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Synthesis of a Benzotriazole Bearing Alternating Copolymer For an Organic Photovoltaic Application

Cagla Istanbulluoglu, Seza Göker, Gonul Hizalan, Serife O. Hacioglu, Yasemin Arslan Udum, Esra D. Yildiz, Ali Cirpan and Levent Toppare

A low band gap donor–acceptor (D–A) copolymer PTBTBDT namely poly(2-dodecyl-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazole-alt-4,8-bis(2-ethylhexyl)oxy)benzo[1,2-b:4,5-b′]dithiophene) was designed and synthesized via Pd-catalyzed Stille polycondensation reaction. The polymer was characterized by 1H NMR spectroscopy, UV–Vis absorption spectroscopy, cyclic voltammetry, and gel permeation chromatography (GPC). PTBTBDT has good solubility in common organic solvents, good thermal stability, broad absorption, low band gap and exhibits not only high hole mobilities but also moderate photovoltaic properties. PTBTBDT revealed broad absorption in the wavelength range of 300 nm to 630 nm, and the HOMO and LUMO energy levels were calculated as -4.98 eV and -3.34 eV, respectively. Bulk heterojunction solar cells were fabricated using PTBTBDT as the electron donor and PC71BM as the acceptor. The device exhibits a power conversion efficiency of 2.12% with a current density of 5.45 mA/cm2, an open-circuit voltage of 0.72 V, and a fill factor of 54% under illumination of AM 1.5 G, 100 mW cm−2. Under similar device fabrication conditions, PTBTBDT based device showed much improved efficiency among its previously synthesized counterparts i.e. PBDTDTBTz, and PBDTDTz based devices with 1.7% and 1.4% efficiencies. The hole mobility of PTBTBDT:PC71BM (1:2 w/w) blend reached up to 1.47 x10−4 cm2 V−1 s−1 as calculated by the space-charge-limited current (SCLC) method. By side-chain engineering, this study demonstrates a good example for tuning absorption range, energy level, charge transport, and photovoltaic properties of the polymers.

Introduction

Conducting polymers have received considerable interest as active materials for organic photovoltaics (OPVs),1,2 organic light-emitting diodes (OLEDs),3,4 organic field effect transistors (OFETs),5,6 and electrochromic devices (ECDs).7,8 Due to the unique advantages of polymer solar cells (PSCs), like low cost, solution processability, application to flexible substrates, there is a growing interest towards the development of novel materials for polymer solar cell (PSC) applications.9–14 Power conversion efficiencies (PCE) of 9% for single junction architecture15–17 was improved to 10.6% with tandem cells.18 These results have been achieved with the development of novel donor acceptor moieties together with the device processing innovations.16,19–21 Recent research has focused on the development of new materials and morphology control of the active layer. Ideal polymer should have broad absorption spectrum for enhancement of sunlight harvesting, appropriate HOMO and LUMO levels for high open circuit voltage (Voc) (and efficient charge separation) and high hole mobility. Apart from optical and electronic properties, polymer PCBM blend should form interpenetrated network morphology on nanoscale.24 In order to improve the performance of the PSC, the synthetic versatility of organic chemistry is used for the development of novel materials. Over the past several years 4,8-bis(2-ethylhexyl)oxy)benzo[1,2-b:4,5-b′]dithiophene (BDT) has been incorporated in the polymer backbone extensively as the donor unit. Since the first introduction of BDT unit, it was coupled with thieno[3,4-b]thiophene (TT),25,26 diithiophene-2-yl-2,1,3-benzothiadiazole (DTBT),27 thieno[3,4-c]pyrrole-4,6-dione (TPD)28–30 and diketopyrrolopyrrole (DPP) to form copolymers.31 BDT unit offers several advantages like strong electron donating ability, large planar structure providing high hole mobility and strong intramolecular charge transfer.32–36 Therefore, in this study, 4,8-bis(2-alkoxy)benzo[1,2-b:4,5-b′]dithiophene (BDT) was incorporated in benzotriazole (BTZ) and thiophene bearing polymer backbone due to aforementioned properties. Previously, Zou et al reported BTZ and BTD containing polymers with a highest PCE of 1.7%.37 In this work, electrochemical, optical and photovoltaic properties of the PTBTBDT were investigated.
Experimental

Materials

1H-Benzotriazole, 1-bromododecane, potassium tert-butoxide, tributyltin chloride, ammonium chloride, bis(triphenylphosphine)palladium(II) dichloride, N-bromosuccinimide, sodium bicarbonate, bromine, hydrobromic acid, triphenylphosphine, magnesium sulphate, acetic acid, methanol, dichloromethane, hexane, chloroform, 2,6-bis(trimethylstannyl)-4,8-bis(2-ethylhexyl)oxy)benzo[1,2-b:4,5-b’]dithiophene were purchased from Sigma Aldrich Chemical Co. Ltd and used without further purification. The PCBM was obtained from Solenne. All reactions were carried out under argon atmosphere unless otherwise mentioned. Tetrahydrofuran (THF) was freshly distilled over Na/benzophenone ketyl. Tributyl(thiophene-2-yl)stannane, 2-dodecylbenzotriazole and 2-dodecyloxy-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazole (TBT) were synthesized according to previously described methods. 38

Characterization

For cyclic voltammetry studies, polymer was dissolved in CHCl₃ (5mg/mL) and spray coated onto ITO coated glass substrate using an Omni spray coating gun. The polymer thickness was less than a micron in order to be able to study its electrochromic properties. Three electrode system was constructed, ITO substrate was used as the working electrode, Pt wire as the counter electrode and Ag wire as the reference electrode which was calibrated against Fc/Fc’. Cyclic voltammetry studies were carried out in a solution of 0.1 M TBAPF₆ in acetonitrile. Ferrocene was purchased from Aldrich and used as the supporting electrolyte. In the spectroelectrochemistry studies, polymer film was coated on ITO electrode and dipped into monomer free solution. 1H NMR and 13C NMR spectra were recorded using a Bruker SpectroSpin Avance DPX-400 spectrometer, with tetramethylsilane (TMS) as the internal reference; chemical shifts were recorded in ppm. The UV-Vis spectra were recorded on Varian Cary 5000 UV-Vis spectrophotometer at room temperature. Cyclic voltammetry studies were carried out in a solution of 0.1 M of tetrabutylammonium hexafluorophosphate in anhydrous acetonitrile (ACN) solution at a scan rate of 100 mV/s. A Gamry 600 potentiostat was used with a three-electrode cell consisting of an ITO-coated glass substrate as the working electrode, Pt wire as the counter electrode, and Ag wire as the reference electrode which was calibrated against Fc/Fc’ (0.3V). HOMO and LUMO energy levels were calculated from the onset oxidation and onset reduction potentials. Molecular weight and polydispersity index of the polymer was determined by gel permeation chromatography (GPC) analysis.

Fabrication and Characterization of Organic Solar Cell

ITO glass substrates were purchased from Visiontek Systems. ITO glass substrates were etched with acid solution and sonicated for 15 minutes with detergent, distilled water, acetone, and isopropanol, consecutively. Oxygen plasma cleaning was performed to remove organic impurities from ITO surface. Poly(3,4-ethylenedioxythiophene) (PEDOT-PSS) solution was spin-coated on cleaned ITO surface with a thickness of 40 nm. The substrates were heated for 10 minutes at 150°C to remove residual water. Polymer PCBM blends, were prepared at different weight ratios and spin-coated under N₂ atmosphere. Cathode materials (0.8 nm LiF and 100 nm Al) were thermally evaporated with an average rate of 0.08 and 1 Å/s respectively in the glove box. I–V curves were recorded with a Keithley 2400 source meter under simulated AM 1.5 G illumination of 100mW/cm². Incident photon to current efficiencies (IPCE) of solar cells was recorded by the Oriel Quantum Efficiency Measurement system.

Syntheses

Tributyl(thiophen-2-yl)stannane (1)

Thiophene (2.00 g, 23.8 mmol) and freshly distilled THF (25 ml) were added in a 100 ml three-necked flask under argon atmosphere. n-Butyl lithium (9.50 ml, 2.5 M in hexane, 23.8 mmol) was added drop wise at -78 °C. After that the solution was stirred for 1h at room temperature. After cooling to -78 °C, tributyltin chloride (23.8 ml, 28.5 mmol) was added drop wise. The mixture was allowed to reach room temperature and stirred overnight. After evaporation of solvent under reduced pressure, dichloromethane was added to the crude product and the mixture was washed with NH₄Cl (saturated), brine (saturated) and distilled water until clear solution was obtained. The organic layer was dried over anhydrous MgSO₄. After removal of solvent, a light yellow liquid was obtained. Yield: 94%

1H NMR (400 MHz, CDCl₃ ppm): δ 7.57 (d, J= 4.6 Hz, 1H), 7.19 (t, J= 3.2 Hz, 1H), 7.12 (d, J= 3.2 Hz, 1H), 1.50 (m, J=7.2 Hz, 6H), 1.26 (m, J= 7.4 Hz, 6H), 1.03 (t, J= 8.4 Hz, 6H), 0.82 (t, J= 7.7 Hz, 9H)

13C NMR (100 MHz, CDCl₃): δ 135.2, 130.6, 127.8, 29.28, 29.95, 27.41, 27.24, 13.71, 13.64, 10.81, 8.772

2-dodecyl-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazole (3)

4,7-Dibromo-2-dodecylbenzotriazole (600 mg, 1.35 mmol), and tributyl(thiophen-2-yl) stannane (1.39 g, 4.05 mmol) were dissolved in anhydrous THF (40 ml) and bis(triphenylphosphine)palladium(II) dichloride was added to the reaction medium. The mixture was refluxed for 2 days under inert atmosphere at 125 °C. After solvent evaporation under vacuum, the crude product was purified by column chromatography on silica gel to obtain green solid.

Yield: 85%
4,7-bis (5-bromo-thiophen-2-yl)-2-dodecyl-2H-benzo[d][1,2,3]triazole (4)

2-Dodecyl-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazole (450 mg, 1.0 mmol) and N-bromosuccinimide (2.5 mmol, 445.0 mg) were dissolved in chloroform (20 ml) and glacial acetic acid (20 ml) mixture. The mixture was stirred overnight at room temperature in dark. The mixture was washed with NaHCO₃ and distilled water three times. The organic phase was dried over MgSO₄. After solvent removal, the crude product was recrystallized with ethanol to obtain yellow solid. Yield: 78%

¹H NMR (400MHz, CDCl₃, ppm): δ 7.73 (d, J = 3.9 Hz, 2H), 7.45(s,2H), 7.06 (d, J = 3.9 Hz, 2H), 4.73 (t, J = 7.2 Hz, 2H), 2.11(q, J = 7.1 Hz, 2H), 1.33-1.17 (m, J = 5.2 Hz, 18H), 0.80 (t, J = 6.6 Hz, 3H)

¹³C NMR (100 MHz, CDCl₃, ppm): δ 138.8, 128.3, 124.5, 119.5, 54.53, 29.50, 27.50, 27.00, 26.51, 24.10, 20.31, 11.60

P-TBTBDT

4,7-Bis(5-bromothiophen-2-yl)-2-dodecyl2Hbenzo[d][1,2,3]triazole (250 mg, 0.41 mmol), 2,6-bis(trimethylstannyl)-4,8-bis(2-ethylhexyloxy)bdenzo[1,2-b;4,5-b']dithiophene (316.8 mg, 0.41 mmol) and bis(triphenylphosphine)palladium(II) dichloride (5 mol%) were refluxed at 110 °C under an argon atmosphere for 2 days. The solvent was removed under reduced pressure. To remove oligomers, the crude product was washed with methanol, acetone, and hexane using Soxhlet extractor. To extract the polymer, chloroform was used and a red solid was obtained after precipitation with cold methanol. Yield: 37%

¹H NMR (400MHz, CDCl₃, δ: ppm) 7.56 (BTz), 7.31 (BDT), 7.66 (thiophene), 4.77(1-OCH₃), 3.23 (N-CH₃), 2.27 (-CH), 1.96-1.68 (-CH₂), 1.18-0.79 (-CH₃).

Mn: 34 kDa, Mw: 42 kDa, PDI: 1.2

Polymer synthesis and characterization

The synthetic route toward monomer and polymer is shown in scheme 1. 4,7-Dibromo-2-dodecyl-2H-benzo[d][1,2,3]triazole (2) was synthesized according to reported procedures in literature.²⁹ Compound 2 was coupled with compound 1 via Stille coupling to obtain 2-Dodecyl-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazole (3). Then bromination of compound (3) was performed in the presence of N-bromosuccinimide (NBS) and CHCl₃ to give compound (4). The Stille polymerization between 2,6-bis(trimethylstannyl)-4,8-bis(2-ethylhexyloxy)bdenzo[1,2-b;4,5-b']dithiophene and monomer (4) in the presence of bis(triphenylphosphine)palladium(II) dichloride afforded the copolymer PTBTBDT. Soxhlet extraction was performed with methanol, hexane, and acetone to remove residual catalyst. After extraction with several organic solvents, the polymer was precipitated in cold methanol. Resulting polymer has superior solubility in organic solvents like chloroform, dichlorobenzene and o-dichlorobenzene due to presence of alkyl chains on the polymer backbone. Molecular weight of the polymer was determined by gel permeation chromatography (GPC) using CHCl₃ as the eluent and polystyrene standards as the reference. Number average molecular weight (Mn) and weight average molecular weight (Mw) of the polymer was determined as 34 kDa and 42 kDa respectively, with a polydispersity index (PDI) of 1.2. Thermal property of PTBTBDT was investigated by thermogravimetric analysis (TGA). The polymer showed no degradation up to 300°C with a 65% loss at 500°C. This thermal behaviour is good enough for organic photovoltaic applications.

Scheme 1: Synthetic route of the monomer and polymer

RESULTS AND DISCUSSION

Electrochemical and Optical properties

Cyclic voltammetry studies were performed in order to investigate redox properties of the P-TBTBDT. The polymer was spray coated on ITO glass electrode and single scan cyclic voltammogram of polymer performed in the potential range between -1.60 and 1.20 V. Since polymer has ambipolar (both p and n dopable) character, HOMO and LUMO energy levels were calculated from the onset of the oxidation of p-doping state and onset of the reduction of n-doping state respectively. Cyclic voltammogram of polymer was shown in Figure 1(a). Onset of the oxidation at p-doping state is 0.53 V and onset of the reduction at n-doping state is -1.11 V. From equation 1, HOMO-LUMO energy levels were found as -4.98 eV and -3.34 eV respectively and electronic band gap was found as 1.6 eV which is the difference between HOMO and LUMO energy levels. Relatively low HOMO energy level is beneficial to obtain high open circuit voltage (V₉ₒ) value, since V₉ₒ is proportional to the difference between the LUMO of the acceptor and the HOMO of the donor. Table 1 summarizes optoelectronic properties of the polymer and
Figure 3 shows the energy level diagram of organic solar cell device construction.

**TABLE 1: Summary of Optical and Electrochemical Properties of PTBTBDT**

<table>
<thead>
<tr>
<th>Properties</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>$E_g^{ee}$ (eV)</th>
<th>Thin film $\lambda_{\text{max}}$ (nm)</th>
<th>Solution $\lambda_{\text{max}}$ (nm)</th>
<th>$E_g^{op}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTBTBDT</td>
<td>-4.98</td>
<td>-3.34</td>
<td>1.64</td>
<td>493/530</td>
<td>473/510</td>
<td>1.90</td>
</tr>
</tbody>
</table>

HOMO = $-(E_{\text{ox.onset}} + 4.75 - 0.30)$ eV

LUMO = $-(E_{\text{red.onset}} + 4.75 - 0.30)$ eV

Optical properties of copolymer were investigated in thin film and as o-DCB solution [Fig. 1(b)]. Polymer has a strong absorption between 300 nm and 630 nm. The maximum absorption peaks in solution and in thin film are located at 473/510 nm and 493/530 nm respectively. Due to the planarity effect of the π-conjugated polymer backbone in the solid state and enhanced intermolecular interactions between the polymer main chains, a 20 nm red shift was observed in UV–VIS absorption spectra. Optical band gap of polymer ($E_g^{op}$) was calculated from absorption spectra according to $E_g^{op} = 1241/\lambda$. The $E_g^{op}$ was found as 1.9 eV.

**Spectroelectrochemical Studies**

In order to investigate the electronic transitions and optical changes upon doping, benzotriazole bearing copolymer (PTBTBDT) was subjected to incrementally increasing applied potential while recording UV–Vis spectra. Polymer film was coated on ITO electrode and dipped into monomer free solution of 0.1M TBAPF$_6$/ACN. The polymer has electrochromic characteristics of reversible color change upon external potential. As shown in figure 3, an absorption band was observed at around 500 nm for copolymer film at the neutral state which corresponded to the π-π* inter band transition. The applied potential was increased, the absorption of π-π* transition decreased meanwhile the new absorption bands started at around 700 nm and 1370 nm. The formation of this new bands observed at longer wavelengths due to the formation polaronic and bipolaronic charge carriers on the polymer backbone.

Figure 1: a) Cyclic voltammogram of PTBTBDT in a monomer free solution of 0.1M TBAPF$_6$/ACN and b) Normalized UV-Vis spectra of PTBTBDT in o-DCB solution and in thin film.

Figure 2: Energy level diagram of organic solar cell device.

Figure 3: Electronic absorption spectra of polymers in 0.1 M TBAPF$_6$/ACN solution between 0.0 V and 1.3 V for PTBTBDT.
Kinetic studies were performed to determine switching times and percent transmittance changes (ΔT%) of the polymer. Switching time is the time between the colored and bleached states of the electrochromic material at a 95% contrast value. The measurement was done between the neutral and fully oxidized states of the polymers with 5 s time intervals. As shown in figure 4 the copolymer film revealed 18% optical contrast with a switching time of 0.4 s at 500 nm, 14% optic contrast with a switching time of 0.5 s at 700 nm and 36% optical contrast with 0.4 s switching time at 1370 nm.

**Figure 4:** Percent transmittance change for PTBTBDT.

**Photovoltaic properties**

In order to investigate photovoltaic properties of the polymer, bulk heterojunction solar cells were fabricated with a device architecture of ITO/PEDOT:PSS (Clevios) (40 nm)/polymer:PC_{70}BM/LiF(0.8 nm)/Al(100 nm). The performance of PTBTBDT based devices was optimized by the ratio of donor acceptor, spin coating speed (thickness of the active layer), thermal annealing treatment and addition of an additive. Since organic solar cell applications highly depend on solubility and film formation of the polymer fullerene blend, optimization of solvent is a crucial step in organic solar cell applications. In this context, dissolving polymer and PC_{70}BM in o-DCB resulted in the best morphology. PC_{70}BM was preferred as the acceptor to enhance absorption of blend due to broad absorption range of PC_{70}BM in visible region. Current density/ Voltage (J/V) characteristics of the optimized OSCs were shown in Figure 5(a). The best performance was obtained with device construction of 1:2 polymer:PC_{70}BM ratio. As summarized in Table 2, increasing PC_{70}BM ratio from 1:1 to 1:2 was improved charge transport as a result power conversion efficiency (PCE) was enhanced. However increasing PC_{70}BM ratio from 1:2 to 1:3 decreased the short circuit current (Isc) due to less contribution of the polymer on absorption. Moreover, it decreased the hole transport ability of the active layer. Hence, optimum ratio was found as 1:2 polymer:PC_{70}BM. In addition to this, active layer thickness should be optimized to balance the absorption and charge transport. Since, the absorption of sun light is enhanced as the thickness of active layer increases which in return, results in higher charge production. On the other hand, active layer thickness is limited to a few hundreds of nanometers due to low diffusion lengths of organic materials which is around 10-20 nm. The optimum active layer thickness was found as 116 nm which was determined by AFM (Atomic Force Microscopy) (fig.6 a and b). PSCs showed the highest photovoltaic performance of 2.12% with Voc of 0.72 V, Jsc of 5.40 mA/cm² and FF (fill factor) of 54%.

Pre and post annealing treatments, addition of additive can be carried out to improve the morphology of the active layer.

In this study, pre-annealing treatments were carried out to increase device performance. Active layer coated ITO substrates were annealed at different temperatures for different time periods. However, power conversion efficiency decreased from 2.12% to 1.53%. To investigate the pre-annealing treatment effect on morphology, Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM) measurements were carried out. Due to the higher electron density of PC_{70}BM compared to polymer, the dark areas correspond to PC_{70}BM domains in TEM images. As depicted in Figures 6 c and d, nanoscale morphology was adversely affected with thermal annealing. Voc value was decreased from 5.45 mA/cm² to 3.37 mA/cm² due to the formation of less interconnected donor-acceptor network upon annealing. According to AFM results Fig. 6 a and b, the blend film root mean square roughness (Rms) were determined as 6.79 nm and 6.47 nm. For further optimization, addition of 1% 1,8-diiodooctane (DIO) to polymer PCBM blend did not make any improvement on PCE. Incident photon to electron conversion efficiency (IPCE) measurements were performed and 40% IPCE was obtained with the device showing the highest PCE%. External quantum efficiencies of PTBTBDT based devices as a function of wavelength from 350 nm to 750 nm matches well with UV-Vis absorbance range of polymer PC_{70}BM blend.

Two benzotriazole-based polymers, PBTDTBTz and PBBDTBTz, were previously synthesized by Zou et al. The photovoltaic devices based on these polymers demonstrated a power conversion efficiency of 1.7% and 1.4%, respectively for PBTDTBTz and PBBDTBTz, under the illumination of AM 1.5, 100 mW cm². In our work, PTBTBDT comprising thiophene unit as a π bridge revealed a power conversion efficiency of 2.12% which is higher than previously synthesized polymer based photovoltaic device. The absorption edges of previously synthesized polymers were at 625 nm and 635 nm and the band gaps were determined as 2.0 eV and 1.95 eV. For PTBTBDT, the absorption edge is at 653 nm with band gap of 1.9 eV. The lower band gap of this polymer resulted from the red shift in the absorption. PTBTBDT can harvest more visible light due to higher absorption edge.
on ITO/PEDOT: PSS annealed at 110°C for 10 min c) TEM image of PTBTD:PC70BM blend d) TEM image of PTBTD:PC70BM blend annealed at 110°C for 10 min. Scale bars in AFM and TEM images are 500nm.

**TABLE 2**: Photovoltaic Properties of PTBTD

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>Voc (V)</th>
<th>Jsc (mA cm⁻²)</th>
<th>FF</th>
<th>PCE (%)</th>
<th>Mobility (cm²V⁻¹s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P:PC70BM 1:1</td>
<td>102</td>
<td>0.71</td>
<td>4.45</td>
<td>52</td>
<td>1.64 (1.60) 3.85x10⁻⁴</td>
</tr>
<tr>
<td>P:PC70BM 1:2</td>
<td>116</td>
<td>0.72</td>
<td>5.45</td>
<td>54</td>
<td>2.12 (2.03) 1.47x10⁻⁵</td>
</tr>
<tr>
<td>P:PC70BM 1:3</td>
<td>125</td>
<td>0.71</td>
<td>4.00</td>
<td>52</td>
<td>1.48 (1.40) 6.54x10⁻⁵</td>
</tr>
<tr>
<td>P:PC70BM 1:2</td>
<td>108</td>
<td>0.73</td>
<td>5.34</td>
<td>50</td>
<td>1.82 (1.75) 1.14x10⁻⁵</td>
</tr>
<tr>
<td>P:PC70BM 1:3</td>
<td>108</td>
<td>0.74</td>
<td>4.70</td>
<td>57</td>
<td>2.00 (1.83) 1.28x10⁻⁵</td>
</tr>
<tr>
<td>P:PC70BM 1:2</td>
<td>113</td>
<td>0.76</td>
<td>3.37</td>
<td>59</td>
<td>1.53 (1.47) 9.88x10⁻⁵</td>
</tr>
</tbody>
</table>

*annealed at 110°C for 10 min

The values in the parenthesis are the average values of PCEs based on measurements for 8 cells.

**Hole Mobility**

Charge carrier mobility of the polymer was investigated by the space charge limited current (SCLC) theory. It is related with the current density-voltage characteristics (J–V curve) under dark. J–V curve follows Child’s law:

\[
J_{SCL} = \frac{9}{8} \epsilon_0 \epsilon_r \mu \left( \frac{V}{L} \right)^2
\]

Eq. 2

where L is the thickness of polymer, V is applied voltage, \( \mu \) is the carrier mobility, \( \epsilon_r \) (3 for polymer) is the relative permittivity and \( \epsilon_0 \) permittivity of free space. Figure 6 shows log J vs. log V plots with different active layer thicknesses of ITO/PEDOT: PSS/PC70BM/LiF/Al solar cells under dark. The hole mobilities were calculated using eq. 2 and summarized in Table 2.
Figure 7: J-V plots of devices with different thicknesses of active layer in dark medium. *annealed at 110°C for 10 min

**Conclusion**

A benzodithiophene based new donor-acceptor type alternating copolymer was synthesized via palladium catalyzed Stille coupling reaction. The polymer exhibits good electrochemical and spectroelectrochemical properties, good solubility in common organic solvents, high thermal stability up to 300°C and broad absorption from 300 nm to 630 nm. Bulk heterojunction polymer solar cells with PTBTBDT as the active layer were fabricated and optimized systematically. The organic solar cell device based on PTBTBDT: PC$_70$BM (1:2, w/w) exhibited the best PCE of 2.12% with a Voc of 0.72 V, a Jsc value of 5.45 mA/cm$^2$, and a FF of 54% under the illumination of AM 1.5 G, 100 mW/cm$^2$. The hole mobility of the polymer was estimated through space charge limited current (SCLC) model and calculated as 1.47 x10$^{-3}$ cm$^2$/V·s$^{-1}$. Hole mobility results are consistent with PCE of PTBTBDT based photovoltaic device. The results indicate that synthesized polymer is a promising donor for organic photovoltaics.

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