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Synthesis of the Conjugated Polymer with Fluoronated Carbazole Donor and Benzothiadiazole Acceptor Linked Through Thienothiophene

Mohd Sani Sarjadi[1,*], Shu Er Tan[1], Xin Lin Wong[1] and Ahmed Iraqi[2]
[1]*Faculty of Science and Natural Resources, Universiti Malaysia Sabah, Jalan UMS, 88400 Kota Kinabalu, Sabah, Malaysia*

[2]*Department of Chemistry,University of Sheffield, Sheffield S37HF, United Kingdom*

Polymer solar cells have emerged as outlook clean and low-cost renewable energy technology due to its characteristic such as flexibility and lightweight materials, capability and easy fabrication to be produced on large area flexible substrates. In this study we present the preparation and characterisation of new materials for application in this area and an investigation of the photophysical and electronic properties of conjugated polymer based on carbazole derivative with thienothiophene and benzothiadiazole repeat units. A new material of alternating donor/acceptor copolymers comprising fluorinated carbazole-based units and thienothiophene substituted benzothiadiazole repeat units was prepared by using Suzuki coupling method and characterized with suitable analysis techniques. Morphological, spectroscopic and charge-transport measurements are used to investigate the influence of either the thienothiophene substituted benzothiadiazole moieties on the structure and photophysical properties of the copolymer rationalise the solar cell characteristics. Their electronic and photovoltaic properties in bulk heterojunction solar cells in blends with carbazole derivative acceptors will be discussed in this contribution. This research will give further understanding to the structure-property relationship of polymers which might be useful in the future design of polymer solar cells.

Keywords: Conjugated polymers, carbazole, thienothiophene, benzothiadiazole, Suzuki cross coupling, solar cells

I. INTRODUCTION

Solar energy is the most abundant and cleanest renewable energy resource (Koizumi et al., 2013). Solar planar is an essential technology that uses to harvest the solar energy and convert it into usable electricity. The photovoltaic performance of solar cell was found to be influenced by several factors such as the optical band gap, fill factor, open circuit voltage, short-circuit current and etcetera (Zhou et al.,2012). The efficiency of the polymer solar cell is evaluated from value of the power conversion efficiency (PCE).

The active layer of bulk heterojunction (BHJ) polymer solar cell, as shown in Figure 1, made up of both electron donating conjugated polymer and fullerene or non-fullerene-based

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[*] Corresponding author’s e-mail: msani@ums.edu.my

electron accepting material. The designed conjugated polymers were used as the electron donating material for the active layer of polymer solar cell (Zhou et al., 2012).

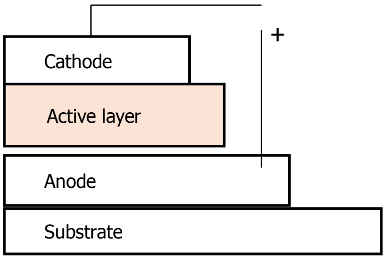


Figure 1. The bulk heterojunction (BHJ) polymer solar cell.

II. PAST REVIEW

In the past few decades, various kinds of conjugated polymers were designed and synthesized to improve the photovoltaic (PV) performance of polymer solar cells (PSC) (Leclerc et al.,2016). Up to now, a variety of donors and acceptors have been disclosed as the building block of conjugated polymer. Amongst these monomers, the carbazole and benzothiadiazole are still remained as the common choices for donor and acceptor, respectively. The features of both monomers have been extensively studied, modified and reviewed during the last decade (Biniek et al.,2009 ;Tan et al.,2016). Recently, several new monomers with promising features have been discovered and applied during designation of the polymeric backbone, yet carbazole and benzothiadiazole are still taking the precedent choice for researchers as they are relatively lower cost and easier to be handled during the synthesis as compared to the others (Figure 2).

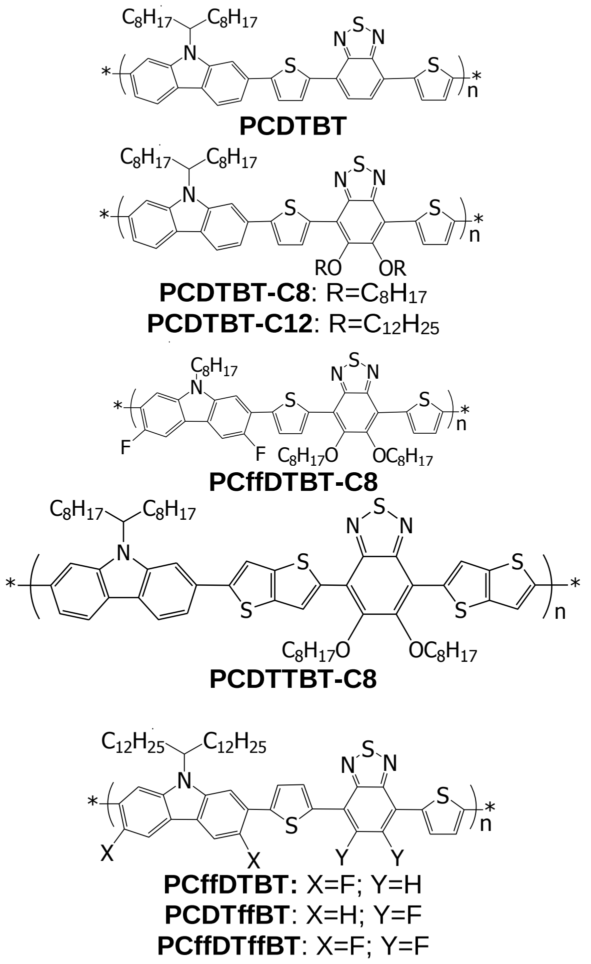


Figure 2. The chemical structure of the parent PCDTBT and modified polymers.

In 2007, Blouin's research group reported a novel (PCDTBT) polymer, namely poly[N-9'-heptadecanyl-2,7-carbazole-*alt*-5,5- (4',7'-di-2-thienyl-2',1',3'-benzo- thiadiazole)], which the carbazole and benzothiadiazole were polymerized in alternating donor-acceptor (D-A) arrangement with thiophene spacer (Blouin,2007). The features exhibited by this parent PCDTBT polymer has been intensively studied by researchers during the past decade (Moon et al., 2012 ; Parlak et al.,2013. Besides that, various modifications also have been done on PCDTBT. The researchers have strived hard to improve the overall performance of the

PCDTBT-based polymer solar cells by substituted the monomers with different substituents or replacement of the thiophene spacer and 9-heptadecanyl side chain with other alternative compounds.

During the last decade, the chemical structure of parent PCDTBT has undergone various modifications. In 2010s, researchers alkoxylated the benzothiadiazole acceptor at 5th- and 6th- positions with $-OC_8H_{17}$ [24] and $–OC_{12}H_{25}$ [25], resulted in PCDTBT-C8 and PCDTBT-C12, respectively. The incorporation of alkoxyl chains on benzothiadiazole improves the solubility and planarity.

There was a past research reported a PCffDTBT-C8 polymer, which is modified from the parent PCDTBT by fluorinated the 3rd- and 6th- positions of the carbazole and the symmetrically branched *N*-alkyl chain has been replaced with a linear alkyl chain. This work shows that the incorporation of two fluorine atoms on the carbazole helps to lower the HOMO and LUMO energy levels. Besides that, the this modified polymer possesses smaller bandgap, higher Voc and Jsc value than the parent PCDTBT (Du et al.,2013).

In 2014, Pearson and co-workers replaced the thiophene spacers of PCDTBT-C8 with thienothiophene. This newly synthesized PCDTTBT-C8 was found to have better photovoltaic efficiency than its counterpart with the thiophene spacers. This is because the thienothiophene has better π-bridge conjugation than thiophene [27].

Recently, Cartwright and co-workers (2016) fluorinated the PCDTBT to study the optical, electrochemical, thermal, and molecular arrangement. The three fluorinated PCDTBT are PCffDTBT, PCDTffBT, and PCffDTffBT. Interestingly, the result shown that the decomposition temperature (T_d) for these three copolymers improved when the molecular weight (M_n) increased. The T_d and M_n of these polymers increased from PCffDTffBT, PCDTffBT, to PCffDTBT. Moreover, the XRD study discovered that the polymers with fluorinated benzothiadiazole unit have the ability to promote the π-π stacking of the solid state copolymeric backbones, which in turn improve the molecular ordering of the polymer (Carwright et al.,2016). Amongst these three polymers, the PCffDTBT has the lowest optical bandgap which indicates that PCffDTBT able to harvest more photons from the solar spectrum than its counterparts. In this study we present the preparation and characterisation of new materials for application in this area and an investigation of the photophysical and electronic properties of conjugated polymer based on carbazole derivative with thienothiophene and benzothiadiazole repeat units.

III. MATERIALS AND METHODS

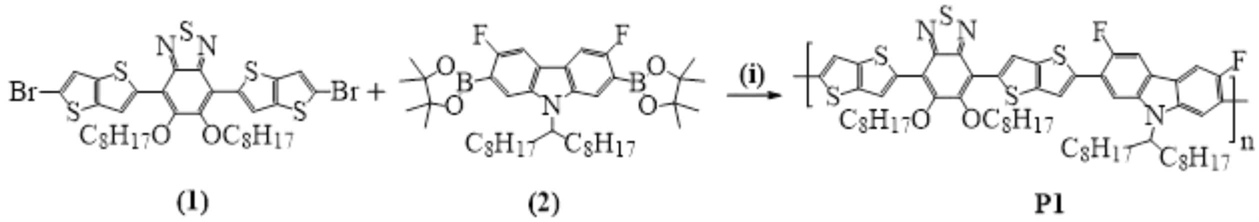
A. Materials

All chemicals and reagents were purchased from commercial suppliers and used without further purification, unless otherwise stated. The toluene and acetonitrile (HPLC grade) used were dried and distilled over sodium and phosphorus pentoxide, respectively, under argon atmosphere and stored over molecular sieves, 3Å.

B. Synthesis of Polymer P1

4,7-Bis(5-bromothieno[3,2-b]thiophen-2-yl)-5,6-bis(octyloxy)benzo [c][1,2,5]thiadiazole **(1)** (Bouffard & Swager, 2008; Ding *et al.,* 2011) and 3,6-difluoro-9-(heptadecan-9-yl)-2,7-bis(4,4,5,5-tetrameth yl-1,3,2-dioxaboro lan-2-yl)-9*H*-carbazole **(2)** (Du *et al.,* 2013; Cartwright *et al.,* 2016) were prepared according to the literature procedures. The synthesis route of poly(3,6-difluoro-9-(heptadecan-9-yl)-9H-carbazole- alt-5,6-bis(octyloxy)-4,7-di(thieno[3,2-b]thiophen-2-yl)benzo [c][1,2,5]thiadiazole) (P1) was outlined in **Scheme 1**. 4,7-Bis(5-bromothieno[3,2-b]thiophen-2-yl)-5,6-bis(octyloxy)benzo[c][1,2,5]thiadiazole **(1)** (0.1433 g, 0.173 mmol) and 3,6-Difluoro-9-(heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*- carbazole **(2)** (0.120 g, 0.173 mmol) were introduced to 100 mL round bottom flask under argon. To the mixture was added toluene (5.0 ml) and the mixture was degassed. Then 20 wt % tetraethyl ammonium hydroxide, $Et_4N{\cdot}OH$ (1.0 ml, previously degassed) was added. To this mixture was added $Pd(OAc)_2$ (1.2 mg, 4.9 x 10-3 mmol) and tri(o-tolyl)phosphine, P(o-Tol) (3.54 mg, 1.2 x 10-3 mmol) under an inert argon atmosphere and it was heated to 95 °C for 96 h. The mixture was cooled to room temperature and bromobenzene (0.05 ml, 61 mg; 0.3877 mmol) was added. It was then degassed and heated to 90 °C for 1 h. The mixture was cooled to room temperature and phenylboronic acid (50 mg; 0.4076 mmol) was added. The mixture was degassed and heated to 90 °C for 1h. After cooling to room temperature, $CHCl_3$ (200 ml) was added to solubilize the polymer. An ammonium hydroxide solution (28% in H_2O, 50 ml) was then added and the mixture was stirred overnight. The organic phase was separated and washed with distilled water (2 x100 ml). It was then concentrated to about 50 ml in volume and drop-wise into a methanol/water mixture (10: 1, v/v, 300 ml). The resulting mixture was then stirred overnight and filtered through a membrane filter. The collected solid was cleaned using a Soxhlet extraction under an inert argon using a Soxhlet extraction under an inert argon atmosphere with methanol (250 ml), acetone (250 ml), hexane (250 ml), toluene (250 ml) and chloroform (250 ml), respectively. The toluene and chloroform fractions were concentrated to about 50 ml and then poured into degassed methanol (200 ml). The resulting mixture was stirred overnight and the solid collected by filtration to afford polymer P9 fractions as a dark red powder. Yield: 115.1 mg (60 %). Toluene fraction: 53.7 mg, 28 %, GPC (1, 2, 4-trichlororbenzene at 100 °C): Mw = 4600, Mn = 1900, PD = 2.4. Chloroform fraction: 61.4 mg, 32 %, GPC (1, 2, 4-trichlororbenzene at 100 °C): Mw = 62900, Mn = 26200, PD = 2.4. 1H NMR ($C_2D_2Cl_4$), (δH/ppm): 8.72 (d, 2H); 8.62 (d, 2H); 7.72 (bm, 2H); 7.32 (b, 2H); 4.49 (b, 1H); 4.18 (b, 4H); 2.24 (b, 4H); 1.96 (b, 4H);

1.58-1.02 (bm, 44H); 0.91-0.74 (bm, 12H). FT-IR (cm-1): 3113, 2949, 2923, 2949, 2159, 2018, 1977, 1628, 1587, 1565. Elemental analysis (%) calculated for $C_{63}H_{77}F_2N_3O_2S_5$: C, 68.38; H, 7.01; N, 3.80; Br, 0.00. Found: C, 70.10; H, 6.66; N, 3.11; Br, 0.00.



Scheme 1. Synthetic routes using the Suzuki cross-coupling polymerization reaction. (i) Pd(OAc)2, P(o-Tol), Et4N.OH, toluene, Ar, 95 °C, 96 hr

IV. RESULTS AND DISCUSSIONS

The data of NMR, UV-Vis, CV, TGA, and DSC analysis were explained in this section.

A. The Nuclear Magnetic Resonance (NMR) Spectroscopy Analysis

The ^{1}H-NMR studies conducted at 100 °C in 1,1,2,2-tetra chloroethane-d$_2$ on **P1** confirmed its assigned structure. The ^{1}H-NMR spectrum of **P1** is shown in Figure 3, it reveals in the aromatic region the proton of the carbazole hydrogen with multiplet signal at 8.76 ppm, and 8.62 ppm assigned to protons a and b respectively.

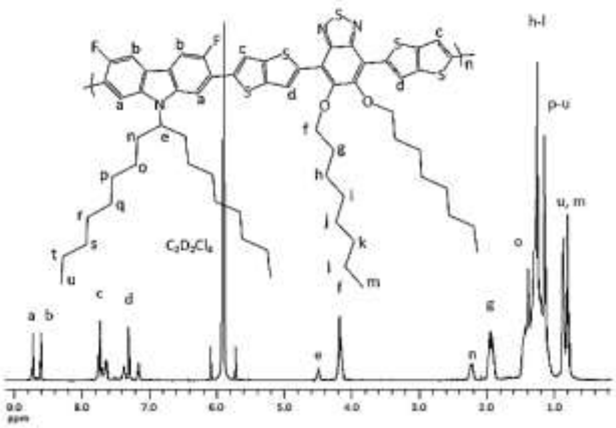


Figure 3. The ^{1}H-NMR spectra of P1 in 1,1,2,2-tetrachloroethane-d$_2$ ($C_2D_2Cl_4$) at 100 °C.

B. The UV-Visible (UV-Vis) Absorption Spectroscopy Analysis

The UV-Vis absorption spectra of the polymer were measured in chloroform and in solid state as thin films. UV-Vis analysis of **P1** in Figure 4 shows two absorption band at $\lambda_{max\ 1}$ = 344 nm and $\lambda_{max\ 2}$ = 486 nm in chloroform solution, and at $\lambda_{max\ 1}$ = 390 nm and $\lambda_{max\ 2}$ = 512 nm in solid state. The optical band gaps were calculated from the onset of absorption of the polymers in the solid state The optical band gap of polymer **P1** as determined from the onset of its absorption spectra in the solid state has a value E_g = 2.03 eV.

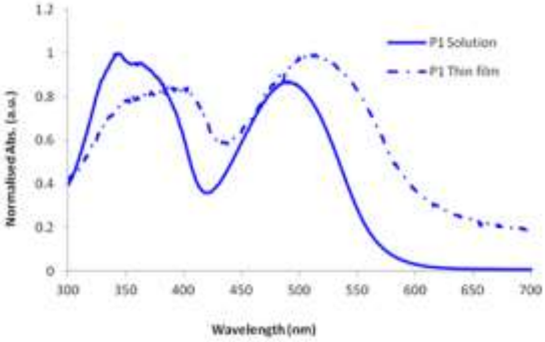


Figure 4. Normalized UV-Vis spectra of P1 in chloroform (solid line) and a thin film (dotted line)

C. Cyclic Voltammetry (CV) Analysis

Based on the cyclic voltammogram of the polymer **P1** as illustrated in Figure 5, it can be concluded that the P1 exhibits an oxidation wave at E_{pa} = 0.70 V and a reduction wave at E_{pa} = -1.36 V, and their associated reduction and oxidation waves at E_{pc} = 0.64 V and E_{pc} = -1.81 V, respectively.

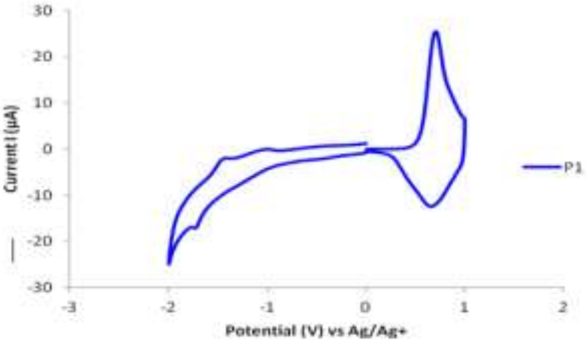


Figure 5. Normalized cyclic voltammogram of P1.

$E_{onset, ox}$ (V)[a]	$E_{onset, red}$ (V)[a]	HOMO (eV)	LUMO (eV)	Band gap (eV)
0.47	-1.64	-5.27	-3.16	2.11

[a] *vs. Ag/Ag⁺*

D. Thermogravimetry (TGA) and Differential Scanning Calorimetry (DSC) Analysis

The TGA curves for of the thermal degradation of the polymer **P1**, the onset of the degradation occurs at 324 °C, the onset of second degradation is 442 °C with a weight loss of 52.3 %. The percentage of residual weight 47.7 % is consistent with percentage weight of PDI units and polymer backbone. TGA analysis measurements revealed the remarkable stability of the polymer up to 442 °C, which indicated that these polymers are thermally very stable. The subsequent degradation and weight loss of the polymer beyond 442 °C was proportional to the mass of its alkyl-group substituents. The polymer did not show any further weight loss up to a temperature of 800 °C. The data for both TGA and DSC analysis were enclosed in Table 2.

Table 1. Voltammetry result and band gap of P1

TGA Analysis			DSC Analysis
Onset degradation temp. / °C		Weight loss at 800 °C (wt. %)	T_g / °C
1st degradation	2nd degradation		
324	442	52.3	71

From the onset of oxidation (0.47 V) and the onset of reduction (-1.64 V), the HOMO level is at -5.27 eV and the LUMO level is at -3.16 eV for the polymer backbone (on the basis that ferrocene/ferrocenium has an IP of 4.8 eV below the vacuum level and the oxidation occurs at 0.082 V relative to Ag/Ag⁺), therefore the electrochemical band gap of the polymer is 2.11 eV.

V. SUMMARY

Poly(3,6-difluoro-9-(heptadecan-9-yl)-*9H*-carbazole-*alt*-5,6-bis(octyloxy)-4,7-di(thieno[3,2-*b*]thiophen-2-yl)benzo[c][1,2,5]thiadiazole) **(P1)** composed of alternating carbazole donor unit and acceptor unit were successfully prepared. The polymer was synthesized by Suzuki's cross coupling reaction, in order to investigate its suitability for application in photovoltaic cell.

VI. ACKNOWLEDGMENT

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[1] Y. Koizumi, M. Ide, A. Saeki, C. Vijayakumar, B. Balan, M. Kawamoto, S. Seki, Thienoisoindigo-based low-band gap polymers for organic electronic devices, Polym. Chem. 4 (2013) 484–494. doi:10.1039/C2PY20699D.

[2] H. Zhou, L. Yang, W. You, Rational Design of High Performance Conjugated Polymers for Organic Solar Cells, Macromolecules. 45 (2012) 607–632. doi:10.1021/ma201648t.

[3] N. Leclerc, P. Chávez, O.A. Ibraikulov, T. Heiser, P. Lévêque, Impact of Backbone Fluorination on π -Conjugated Polymers in Organic Photovoltaic Devices : A Review, (2016). doi:10.3390/polym8010011.

[4] Y. Cheng, S. Yang, C. Hsu, Synthesis of Conjugated Polymers for Organic Solar Cell Applications, Chem. Rev. 109 (2009) 5868–5923. doi:10.1021/cr900182s.

[5] Q. Wang, Y. Xie, F. Soltani-kordshuli, M. Eslamian, Progress in emerging solution-processed thin film solar cells – Part I : Polymer solar cells, Renew. Sustain. Energy Rev. 56 (2016) 347–361. doi:10.1016/j.rser.2015.11.063.

[6] S. Günes, H. Neugebauer, N.S. Sariciftci, Conjugated Polymer-Based Organic Solar Cells, Chem. Rev. 107 (2007) 1324–1338. doi:10.1021/cr050149z.

[7] J.W. Jung, J.W. Jo, E.H. Jung, W.H. Jo, Recent progress in high efficiency polymer solar cells by rational design and energy level tuning of low bandgap copolymers with various electron-withdrawing units, Org. Electron. Physics, Mater. Appl. 31 (2016) 149–170. doi:10.1016/j.orgel.2016.01.034.

[8] T. Biniek, L., Chochos, C. L., Leclerc, N., Hadziioannou, G., Kallitsis, J. K., Bechara, R., Lévêque, P., Heiser, A [3,2-b]thienothiophene-alt-benzothadiazole copolymer for photovoltaic applications: design, synthesis, material characterization and device performances, J. Mater. Chem. 19 (2009) 4946–4951. doi:10.1039/b819177h.

[9] P. Anant, H. Mangold, N.T. Lucas, F. Laquai, J. Jacob, Synthesis and characterization of donor–acceptor type 4,4′-bis(2,1,3-benzothiadiazole)-based copolymers, Polymer (Guildf). 52 (2011) 4442–4450. doi:10.1016/j.polymer.2011.07.053.

[10] R. Qin, J. Yang, P. Li, Q. Wu, Y. Zhou, H. Luo, F. Chang, Structure property relationship for carbazole and benzothiadiazole based conjugated polymers, Sol. Energy Mater. Sol. Cells. 145 (2016) 412–417. doi:10.1016/j.solmat.2015.11.005.

[11] A. Casey, R.S. Ashraf, Z. Fei, M. Heeney, Thioalkyl-Substituted Benzothiadiazole Acceptors: Copolymerization with Carbazole Affords Polymers with Large Stokes Shifts and High Solar Cell Voltages, Macromolecules. 47 (2014) 2279–2288. doi:10.1021/ma5000943.

[12] G. Sathiyan, E.K.T. Sivakumar, R. Ganesamoorthy, R. Thangamuthu, P. Sakthivel, Review of carbazole based conjugated molecules for highly efficient organic solar cell application, Tetrahedron Lett. 57 (2016) 243–252. doi:10.1016/j.tetlet.2015.12.057.

[13] S.E. Tan, M.S. Sarjadi, A Review of the Modification of PCDTBT Structure Used in the Polymeric Solar Cells, Res. Rev. J. Chem. 5 (2016) 1–15.

[14] N. Blouin, A. Michaud, M. Leclerc, A Low-Bandgap Poly(2,7-Carbazole) Derivative for Use in High-Performance Solar Cells, Adv. Mater. 19 (2007) 2295–2300. doi:10.1002/adma.200602496.

[15] J.S. Moon, J. Jo, A.J. Heeger, Nanomorphology of PCDTBT:PC70BM Bulk Heterojunction Solar Cells, Adv. Energy Mater. 2 (2012) 304–308. doi:10.1002/aenm.201100667.

[16] P.A. Staniec, A.J. Parnell, A.D.F. Dunbar, H. Yi, A.J. Pearson, T. Wang, P.E. Hopkinson, C. Kinane, R.M. Dalgliesh, A.M. Donald, A.J. Ryan, A. Iraqi, R.A.L. Jones, D.G. Lidzey, The Nanoscale Morphology of a PCDTBT:PCBM Photovoltaic Blend, Adv. Energy Mater. 1 (2011) 499–504. doi:10.1002/aenm.201100144.

[17] Y. Zhang, E. Bovill, J. Kingsley, A.R. Buckley, H. Yi, A. Iraqi, T. Wang, D.G. Lidzey, PCDTBT based solar cells: one year of operation under real-world conditions., Sci. Rep. 6 (2016) 21632. doi:10.1038/srep21632.

[18] D.H. Wang, K.H. Park, J.H. Seo, J. Seifter, J.H. Jeon, J.K. Kim, J.H. Park, O.O. Park, A.J. Heeger, Enhanced Power Conversion Effi ciency in PCDTBT / PC 70 BM Bulk Heterojunction Photovoltaic Devices with Embedded Silver Nanoparticle Clusters, (2011) 766–770. doi:10.1002/aenm.201100347.

[19] Y. Xiao, H. Wang, S. Zhou, K. Yan, W. Xie, Z. Guan, S.W. Tsang, J. Bin Xu, Efficient ternary bulk heterojunction solar cells with PCDTBT as hole-cascade material, Nano Energy. 19 (2016) 476–485. doi:10.1016/j.nanoen.2015.11.016.

[20] M. Tong, N.E. Coates, D. Moses, A.J. Heeger, S. Beaupré, M. Leclerc, Charge carrier photogeneration and decay dynamics in the poly (2 , 7-carbazole) copolymer PCDTBT and in bulk heterojunction composites with PC 70 BM, (2010) 1–6. doi:10.1103/PhysRevB.81.125210.

[21] Y. Zhang, E. Bovill, J. Kingsley, A.R. Buckley, H. Yi, A. Iraqi, T. Wang, D.G. Lidzey, PCDTBT based solar cells: one year of operation under real-world conditions, Sci. Rep. 6 (2016) 21632. doi:10.1038/srep21632.

[22] V. Sharma, V. Singh, M. Arora, S. Arora, R.P. Tandon, Degradation analysis of PCDTBT:PC71BM organic solar cells-an insight, Curr. Appl. Phys. 16 (2016) 273–277. doi:10.1016/j.cap.2015.12.007.

[23] E.A. Parlak, T. AslTumay, N. Tore, Ş. Saroğlan, P. Kavak, F. Türksoy, Efficiency improvement of PCDTBT solar cells with silver nanoparticles, Sol. Energy Mater. Sol. Cells. 110 (2013) 58–62. doi:10.1016/j.solmat.2012.12.002.

[24] P. Ding, C.-C. Chu, Y. Zou, D. Xiao, C. Pan, C.-S. Hsu, New low bandgap conjugated polymer derived from 2, 7-carbazole and 5, 6-bis(octyloxy)-4, 7-di(thiophen-2-yl) benzothiadiazole: Synthesis and photovoltaic properties, J. Appl. Polym. Sci. 123 (2011) 99–107. doi:10.1002/app.34439.

[25] J. Sun, Y. Zhu, X. Xu, L. Lan, L. Zhang, P. Cai, J. Chen, J. Peng, Y. Cao, High efficiency and high voc inverted polymer solar cells based on a low-lying HOMO polycarbazole donor and a hydrophilic polycarbazole interlayer on ITO cathode, J. Phys. Chem. C. 116 (2012) 14188–14198. doi:10.1021/jp3009546.

[26] C. Du, W. Li, Y. Duan, C. Li, H. Dong, J. Zhu, W. Hu, Z. Bo, Conjugated polymers with 2,7-linked 3,6-difluorocarbazole as donor unit for high efficiency polymer solar cells, Polym. Chem. 4 (2013) 2773. doi:10.1039/c3py00177f.

[27] A.J. Pearson, D.C. Watters, H. Yi, M.S. Sarjadi, L.X. Reynolds, P.P. Marchisio, J. Kingsley, S.A. Haque, A. Iraqi, D.G. Lidzey, Impact of dithienyl or thienothiophene units on the optoelectronic and photovoltaic properties of benzo[1,2,5]thiadiazole based donor–acceptor copolymers for organic solar cell devices, RSC Adv. 4 (2014) 43142–43149. doi:10.1039/C4RA07186G.

[28] L. Cartwright, H. Yi, A. Iraqi, Effect of fluorination pattern and extent on the properties of PCDTBT derivatives, New J. Chem. 40 (2016) 1655–1662. doi:10.1039/C5NJ02394G.

[29] J. Bouffard, T.M. Swager, Fluorescent conjugated polymers that incorporate substituted 2, 1, 3-benzooxadiazole and 2, 1, 3-benzothiadiazole units, Macromolecules. 41 (2008) 5559–5562. doi:10.1021/ma8010679.