Synthesis of Polymers Containing 1,2,4-Oxadiazole as an Electron-Acceptor Moiety in Their Main Chain and Their Solar Cell Applications

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ABSTRACT: To explore the aptitude of 1,2,4-oxadiazole-based electron-acceptor unit in polymer solar cell applications, we prepared four new polymers (P1–P4) containing 1,2,4-oxadiazole moiety in their main chain and applied them to solar cell applications. Thermal, optical, and electrochemical properties of the polymers were studied using thermogravimetric, absorption, and cyclic voltammetry analysis, respectively. All four polymers showed high thermal stability (5% degradation temperature over 335 °C), and the optical band gaps were calculated to be 2.20, 1.72, 1.37, and 1.74 eV, respectively, from the onset wavelength of the film-state absorption band. The energy levels of the polymers were found to be suitable for bulk heterojunction (BHJ) solar cell applications. The BHJ solar cells were prepared by using the synthesized polymers as a donor and $PC_{71}BM$ as an electron acceptor with the configuration of ITO/PEDOT:PSS/polymer:$PC_{71}BM$ (1:3 wt %)/LiF/Al. One of the polymers was found to show the maximum power conversion efficiency of 1.33% with a Jsc of 4.95 mA/cm^2, a V_{oc} of 0.68 V, and a FF of 40%, measured using AM 1.5 G solar simulator at 100 mW/cm$_2$ light illumination. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 2131–2141

KEYWORDS: bulk heterojunction solar cells; conjugated polymers; copolymerization; oxadiazole-based polymers; pyrrole-based polymers; solar cells

INTRODUCTION Polymer solar cells (PSCs) are considered as a green energy production technique and PSCs based on the bulk heterojunction (BHJ) structure are competing with inorganic-based solar cells, which are already commercialized, due to their advantages in that they can be fabricated at low cost, light weight, flexibility, and most notably, very fast modes of production to large area by standard roll-to-roll (R2R) printing techniques.[1,2] So far, the power conversion efficiency (PCE) of the PSCs was significantly improved by three different ways such as developing structurally new donor polymer that have the capability to absorb the sunlight efficiently,[3–7] replacing the existing acceptor ($PC_{71}BM$) with new acceptor unit that has the increased lowest unoccupied molecular orbital (LUMO) energy level[8] or changing the device architecture to inverted[9] or tandem structured PSCs.[10,11] After many efforts, the PCE of the single layer PSCs was improved to 7.5%[3–7] and that of tandem structured PSCs containing two different photoactive layers was enhanced in the range of 8–10.6%.[9–11] The theoretical studies implied that the maximum PCE could be reach up to 17% for single layer PSC and 24% for tandem PSCs.[12] In our attempt to improve the PCE of PSCs, we were interested in synthesizing new donor polymers that have the appropriate energy levels with broad absorption band in entire part of the visible spectrum.

The broad absorption polymers were usually synthesized by copolymerizing the electron rich and electron deficient unit in alternate fashion, thereby decreasing the band gap due to the combined electronic transition, such as π–π* electronic transition in the donor and internal charge transfer (ICT) between the donor and acceptor moiety.[13–20] So far, benzothiadiazole and quinoxaline derivatives were widely used as an electron deficient unit in the low band-gap polymer preparation and the photovoltaic studies of those polymers showed maximum PCE of 6%.[21–28] Recently, a variety of new electron-accepting heteroaromatic units were incorporated in polymer main chain and the PCE of single layer PSCs were significantly improved up to 7.5% by using them as a donor polymer[29–34] in PSC studies. The later results indicate that changing the electron-acceptor unit in polymer main chain can show big difference in the optoelectrical and photovoltaic properties of the polymer due to the different electron-accepting strength and carrier mobility. In this instance, finding new acceptor unit to prepare structurally new polymers for PSC applications is quite important. In heterocyclic chemistry, the planar structured oxadiazoles are known to be a strong electron-accepting moiety[35,36] and, consequently, PSC applications of polymers containing oxadiazole moiety would be quite interesting. Recently, polymers containing electron-withdrawing 1,3,4-oxadiazole side chains were investigated for their photovoltaic properties.[37] However, to the best of our knowledge, polymers containing oxadiazole moiety in the polymer main chain have not been studied for any optoelectronic applications so far. In this study, we elucidate the possible utility of oxadiazole moiety as an electron-acceptor unit in polymer main chain for polymer solar cell applications. As an oxadiazole moiety, we selected 1,2,4-oxadiazole because its derivative can be easily prepared from commercially available materials. In this study, we prepared four new polymers containing 1,2,4-oxadiazole moiety in their main chain. Here, we report the synthesis and optical, electrical, and photovoltaic properties of the four new polymers.

EXPERIMENTAL

Materials and Instruments

The commercially available reagents were received from Aldrich or TCI chemicals and used without further purification. The anhydrous grade solvents were purchased from Aldrich or Fluka and the common organic solvents such as dichloromethane, tetrahydrofuran, and diethyl ether were distilled and handled in a moisture-free atmosphere. The compounds were purified by column chromatography on 70–230 mesh silica gel (Merck Kieselgel 60, 70–230 mesh ASTM). The nuclear magnetic resonance (NMR) spectra of the compounds were recorded using Varian Mercury Plus spectrometer (300 and 75 MHz, respectively for ^{1}H and ^{13}C) in $CDCl_3$. Gel permeation chromatography (GPC) analyses were conducted on an Agilent 1200 Infinity Series separation module using polystyrene as a standard and chloroform as an eluent to determine the molecular weight and polydispersity (PDI) of the polymers. Thermogravimetric analyses (TGA) were conducted with a TA instrument Q500 at a heating rate of 10 °C/min under nitrogen. The absorption studies of the polymers were performed on JASCO V-570 spectrophotometer at 25 °C in chloroform or as thin films on glass. Cyclic voltammetry (CV) measurements were performed using a CH Instruments Electrochemical Analyzer with a standard three-electrode electrochemical cell (Ag/AgCl: reference electrode, platinum: working electrode, platinum wire: counter electrode) in a 0.1 M tetrabutylammonium tetrafluoroborate (Bu_4NBF_4)/chloroform as the supporting electrolyte at room temperature. During the CV measurements, the redox couple ferrocene/ferrocenium ion (Fc/Fc+) was used as an external standard. Atomic force microscopy (AFM) images of blend films were obtained on a Veeco-Multimode AFM operating in the tapping mode.

Device Preparation

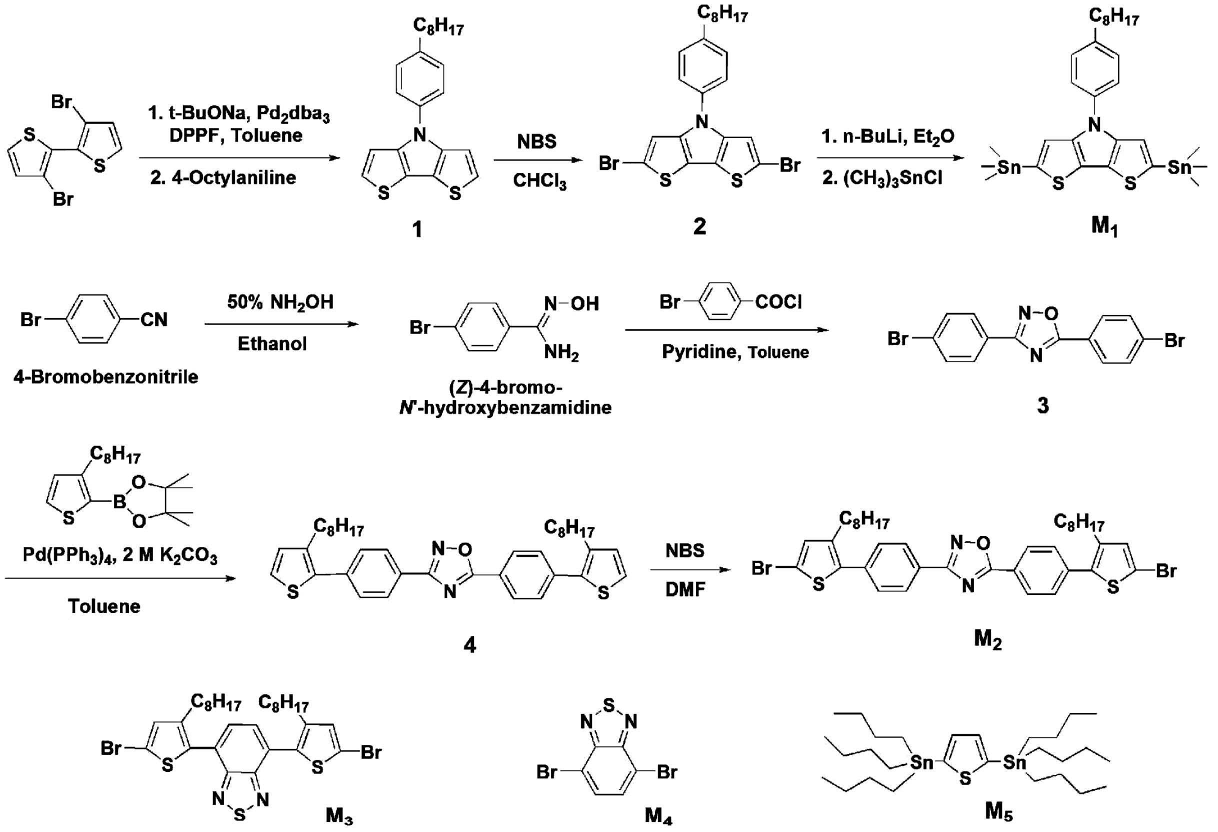
The polymer solar cells were prepared and characterized as we described below. Indium tin oxide (ITO)-coated glass substrates were cleaned stepwise by acetone, deionized water, and isopropyl alcohol in an ultrasonic bath. Followed by 50-nm poly(ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) (Clevious P VP Al 4083) buffer layer was spin-coated on the top of ITO substrate at 3000 rpm for 30 s and dried at 150 °C for 20 min under vacuum to remove the residual water. The active layer of polymer and $PC_{71}BM$ blend (1:3 wt/wt) was spin-coated at 2000 rpm from dichlorobenzene (DCB) solution on the top of ITO/PEDOT:PSS substrate. The ITO/PEDOT:PSS/Polymer:$PC_{71}BM$ substrate was allowed to dry for 2 h in a glove box and then subjected to preannealing at 150 °C for 20 min. The corresponding active layer thickness was found to be around 80 nm. The ITO/PEDOT:PSS/Polymer:$PC_{71}BM$ substrate was transferred into the vacuum chamber and around 0.7-nm-thick layer of LiF was deposited on the substrate. Subsequently, 120-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 (1.2×10^{-6} torr). The top metal electrode area, comprising the active area of the solar cell, was found to be 0.36 cm^2. The BHJ solar cell performance was measured using a AM 1.5G solar simulator (Oriel 300 W) at 100 mW/cm^2 light illumination after adjusting the light intensity using Oriel power meter (model No. 70260 which was calibrated using laboratory standards that are traceable to the National Institute of Standards and Technologies). Current–voltage (*J*–*V*) characteristics of the polymer BHJ solar cell devices were measured using a standard source measurement unit (Keithley 236). All fabrication steps and characterization measurements were performed in an ambient environment without a protective atmosphere. The thickness of the thin films was measured using a KLA Tencor Alpha-step IQ surface profilometer with an accuracy of ±1 nm.

Synthesis

The general synthetic strategy for monomers **M1** and **M2** and polymers **P1-P4** are outlined in Schemes 1 and 2, respectively. Monomer **M3**, 4,7-bis(5-bromo-3-octyl-2-thienyl)-2,1,3-benzothiadiazole,[38] and monomer **M4**, 4,7-dibromo-2,1,3-benzothiadiazole,[39] were synthesized via the reported procedures. Monomer **M5**, 2.5-bis(tributylstannyl)thiophene, is commercially available from Sigma-Aldrich. The detailed synthetic procedures for monomers **M1** and **M2** and polymers **P1–P4** were described below.

Synthesis of *N*-[4-Octylphenyl]dithieno[3,2-*b*:2′,3′-*d*]pyrrole (1)

A stirred solution of 3,3′-dibromo-2,2′-bithiophene (5.2 g, 16 mmol), which was prepared via the known procedure,[40] in 40 mL of toluene was purged well with argon for 15 min, and then NaO*t*Bu (3.7 g, 38.5 mmol), Pd_2dba_3 (0.4 g, 0.44 mmol), and 1,1′-bis(diphenylphosphine)ferrocene (DPPF, 1.0



SCHEME 1 Synthetic route for the synthesis of monomers **M1** and **M2** and the structures of monomers **M3**, **M4**, and **M5**.

g, 1.8 mmol) were added in sequence. Then, 4-octylaniline (4.0 mL, 18 mmol) was added, and the mixture was refluxed for 12 h. The mixture was allowed to cool down, and the solvent was removed by rotary evaporation. The solid residue was dissolved in dichloromethane and the insoluble precipitates were filtered off. The organic solution was washed with water and then brine, and 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, 90/10) to afford compound **1** as a white solid.

Yield: 5.4 g (92%). mp 79–80 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.49 (d, 2H), 7.33 (d, 2 H), 7.17 (s, 4 H), 2.68 (t, 2H), 1.60–1.74 (m, 2 H), 1.22–1.44 (m, 10 H), 0.90 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 144.4, 141.2, 137.8, 129.9, 123.5, 122.8, 116.8, 112.5, 35.8, 32.1, 31.7, 29.7, 29.6, 29.5, 22.9, 14.4; HRMS (EI$^+$, *m/z*) [M$^+$] Calcd. for $C_{22}H_{25}NS_2$ 367.1428, found 367.1434.

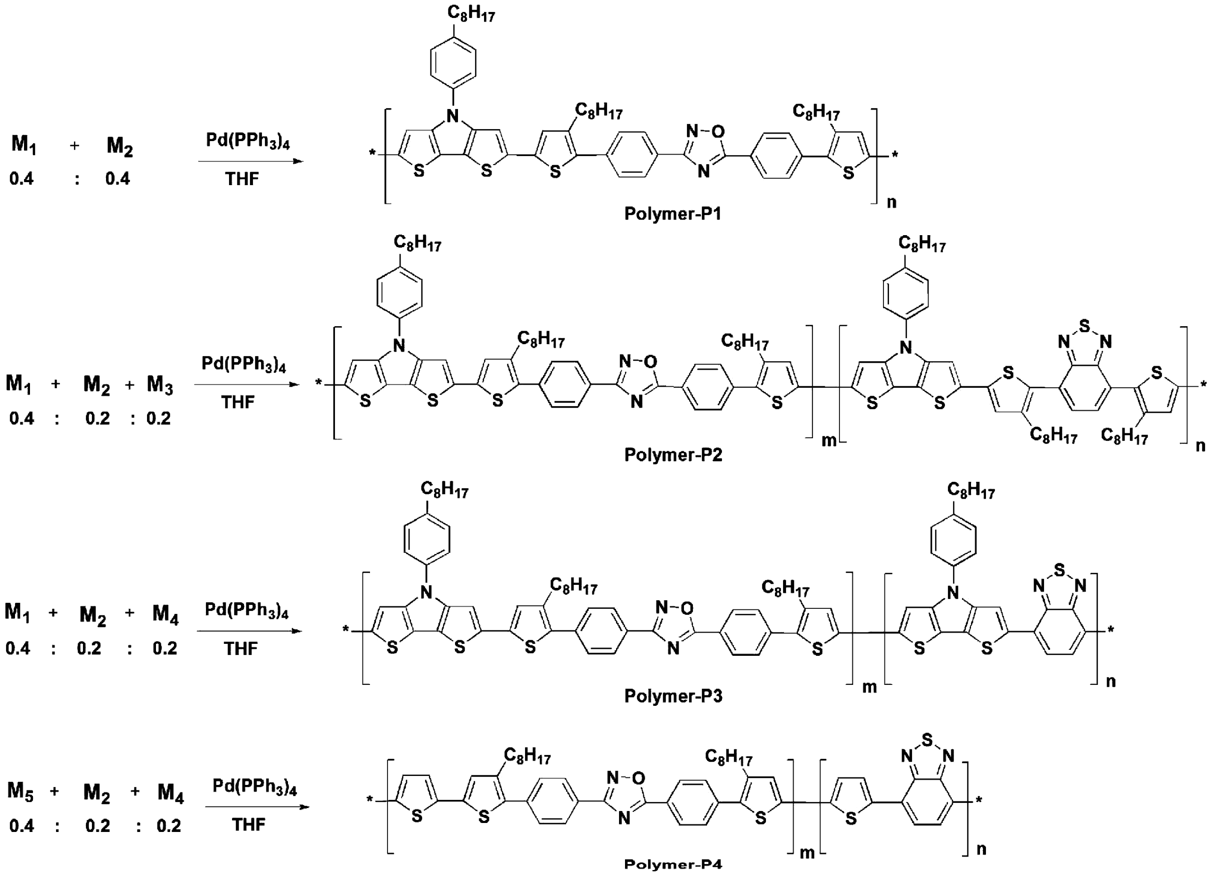
Synthesis of 2,6-Dibromo-*N*-[4-octylphenyl]dithieno[3,2-*b*:2′,3′-*d*]pyrrole (2)

Compound **1** (4.0 g, 10.8 mmol) was dissolved in chloroform (30 mL) and cooled to 0 °C in ice bath under argon. *N*-Bromosuccinimide (NBS) (4.25 g, 23.9 mmol) was added in one portion to the stirred solution. After 15 min, the mixture was allowed to warm to room temperature and stirred for 5 h. The organic mixture was washed with water, brine, and dried over anhydrous Na_2SO_4. The solution was filtered and evaporated by rotary evaporation and the crude product was purified by column chromatography (silica gel, hexane:CH_2Cl_2, 90/10) to afford pure compound **2** as a yellowish solid.

Yield: 5.4 g (92%). mp 121–122 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.49 (d, 2H), 7.32 (d, 2 H), 7.16 (s, 2 H), 2.67 (t, 2H), 1.60–1.74 (m, 2 H), 1.22–1.44 (m, 10 H), 0.89 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 142.1, 141.1, 136.8, 130.0, 123.0, 116.6, 115.7, 110.5, 35.7, 32.1, 31.7, 29.7, 29.6, 29.5, 22.9, 14.4; HRMS (EI$^+$, *m/z*) [M$^+$] Calcd. for $C_{22}H_{23}Br_2NS_2$ 522.9639, found 522.9647.

Synthesis of 2,6-Di(trimethyltin)-*N*-[4-octylphenyl]dithieno[3,2-*b*:2′,3′-*d*]pyrrole (M1)

Under argon atmosphere, a solution of compound **2** (2.52 g, 4.8 mmol) in dry diethyl ether (40 mL) was cooled to 0 °C in ice bath for 20 min. To the stirred solution, *n*-BuLi (4.2 mL, 10.5 mmol, 2.5 M solution in hexane) was added dropwise, resulting in the formation of a white precipitate. The mixture was allowed to reach room temperature, and after stirring for 20 min, a solution of Me_3SnCl (10.5 mL, 10.5 mmol, 1 M solution in hexane) was added. The initial white precipitates disappeared, and the clear solution was obtained, from which another white precipitates were formed. After stirring at room temperature for 1 h, the solvent was removed. Hexane was added, and the white precipitates were filtered off. The filtrate was passed through the neutral alumina packed (5 cm in height) on sintered crucible



SCHEME 2 Synthetic route for the synthesis of polymers **P1**–**P4**.

under vacuum. The filtrate was concentrated by rotary evaporation and dried under vacuum to afford monomer **M1** as a yellow solid material.

Yield: 2.85 g (86%). mp 85–86 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.52 (d, 2H), 7.34 (d, 2 H), 7.15 (s, 2 H), 2.68 (t, 2H), 1.60–1.74 (m, 2 H), 1.22–1.44 (m, 10 H), 0.90 (t, 3H), 0.39 (s, 18 H); ^{13}C NMR (75 MHz, CDCl3): δ (ppm) 147.2, 140.8, 138.2, 136.6, 129.8, 122.9, 122.4, 119.3, 35.8, 32.1, 31.8, 29.7, 29.6, 29.5, 22.9, 14.4, −7.9; HRMS (EI$^+$, *m/z*) [M$^+$] Calcd. for $C_{28}H_{41}NS_2Sn_2$ 695.0724, found 695.0726.

Synthesis of 3,5-Bis(4-bromophenyl)-1,2,4-oxadiazole (3)

To a stirred solution of 4-bromobenzonitrile (5.0 g, 27.5 mmol) in ethanol (50 mL), 50% aqueous hydroxylamine solution (6 mL) was added and refluxed for 2 h. The completion of the reaction was confirmed by TLC, and ethanol was removed by rotary evaporation. The crude product was dissolved in ethyl acetate (100 mL) and washed one time with water (20 mL). The organic layer was separated and dried over anhydrous Na_2SO_4. After filtration and removal of the organic solvent by rotary evaporation, (*Z*)-4-bromo-*N*′-hydroxybenzamidine was obtained as a white solid.

Yield: 5.7 g (96%). mp 148–149 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.52 (d, 4 H), 4.83 (brd s, 2 H). (*Z*)-4-Bromo-*N*′-hydroxybenzamidine (5.0 g, 23.3 mmol) was dissolved in 60 mL of toluene, and the solution was cooled to 0 °C in ice bath. After 15 min, pyridine (2 mL, 24 mmol) and 4-bromobenzoyl chloride (5.3 g, 24 mmol) were added and stirred for 2 h in the same bath. The ice bath was removed and the mixture was refluxed for 15 h. The insoluble material was filtered off in hot condition, and the filtrate was concentrated by rotary evaporation. The crude material was purified by column chromatography (silica gel, hexane) to afford pure compound **3** as a white solid material.

Yield: 8 g (90%). mp 179–180 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.07 (d, 2 H), 8.03 (d, 2 H), 7.70 (d, 2 H), 7.65 (d, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 175.3, 168.6, 132.8, 132.4, 129.8, 129.2, 128.2, 126.1, 125.9, 123.2; HRMS (EI$^+$, *m/z*) [M$^+$] Calcd for $C_{14}H_8Br_2N_2O$ 377.9003, found 377.9009.

Synthesis of 3,5-Bis(4-(3-octylthiophen-2-yl)phenyl)-1,2,4-oxadiazole (4)

A stirred solution of compound **3** (3 g, 7.9 mmol) and 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-octylthiophene (5.8 g, 18 mmol), which was prepared via the known procedure,[36] in toluene (50 mL) was purged with argon for 45 min. To the solution, Pd $(PPh_3)_4$ (0.37 g, 4 mol %) and aqueous 2 M K_2CO_3 (7 mL) were added. The whole mixture was refluxed for 24 h under argon. The solution was cooled to room temperature and concentrated by rotary evaporation. The crude product was dissolved in dichloromethane and washed with water and then brine. The organic layer was separated and dried over anhydrous Na_2SO_4. The organic solution was filtered and concentrated by rotary evaporation, and then the residue was purified by column chromatography (silica gel, hexane:ethyl acetate, 9.5/0.5, v/v) to afford pure compound **4** as a yellow liquid material.

Yield: 3.9 g (81%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.27 (d, 2H), 8.23 (d, 2 H), 7.63 (d, 2H), 7.59 (d, 2 H), 7.31 (d, 1 H), 7.27 (d, 1 H), 7.03 (d, 1 H), 7.01 (d, 1 H), 2.66–2.76 (m, 4 H), 1.58–1.70 (m, 4 H), 1.16–1.38 (m, 20 H), 0.87 (t, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 175.7, 169.0, 140.3, 139.8, 138.1, 137.1, 136.5, 132.4, 130.2, 130.0, 129.9, 129.3, 128.6, 127.9, 125.9, 125.1, 124.6, 123.0, 32.1, 31.2, 31.1, 29.7, 29.6, 29.5, 29.1, 29.0, 22.9, 14.3; HRMS (EI$^+$, *m/z*) [M$^+$] Calcd. for $C_{38}H_{46}N_2OS_2$ 610.3052, found 610.3054.

Synthesis of 3,5-Bis(4-(5-bromo-3-octylthiophen-2-yl)phenyl)-1,2,4-oxadiazole (M2)

Compound (**4**) (3 g, 4.9 mmol) was dissolved in dimethylformamide (20 mL) under argon. To the stirred solution was added NBS (1.78 g, 10.0 mmol) in one portion. The resulting solution was stirred at room temperature under argon overnight. The solvent was concentrated by using rotary evaporator and then the crude martial was dissolved in dichloromethane and the organic solution was washed with water and then brine. The organic solution 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:ethyl acetate, 9.5:0.5, v/v) to afford monomer **M2** as a yellow sticky material.

Yield: 3.3 g (88%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.25 (d, 2H), 8.21 (d, 2 H), 7.56 (d, 2H), 7.52 (d, 2 H), 6.98 (s, 1 H), 6.96 (s, 1 H), 2.58–2.68 (m, 4 H), 1.52–1.66 (m, 4 H), 1.12–1.38 (m, 20 H), 0.87 (t, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 175.6, 168.9, 140.9, 140.4, 138.6, 138.5, 138.0, 136.9, 132.9, 132.7, 132.4, 129.9, 129.8, 129.3, 128.7, 128.0, 126.3, 123.3, 32.1, 31.1, 31.0, 29.6, 29.5, 29.4, 29.0, 28.9, 22.9, 14.4; HRMS (EI$^+$, *m/z*) [M$^+$] Calcd. for $C_{38}H_{44}Br_2N_2OS_2$ 766.1262, found 766.1268.

General Procedure for Polymer Synthesis

A solution of respective monomers (shown in Scheme 2) in THF (60 mL) was purged well with argon for 45 min. Then, Pd $(PPh_3)_4$ (0.02 g, 5 mol %) was added to the stirred solution and the mixture was heated to reflux under argon atmosphere. After refluxing for 48 h, the reaction mixture was cooled to room temperature and then poured into the mixed solvent of methanol and water (200 mL:100 mL) containing 2 N HCl (50 mL) with vigorous stirring. The precipitate was recovered by filtration, and then extracted with methanol for 24 h and acetone for 24 h in a Soxhlet apparatus.

P1

Red color. Yield (0.29 g, 74%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.16–8.34 (m, 4 H), 7.48–7.70 (m, 6 H), 7.39 (d, 2 H), 7.00–7.26 (m, 4 H), 2.60–2.80 (m, 6 H), 1.60–1.80 (m, 6 H), 1.10–1.50 (m, 30 H), 0.74–0.98 (m, 9 H).

P2

Black color. Yield (0.36 g, 49%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.10–8.28 (m, 4 H), 7.98–8.10 (m, 2 H), 7.54–7.68 (m, 4 H), 7.42–7.54 (m, 5 H), 7.38 (d, 5 H), 7.00–7.26 (m, 6 H), 2.60–2.80 (m, 12 H), 1.60–1.80 (m, 12 H), 1.14–1.50 (m, 60 H), 0.74–1.00 (m, 18 H).

P3

Black color. Yield (0.25 g, 42%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.36 (s, 1 H), 8.10–8.28 (m, 4 H), 7.84 (s, 1 H), 7.44–7.64 (m, 8 H), 7.28–7.44 (m, 4 H), 6.86–7.24 (m, 6 H), 2.58–2.82 (m, 8 H), 1.60–1.80 (m, 8 H), 1.14–1.50 (m, 40 H), 0.74–1.00 (m, 12 H).

P4

Dark brown color. Yield (0.27 g, 75%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.20–8.32 (m, 4 H), 8.06 (s, 1 H), 7.89 (s, 1 H), 7.56–7.72 (m, 4 H), 7.44–7.56 (m, 2 H), 7.24 (s, 1 H), 7.10 (s, 2 H), 7.04 (s, 1 H), 2.64–2.78 (m, 4 H), 1.60–1.74 (m, 4 H), 1.18–1.44 (m, 20 H), 0.76–0.98 (m, 6 H).

RESULTS AND DISCUSSIONS

Synthesis and Characterization

The synthetic procedures for the monomers and polymers are outlined in Schemes 1 and 2, respectively. In our laboratory, we have been interested in the utilization of pyrrole-based polymers in PSC applications.[38,39,41–44] Recently, we reported acyclic *N*-aryl TPT (thiophene-(*N*-arylpyrrole)-thiophene)-based polymers for PSCs applications and those polymers showed reasonable current density and performance in their photovoltaic studies.[38,39,41–44] These results induced us to develop cyclic *N*-aryl pyrrole monomer because cyclic structure has much better π–π conjugation than acylic structure. In this instance, we prepared a new cyclic *N*-aryl TPT (*N*-aryl DTP) monomer. The electron rich new *N*-aryl DTP monomer **M1**, 2,6-di(trimethyltin)-*N*-[4-octylphenyl]dithieno[3,2-b:2′,3′-d]pyrrole, was synthesized via the procedure similar to that reported by Koeckelberghs et al.[40] The reaction between 3,3′-dibromo-2,2′-bithiophene and 4-octylphenyl aniline in the presence of palladium catalyst afforded compound **1**. And then compound **1** was selectively brominated using NBS to yield compound **2**. The final *N*-aryl DTP monomer (**M1**) was obtained by treating compound **2** with *n*-BuLi followed by Me_3SnCl. On the other hand, compound **3** containing the electron-accepting 1,2,4-oxadiazole moiety was prepared by the reaction between (*Z*)-4-bromo-*N*′-hydroxybenzamidine, which was prepared by treating 4-bromobenzonitirle with 50% hydroxy amine solution, and 4-bromobenzoyl chloride. The Suzuki coupling reaction between compound **3** and 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-octylthiophene afforded compound **4**. Bromination of compound **4** with NBS afforded a new 1,2,4-oxadiazole-based monomer (**M2**). The other monomers (**M3** and **M4**) were synthesized via the known literature procedures.[38,39] All polymers (**P1**–**P4**) were prepared by using the Stille coupling reaction between the respective monomers. Polymer **P1** is alternating copolymer, whereas all other polymers **P2**–**P4** are random copolymers. The copolymerization between monomers **M1** and **M2** afforded polymer **P1** containing

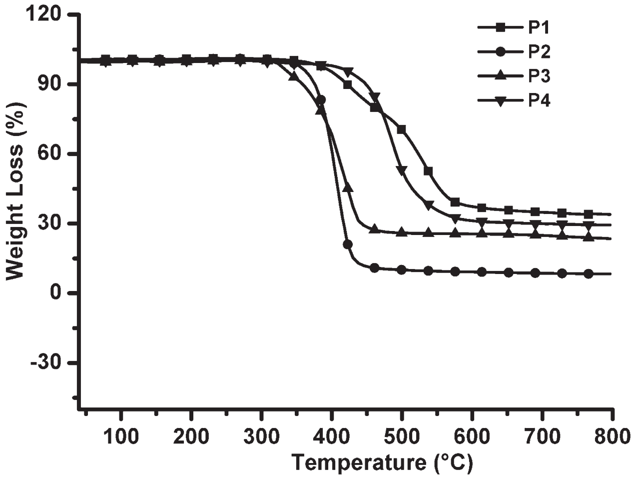


FIGURE 1 TGA curves for polymers **P1**–**P4**.

1,2,4-oxadiazole electron-acceptor unit in the polymer main chain. The absorption study of polymer **P1** shows that the absorption band is extending only up to 550 nm, indicating the electron attracting ability of the 1,2,4-oxadiazole-acceptor unit is not satisfactory. To extend the absorption band of polymer **P1** further, a strong electron-accepting monomer such as **M3** or **M4** was incorporated into the main chain of polymer **P1** by polymerizing three comonomers (**M1** + **M2** + **M3** or **M1** + **M2** + **M4**) at the ratio of 2:1:1 to yield random copolymers **P2** and **P3**. For the preparation of polymer **P4**, thiophene derivative (**M5**) used as an electron rich comonomer instead of **M1** was polymerized with **M2** and **M4**. The structures of polymers **P1**–**P4** were characterized by NMR and absorption studies. The ratios of the two different repeating units [oxadiazole (*m*) and benzothiadiazole (*n*)-based repeating units] in polymers **P2**, **P3**, and **P4** were found to be 1:0.8, 0.7:1, and 1:1, respectively. The solubility of the polymers was tested in the common organic solvents such as chloroform, tetrahydrofuran, chlorobenzene, and dichlorobenzene. All three polymers **P1**, **P2**, and **P3** exhibited good solubility in all solvents, whereas polymer **P4** showed poor solubility in chloroform and tetrahydrofuran. The weight average molecular weights (M_w) of polymers **P1**–**P4** were 2.01×10^4, 1.06×10^4, 5.38×10^3, and 4.89×10^4, and their polydispersities (PDI) were 1.83, 1.88, 1.35, and 2.44, respectively. The thermal stability of the polymers **P1**–**P4** was determined by using TGA, and the 5% decomposition temperature was found to be 399, 361, 338, and 430 °C, respectively. The TGA curves of the polymers **P1**–**P4** were presented in Figure 1. Polymers **P1** and **P4** showed higher thermal stability than polymers **P2** and **P3**. We expect that the high molecular weights of polymers **P1** and **P4** might be responsible for their high thermal stability. The polymerization results and the thermal properties of polymers **P1**–**P4** are summarized in Table 1.

Optical Properties

The UV–vis absorption spectra of the polymers **P1**–**P4** were measured in chloroform and as thin film on glass, and their absorption spectra were presented in Figure 2. The thickness of the copolymer films was estimated to be 88, 90, 85, and 88 nm, respectively. The color image of the polymers **P1**–**P4** films on glass was displayed in Figure 3. All of the four polymers display their absorption band in the visible part of the solar spectrum. Alternating copolymer **P1** shows the absorption band from 300 to 550 nm with maximum absorption peak at 441 and 458 nm, respectively, in solution and film. Random copolymer **P2** shows the absorption band up to 700 nm in film with the maximum absorption peak at 458 and 441 nm, respectively, in film and solution. Polymers **P1** and **P2** show the exactly identical absorption maximum but polymer **P2** shows broader absorption band than polymer **P1**. We expect that **M3** unit in polymer **P2** main chain slightly broadens the absorption band due to the extended π–π delocalization of the repeating units. On the other hand, copolymer **P3** shows broader absorption band in entire part of the visible spectrum with two maximum absorption peaks at 397 and 613 nm in solution and 407 and 626 nm as film. Here, the introduction of **M4** unit in the polymer main chain significantly broadens the absorption band of polymer **P3** and the quite broad absorption is attributed to the combined electronic transitions such as the π–π* transition in the donor unit and the donor–acceptor ICT transition between **M1** and **M4** moiety. In the case of polymer **P4**, monomer **M1** of polymer **P3** was replaced with thiophene monomer **M5**. Polymer **P4** showed the blue shifted absorption maximum (396, 520 nm and 420, 562 nm, respectively, in solution and film) compared to those of polymers **P1** and **P2**. The film-state absorption bands of polymers **P1**–**P4** were found to be slightly broader and their corresponding absorption maxima were red shifted compared with those observed in solution state. The later phenomenon indicates that the polymers are well oriented (better π–π interchain interaction) in film state

TABLE 1 Polymerization Results, Thermal, Optical and Electrochemical Properties of Polymers **P1**–**P4**

	P1	P2	P3	P4
M_w[a]	2.01×10^4	1.06×10^4	5.38×10^3	4.89×10^4
PDI[a]	1.83	1.88	1.35	2.44
m:*n* ratio	–	1:0.8	0.7:1	1:1
TGA[b] (°C)	399	361	338	430
Abs (nm)				
Solution	257, 441	259, 441	261, 397, 613	256, 396, 520
Film[c]	458	458	265, 407, 626	420, 562
E_g[d] (eV)	2.20	1.72	1.37	1.74
HOMO[e] (eV)	−5.06	−5.09	−5.09	−5.39
LUMO[f] (eV)	−2.86	−3.37	−3.72	−3.65

[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 thin film were performed onto the quartz substrate.
[d] Band gap estimated from the onset wavelength of the optical absorption in thin film.
[e] The HOMO levels of the polymers were estimated from cyclic voltammetry analysis.
[f] The LUMO levels of the polymers were calculated using the equation of LUMO = HOMO + E_g.

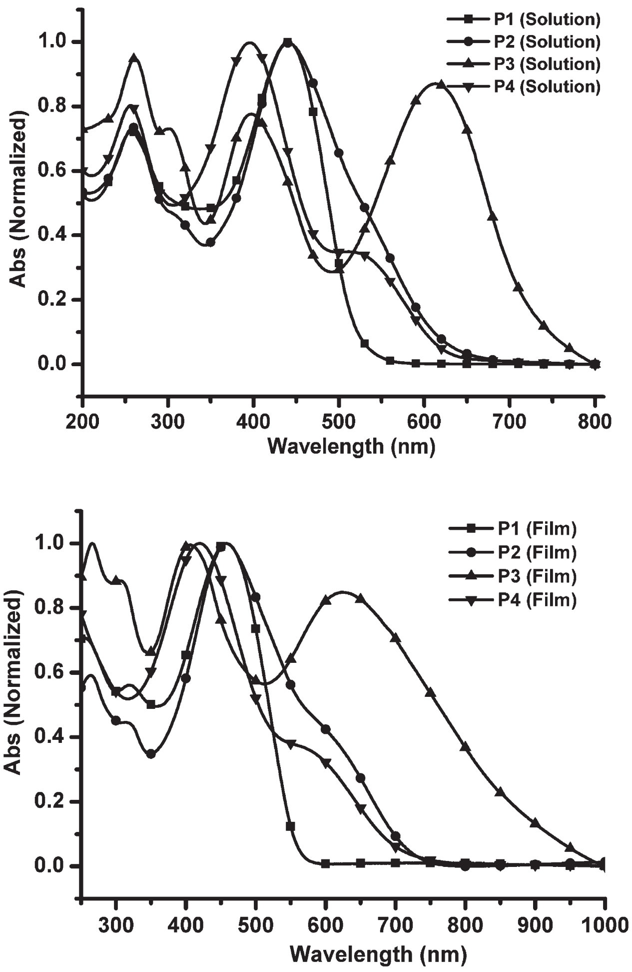


FIGURE 2 UV–visible absorption spectra of polymers **P1**–**P4** in chloroform and thin film.

than those in solution. The optical band gaps of polymers **P1**–**P4** were calculated from the onset wavelength of the optical absorption in thin film to be 2.20, 1.72, 1.37, and 1.74 eV, respectively. The optical properties of polymers **P1**–**P4** are summarized in Table 1.

Electrochemical Properties

Determination of the conduction (HOMO) and valance (LUMO) band energy levels of the synthesized polymers is essential to evaluate their suitability for BHJ solar cell applications. For the efficient electron injection from polymer to $PC_{71}BM$, use of the polymer having higher LUMO energy level than that of $PC_{71}BM$ is most important. The energy levels of the polymers were determined from CV analysis. Figure 4 represents the cyclic voltammograms of polymers **P1**–**P4**. The HOMO energy levels of polymers **P1**–**P4** were calculated from the onset oxidation potentials using the known equation as follows,[38] $E_{\text{HOMO}} = [-(E_{\text{ox, onset vs. Ag/AgCl}} - E_{\text{ferrocene vs. Ag/AgCl}}) - 4.8]$ eV, where 4.8 eV is the energy level of ferrocene below the vacuum level and $E_{\text{ferrocene vs. Ag/AgCl}}$ is 0.51 eV, and $E_{\text{ox, onset}}$ is the onset potential values in volts for oxidation process against Ag/AgCl reference electrode. The onset oxidation potentials ($E_{\text{ox, onset}}$) of polymers **P1**–**P4** were estimated from the cyclic voltammograms shown in Figure 4 to be 0.77, 0.80, 0.80, and 1.10 V, respectively, and the HOMO energy levels of polymers **P1**–**P4** were calculated to be −5.06, −5.09, −5.09, and −5.39 eV, respectively. The LUMO energy levels of the polymers **P1**–**P4** were calculated by using the equation of LUMO = HOMO + E_g, and the LUMO energy levels of polymers **P1**–**P4** were determined to be −2.86, −3.37, −3.72, and −3.65 eV, respectively. The energy-level diagram of polymers **P1**–**P4** and **$PC_{71}BM$** with all other materials used in BHJ solar cell is presented in Figure 5. The conduction bands of all four polymers were located above the conduction band of $PC_{71}BM$ and the energy difference between the LUMO levels of the polymer and $PC_{71}BM$ is estimated to be 1.44, 0.93, 0.58, and 0.65 eV, respectively. According to the literature, 0.2–0.3 eV energy difference is enough for efficient electron transfer.[38,39,41–44] In this instance, the better electron transfer is expected in the order of **P3** > **P4** > **P2** > **P1** for the synthesized polymers **P1**–**P4**. The HOMO and LUMO energy levels of polymers **P1**–**P4** were included in Table 1.

BHJ Solar Cell Properties

The energy conversion abilities of the synthesized polymers were tested by using them as donor materials in PSCs with device structure of ITO/PEDOT:PSS/**P1**–**P4**:$PC_{71}BM$ (1:3 wt/wt)/LiF/Al. The active layer was sandwitched between the hole (PEDOT:PSS) injecting and electron transporting (LiF) layers and covered with ITO anode and Al cathode. The best donor:acceptor blend ratio was fixed by making the PSC devices with each of the synthesized polymers as a donor and $PC_{60}BM$ as an electron acceptor with three different weight ratios such as 1:1, 1:2, and 1:3 wt/wt. The best results were obtained with the PSCs made from 1:3 wt/wt

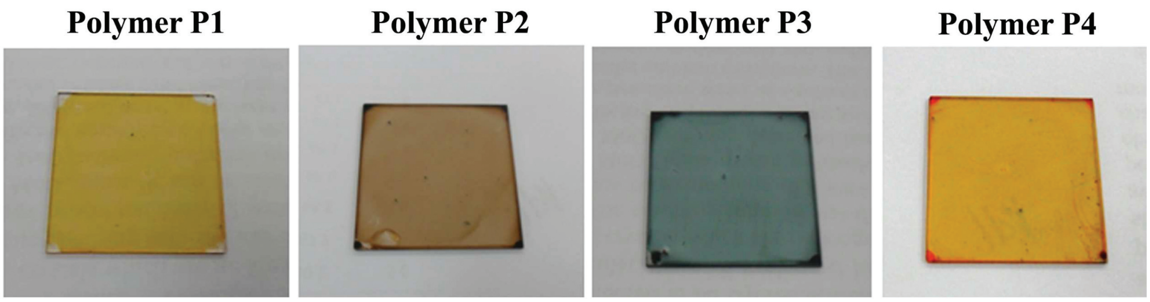


FIGURE 3 The color image of the polymers **P1**–**P4** films on glass.

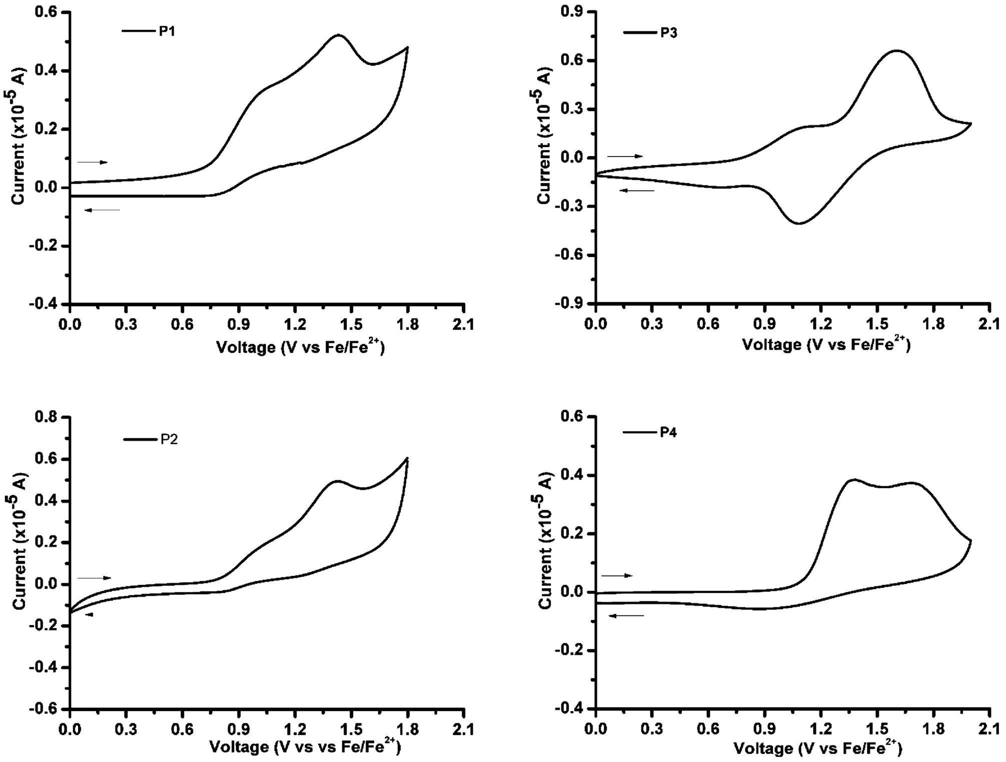


FIGURE 4 Cyclic voltammograms of polymers **P1**–**P4** in chloroform.

blend ratio. Later, the active layer of the PSCs were made with polymer:PC$_{71}$BM (1:3 wt/wt) blend solution and their corresponding characteristic parameters such as open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (*FF*), and PCE are summarized in Table 2. The current density–voltage (*J–V*) characteristics of the PSC devices were measured under the illumination of AM 1.5 G (100 mW/cm^2) solar simulator and their corresponding *J-V* curves are shown in Figure 6. Among the four PSC devices, the PSC made from **P1**:PC$_{71}$BM (1:3 wt/wt) showed the least *PCE* of

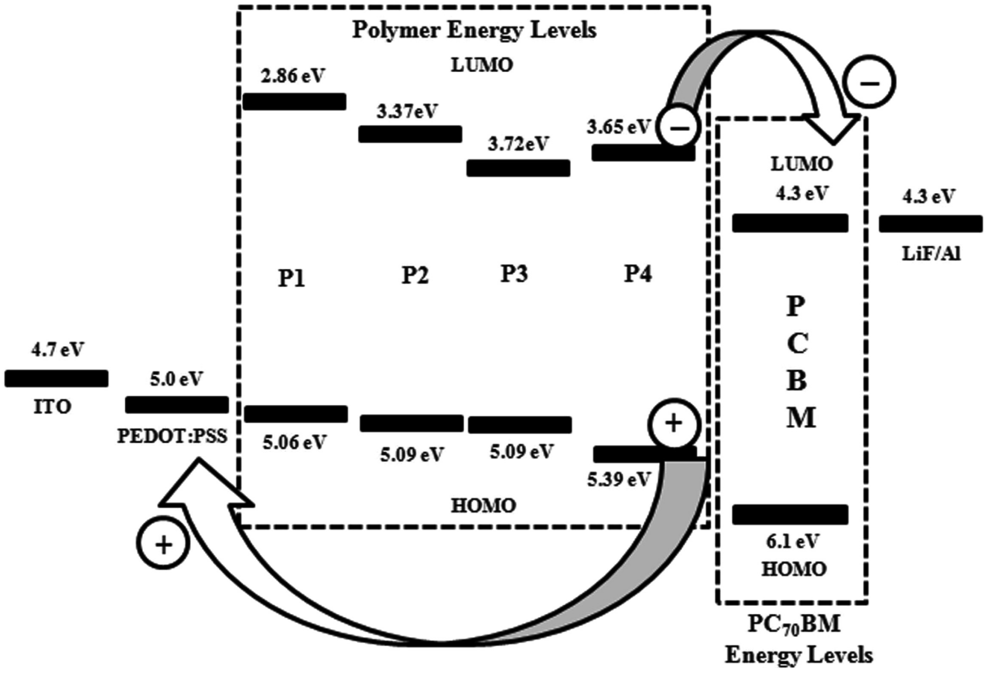


FIGURE 5 The energy level diagram of polymers **P1**–**P4** and **PC$_{71}$BM** with all other materials used in BHJ solar cell.

TABLE 2 Solar Cell Performance of Polymer **P1**–**P4** as Electron Donors with $PC_{71}BM$ as an Electron Acceptor in ITO/PEDOT:PSS/Polymer:$PC_{71}BM$(1:3 wt/wt)/LiF/Al Device

Photoactive Active Layer	V_{oc} (V)[a]	J_{sc} (mA/cm^2)[b]	*FF* (%)[c]	PCE (%)[d]
P1:$PC_{71}BM$ (1:3 wt/wt)	0.61	4.27	28	0.73
P2:$PC_{71}BM$ (1:3 wt/wt)	0.61	4.70	37	1.05
P3:$PC_{71}BM$ (1:3 wt/wt)	0.68	4.95	40	1.33
P4:$PC_{71}BM$ (1:3 wt/wt)	0.72	3.48	32	0.80

[a] Open-circuit voltage.

[b] Short-circuit current density.

[c] Fill factor.

[d] Power conversion efficiency.

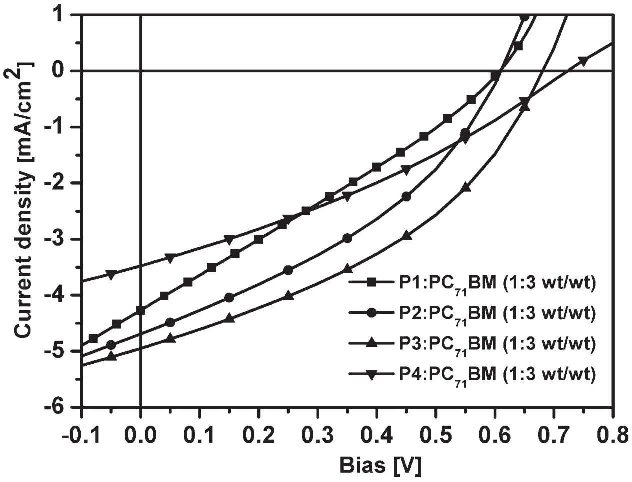


FIGURE 6 *J*–*V* characteristics of BHJ solar cells prepared from ITO/PEDOT:PSS/**Polymer**:$PC_{71}BM$ (1:3 wt/wt)/LiF/Al under AM 1.5 irradiation (100 mW/cm^2).

0.73% with a V_{oc} of 0.61 V, a J_{sc} of 4.27 mA/cm^2, and a *FF* of 0.28. The PSC made from **P2**:$PC_{71}BM$ (1:3 wt/wt) showed higher *PCE* of 1.05% with a V_{oc} of 0.61 V, a J_{sc} of 4.70 mA/cm^2, and a *FF* of 0.37 than the PSC made from **P1**:$PC_{71}BM$ (1:3 wt/wt). The PSC made from **P3**:$PC_{71}BM$ (1:3 wt/wt) showed the best *PCE* of 1.33% with V_{oc} of 0.68 V, a J_{sc} of 4.95 mA/cm^2, and a *FF* of 0.40. Finally, the PSC made from **P4**:$PC_{71}BM$ (1:3 wt/wt) showed the *PCE* value of 0.80% with a V_{oc} of 0.72 V, a J_{sc} of 3.48 mA/cm^2, and a *FF* of 0.32. The V_{oc} values obtained from the PSC devices are in the range of 0.61–0.72 V. The V_{oc} value is highly influenced by several factors, such as voltage loss at the ohmic contacts, molecular weight, and PDI of the donor polymer, carrier mobility of excitons, surface morphology, and quality of heterojunction at donor/acceptor interfaces.[45–47] To consider all those factors, the V_{oc} values achieved in this study are expected to be reasonable. The J_{sc} value of the PSC is mainly correlated with the light harvesting ability of the donor polymer. In this point of view, the J_{sc} values are expected in the

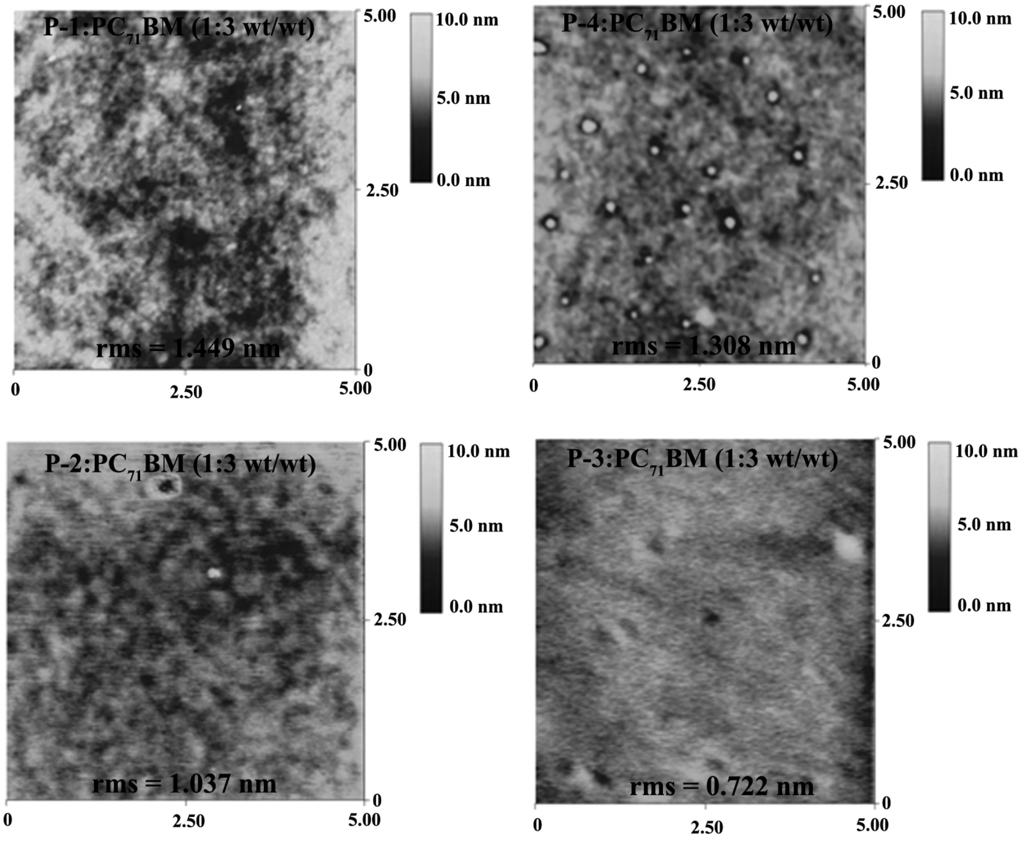


FIGURE 7 AFM image obtained by tapping-mode on the surface for **Polymer**:$PC_{71}BM$ (1:3 wt/wt) spin coated thin film.

following order **P3** > **P2** > **P1** > **P4** for the synthesized polymers, and they are correlated well with the experimental J_{sc} values. However, polymer **P4**-based PSC showed higher *PCE*, V_{oc} and *FF* than polymer **P1**-based PSC. We expect that the relatively high molecular weight of polymer **P4** might be responsible for its better photovoltaic performance than polymer **P1**.[46] In this instance, increasing the molecular weight of polymers **P1**–**P4** is expected to improve their photovoltaic performances, because high-molecular-weight polymers, in general, show enhanced photovoltaic performances compared to those of the low molecular weight polymers.[46] The molecular weight of polymers can be increased by the incorporation of alkyl side chain on the polymer backbone. In our newly synthesized monomer units, we have many chances for the alkyl group incorporation and, consequently, we might improve the molecular weight of the 1,2,4-oxadiazole-based polymers. In PSCs, the surface morphology of the active layer is also important to the photovoltaic performance, and the surface morphology analysis of the active layers might provide the answer for the different photovoltaic performances. Figure 7 shows the AFM images of the active layers of polymer:$PC_{71}BM$ (1:3 wt/wt). The root-mean-square (RMS) roughness is 1.449, 1.037, 0.722, and 1.308 nm, respectively. The RMS roughness of the **P1**:$PC_{71}BM$ (1:3 wt/wt) active layer was found to be higher than those of all other polymer blends, indicating that the surface is relatively more rough than the other active layers surfaces. The higher roughness of **P1**-based active layer might be another reason for the poor photovoltaic performance of polymer **P1** compared to that of polymer **P4**.

CONCLUSIONS

In this study, a series of four new polymers containing 1,2,4-oxadiazole-based electron-acceptor unit in the main chain were synthesized via the Stille polycondensation reaction. The optical study of polymer **P1** containing electron rich **M1** and electron deficient **M2** moieties indicates that the electron attracting ability of 1,2,4-oxadiazole was not satisfactory. Consequently, polymer **P1** showed their absorption band up to only 550 nm. Then, benzothiadiazole-based electron-acceptor unit (**M3** or **M4**) was incorporated in polymer **P1** main chain with the aim of extending the absorption. The absorptions of the new polymers (**P2** and **P3**) were significantly shifted to longer wavelength region of the solar spectrum. In addition, the effect of electron rich comonomer (**M1**) was also investigated by replacing it with thiophene unit (**M5**) to afford polymer **P4**. Each of the four synthesized polymers was used as electron donor material in PSC applications. The PSCs were made with the configuration of ITO/PEDOT:PSS/Polymer:$PC_{71}BM$(1:3 wt/wt)/LiF/Al. Among others, the PSC fabricated with **P3**:$PC_{71}BM$ active layer showed the maximum PCE of 1.33% with a J_{sc} of 4.95 mA/cm^2, a V_{oc} of 0.68 V, and a *FF* of 40%. From this study, we concluded that the incorporation of strong electron-accepting 1,2,4-oxadiazole unit in polymer main chain showed reasonable performances in terms of the converting solar energy into electrical energy. We expect that 1,2,4-oxadiazole-based electron-accepting unit would be more widely utilized in the new polymer synthesis for optoelectronic applications.

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