9.61×10^{-6} $cm^2V^{-1}s^{-1}$, compared with that of the corresponding device made with P(BDT-BOB) and P(BDT-BOB):$PC_{61}BM$ blend ($\mu \sim 3.31 \times 10^{-4}$ $cm^2V^{-1}s^{-1}$ and 4.27×10^{-5} $cm^2V^{-1}s^{-1}$, respectively). The higher hole mobility obtained for P(BDT-BOB)-based device strongly supports the higher *FF* and J_{sc} obtained for P(BDT-BOB)-based PSCs.

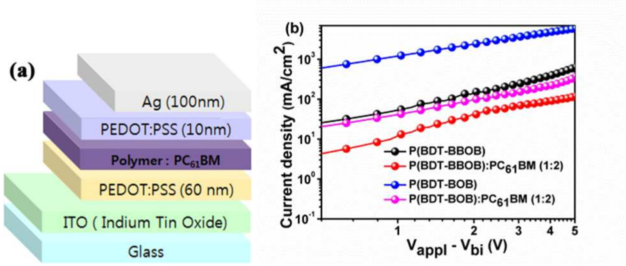

Fig. 6. (a) Schematic diagram of hole-only device. (b) current density–voltage (J–V) characteristics of hole-only devices.

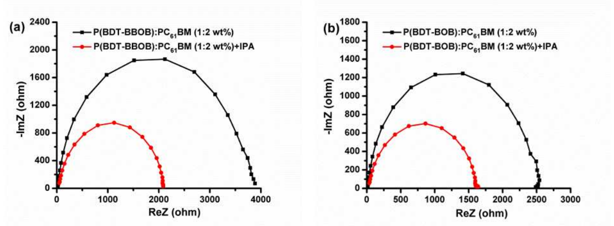

Fig. 7 Electrochemical impedance spectra of PSCs made from P(BDT-BBOB):$PC_{61}BM$ (1:2 wt%) and P(BDT-BOB):$PC_{61}BM$ (1:2 wt%) blends with/without IPA treatment.

In order to investigate the effect of solvent treatment on the interface resistance of the PSCs, the electrochemical impedance spectra (EIS) of the PSCs were measured in the dark condition. Fig. 7 shows the Nyquist plots of the ac impedance of the PSCs based on P(BDT-BBOB) and P(BDT-BOB) without and with solvent treatment at 0 V with frequency range from 1 Hz to 1MHz. The ac impedance consists of a single depressed semicircle for each PSC, which can be used to calculate the internal resistance of the thin film for the PSC. For example, the equivalent resistance of the PSC made from P(BDT-BBOB) with solvent treatment is about 2086 Ω, which is much smaller than the value of about 3886 Ω for the PSC without solvent treatment (see Fig. 6a). This indicates that the solvent treatment layer can improve the contact between photoactive layer and top Al electrode and, consequently, decreases the resistance of whole device. It is worth to notice that the resistance of P(BDT-BOB)-based PSCs are lower than that of P(BDT-BBOB)-based PSCs, which also supports our earlier arguments regarding the higher *FF* values obtained for P(BDT-BOB)-based PSCs.

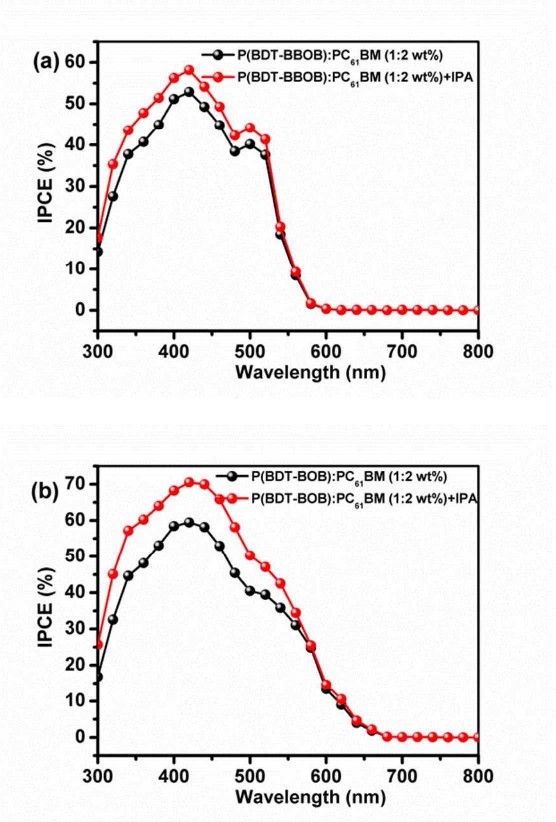

Fig. 8 IPCE spectra of the PSCs made form P(BDT-BBOB):PC$_{61}$BM (1:2 wt%) and P(BDT-BOB):PC$_{61}$BM (1:2 wt%) blends with/without IPA treatment.

The *IPCE* spectra of the PSCs made form P(BDT-BBOB):PC$_{61}$BM (1:2 wt%) and P(BDT-BOB):PC$_{61}$BM (1:2 wt%) blends with and without IPA treatment are displayed in Fig. 8. The *IPCE* responses were found to cover the region of 300 nm–580 nm and 300 nm–650 nm, respectively, for the PSCs made form P(BDT-BBOB) and P(BDT-BOB). The maximum *IPCE* value at 420 nm was appeared to be 53% and 58%, respectively, for the PSCs made from P(BDT-BBOB) without and with IPA treatment. On the other hand, the PSCs made from P(BDT-BOB) without and with IPA treatment showed the *IPCE* maximum of 60% and 70%, respectively, at 420 nm. In both cases, the *IPCE* responses of the PSCs were significantly increased after the IPA treatment. These results strongly agree with the higher J_{sc} values obtained for the PSCs made with IPA treatment and also support the higher J_{sc} values obtained for the PSCs made from P(BDT-BOB) compared with those obtained for the PSCs made from P(BDT-BBOB). The integrated J_{sc} value of the PSCs determined from *IPCE* spectra and the J_{sc} values obtained from *J–V* curve of the PSCs are found to be within 5% error range and the integrated J_{sc} values are summarized in Table 2 for clear comparison.

3.5 Active layer surface morphology

The tapping mode atomic force microscopy (AFM) images of the films made from P(BDT-BBOB):PC$_{61}$BM (1:2 wt%) and P(BDT-BOB):PC$_{61}$BM (1:2 wt%) without and with IPA treatment were recorded as shown in Fig. 9. The rms roughness of the films made from P(BDT-BBOB):PC$_{61}$BM (1:2 wt%) and P(BDT-BOB):PC$_{61}$BM (1:2 wt%) are increased from 0.98 nm to 1.3 nm and from 0.38 nm to 0.58 nm, respectively, after applying the solvent treatment. The rough surface can increase the contact area between the photoactive layer and Al cathode, which may benefit more efficient charge collection at the interface.[41] Moreover, the increased surface roughness may also increase the internal reflection and light collection, increasing the PSCs efficiency.[42]

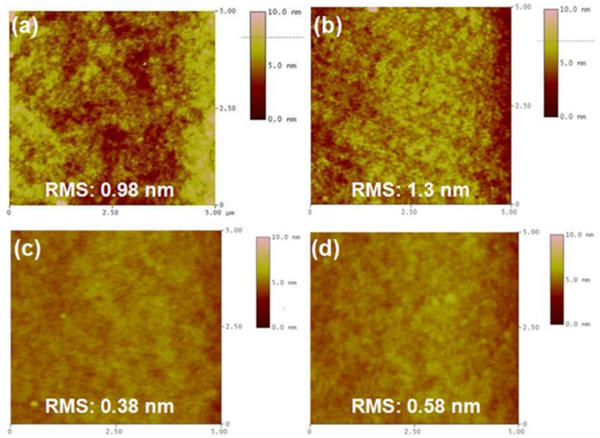

Fig. 9 AFM images of the blend films of P(BDT-BBOB):PC$_{61}$BM (1:2 wt%) and P(BDT-BOB):PC$_{61}$BM (1:2 wt%) without (images a and c, respectively) and with solvent treatment (images b and d, respectively).

4. Conclusions

Two new electron accepting monomers (BBOB and BOB) containing serially connected two different electron deficient units such as 2,1,3-benzothiadiazole (BT) and 1,2,4-oxadiazole (Oxa) are prepared and copolymerized with electron rich distannyl derivative of 4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b′]dithiophene (BDT) to afford polymers P(BDT-BBOB) and P(BDT-BOB), respectively. Polymer P(BDT-BBOB) incorporating two Oxa units on the both sides of BT unit was found to show a blue-shifted absorption with slightly lower HOMO level compared with those of polymer P(BDT-BOB) incorporating one Oxa unit attached to the BT unit. The maximum *PCE* obtained for the PSCs made with the configuration of ITO/PEDOT:PSS/P(BDT-BBOB) or P(BDT-BOB):PC$_{61}$BM (1:2 wt%)/IPA/LiF/Al was 3.31% and 4.21%, respectively, measured using AM 1.5 G solar simulator at 100 mW/cm^2 light illumination. The presence of additional Oxa unit on the polymer main chain was found to decrease the *FF* and J_{sc} values significantly and consequently, gave lower *PCE*. This study concludes that the ratio or configuration of covalently bonded two different electron acceptor units present in the polymer main notably alters the optical, electrical and photovoltaic properties of the polymers. We hope that replacement of the Oxa unit in polymer P(BDT-BOB) with other electron accepting unit such as thiadiazole, tetrazine or thiazole might enhance the *PCE* further and currently the progress is underway.

Acknowledgements

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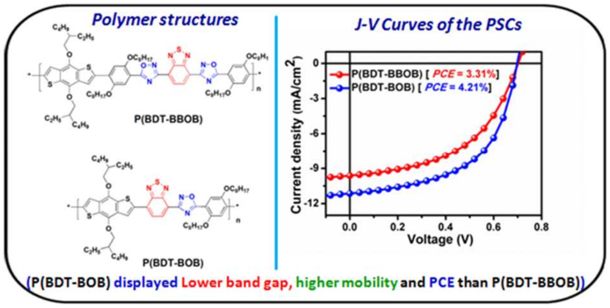
Two novel polymers incorporating covalently bonded two different acceptor units such as 2,1,3-benzothiadiazole and 1,2,4-oxadiazole are prepared. The opto-electrical and photovoltaic properties of the polymers are found to be quite dependent on the configuration of the two acceptor units.



(P(BDT-BOB) displayed Lower band gap, higher mobility and PCE than P(BDT-BBOB))