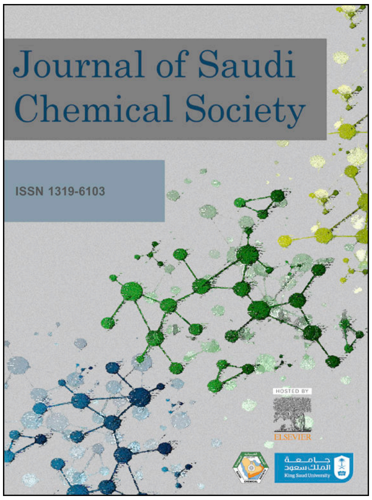
Article:

Alqurashy, B.A., Iraqi, A. orcid.org/0000-0003-3060-6663, Zhang, Y. et al. (1 more author) (2020) Pyrene- benzo[1,2,5]thiadiazole based conjugated polymers for application in BHJ solar cells. Journal of Saudi Chemical Society, 24 (6). pp. 484-491. ISSN 1319-6103

https://doi.org/10.1016/j.jscs.2020.04.004



Original article

Pyrene- benzo[1,2,5]thiadiazole based conjugated polymers for application in BHJ solar cells

Bakhet A. Alqurashy, Ahmed Iraqi, Yiwei Zhang, David.G. Lidzey

PII: S1319-6103(20)30046-6
DOI: https://doi.org/10.1016/j.jscs.2020.04.004
Reference: JSCS 1120

To appear in: *Journal of Saudi Chemical Society*

Received Date: 12 April 2019
Revised Date: 17 October 2019
Accepted Date: 14 April 2020

Please cite this article as: B.A. Alqurashy, A. Iraqi, Y. Zhang, David.G. Lidzey, Pyrene- benzo[1,2,5]thiadiazole based conjugated polymers for application in BHJ solar cells, *Journal of Saudi Chemical Society* (2020), doi: https://doi.org/10.1016/j.jscs.2020.04.004

Pyrene- Benzo[1,2,5]thiadiazole Based Conjugated polymers for Application in BHJ solar cells

Bakhet A. Alqurashy,[1] Ahmed Iraqi,[2] Yiwei Zhang [3] and David. G. Lidzey.[3]

[1]Department of Basic Science and Technologies, Community Faculty, Taibah University, 30002, Al-Madina Al-Mounawara, Saudi Arabia. Email: Bqourasy@taibahu.edu.sa

[2]Department of Chemistry, University of Sheffield, Sheffield S3 7HF, UK, E-mail: a.iraqi@sheffield.ac.uk.

[3]Department of Physics and Astronomy, University of Sheffield, Sheffield S3 7RH, UK, E-mail: d.g.lidzey@sheffield.ac.uk.

Abstract

Ethylhexyloxy-functionalised pyrene (**P$_{EH}$**) was prepared and copolymerised with both dithienyl-benzo[*c*]-[1,2,5]thiadiazole and dibithiophenyl-benzo[*c*]-[1,2,5]thiadiazole *via* a Stille coupling polymerisation method to yield **PP$_{EH}$-DTBT-8** and **PP$_{EH}$-DT2BT-8**, respectively. A comparative study was conducted to assess the impact of substituting thiophene for bithiophene repeat units upon the resulting properties of the conjugated polymers. **PP$_{EH}$-DT2BT-8** which has bithiophene spacers between pyrene and benzothiadiazole repeat units, exhibited a narrower optical and electrochemical band gap relative to **PP$_{EH}$-DTBT-8**; a consequence of the incorporating bithiophene spacer units which promote intramolecular charge transfer between the electron donating and electron accepting moieties. Both **PP$_{EH}$-DTBT-8** and **PP$_{EH}$-DT2BT-8** showed deep HOMO levels of -5.54 and -5.50 eV, respectively. The polymers possess good thermal stabilities with degradation temperatures in excess of 310 °C. The photovoltaic performance of the two polymers was studied by fabricating bulk heterojunction (BHJ) photovoltaic devices using

$PC_{70}BM$ as the acceptor. **PP_{EH}-DTBT-8** and **PP_{EH}-DT2BT-8** demonstrated efficiencies of 0.33 and 1.83%, respectively. The higher efficiency of **PP_{EH}-DT2BT-8** can be attributed to vastly improved FF and J_{sc} values.

Introduction

Organic solar cells based on conjugated polymers have attracted a vast interest from the academic community owing to their attractive advantages such as flexibility, low cost, ease of processing and tunable electronic properties [1], [2]. The most successful architecture for organic solar cells is the bulk heterojunction (BHJ) structure [2], [3]. This architecture possesses a light harvesting active layer that comprises an interdigitated blend of electron-donating and electron-accepting materials. Conjugated polymers are employed as the electron-donor whilst fullerene and its derivatives have found widespread use as the electron-accepting material. The light harvesting properties of the active layer are largely dictated by the conjugated polymer [4], [5]. Conjugated polymers that possess high molecular weights, broad absorption in the UV-vis-NIR region, high charge carrier mobilities and narrow band gaps will often display high efficiencies when fabricated into organic solar cells [6].

Polymers based on the donor-acceptor principle often display the desirable aforementioned characteristics. The intramolecular charge transfer between the alternating electron-rich donor moieties and the electron-deficient acceptor units along polymer chains, enables the energy level and band gap of the conjugated polymer to be finely tuned [7], [8], [9], [10]. 2,1,3-Benzothiadiazole (BT) is one of the most extensively studied electron-accepting units. It has found widespread use in highly efficient bulk heterojunction photovoltaic devices [11], [12], [13]. Polymers that contain BT moieties often exhibit narrow optical band gaps and deep HOMO levels.

Incorporation of thienyl groups at the 4,7-positions of BT decrease steric hindrance between the donor and acceptor units yielding more planar polymers with narrower optical band gap and improved charge mobility [14], [15]. The 4,7-positions of benzothiadiazole have been functionalised with various heterocyclic spacers [16], [17], [18]. Cong Z. *et al* synthesised three copolymers based on benzodithiophene and benzothiadiazole derivatives for use in BHJ solar cells. Devices fabricated from these polymers exhibited efficiencies as high as 8.47% [19]. On the other hand, pyrene-based donor acceptor conjugated polymers have received little interest from researchers. It is suspected that this is due to synthetic challenges encountered during functionalisation of the pyrene ring. Only a few papers have reported the synthesis of pyrene-based donor-acceptor conjugated polymers for use in organic solar cells [20], [21], [22], [23]. The physio-chemical properties of pyrene should, in theory, make it an excellent electron-donating monomer akin to anthracene and naphthalene. The four fused benzene rings yield a symmetrical, planar structure that should exhibit strong $\pi - \pi$ stacking in films, strong absorption in the UV and visible part of the electromagnetic spectrum and high charge mobility [24], [25], [26]. Taking these features into account, coupling 5,6-bis(octyloxy)-4,7-bis(5-(trimethylstannyl)thiophen-2yl)benzo[c][1,2,5]thiadiazole with pyrene units should also lead to materials with deep HOMO energy levels which could translate to devices with high open-circuit voltages. Thus, it is quite interesting to prepare new copolymers that have the pyrene moiety in their backbone for use in BHJ solar cells.

In this study, we report the preparation of two pyrene-alt-benzothiadiazole D-A copolymers, poly{4,5,9,10-tetrakis[(2-ethylhexyl)oxy]pyren-alt-5,6-bis(octyloxy)-4,7-di(thiophen-2-yl)benzo [c][1,2,5]thiadiazole} **(PP_{EH}-DTBT-8)** and poly{4,5,9,10-tetrakis[(2-ethylhexyl)oxy]pyren-alt-4,7-di([2,2'-bithiophen]-5-yl)-5,6-bis(octyloxy)benzo[c][1,2,5]thiadiazole} **(PP_{EH}-DT2BT-8)**.

The addition of octyloxy chains at the 5,6-positions of the BT units are designed to enhance the solubility of the resulting polymers. Previous literature work has also shown that these solubilising substituents increase the planarity of polymer backbones owing to supramolecular S–O interactions [27]. The physical properties of the two polymers were investigated by GPC, TGA, UV−vis absorption, cyclic voltammetry and XRD. The photovoltaic performance of both polymers in BHJ solar cells was evaluated. **PP$_{EH}$-DTBT-8** and **PP$_{EH}$-DT2BT-8** exhibited power conversion efficiencies of 0.33 and 1.83%, respectively.

Experimental

Materials: All materials were purchased from commercial suppliers and used as received, unless otherwise stated. Toluene was dried and distilled over sodium under an inert argon atmosphere. Acetonitrile was dried and distilled over phosphorous pentoxide and stored under an inert atmosphere with molecular sieves (3 Å). 4,7-Bis(5-bromothiophen-2-yl)-5,6-bis(octyloxy)benzo[c][1,2,5]thiadiazole [28] (**1**) and 4,7-bis(5'-bromo-[2,2'-bithiophen]-5-yl)-5,6-bis(octyloxy)benzo[c][1,2,5]thiadiazole [29] (**2**) were prepared according to literature procedures. For supporting information regarding measurements, instrument and fabrication of the devices see reference 24.

Preparation of monomers and polymers:

*5,6-Bis(octyloxy)-4,7-bis(5-(trimethylstannyl)thiophen-2yl) benzo[c][1,2,5]thiadiazole (**M2**):*

Under an inert atmosphere, 4,7-bis(5-bromothiophen-2-yl)-5,6-bis(octyloxy)benzo[c][1,2,5] thiadiazole (**1**) (0.25 g, 0.35 mmol) was dissolved in anhydrous THF (20 mL). The solution was cooled to -78 °C and *n*-BuLi (2.5 M in hexanes, 0.44 ml, 1.1 mmol) was added dropwise. The reaction was stirred for 3 hours at -78 °C. Trimethyltin chloride (0.22 g, 1.1 mmol) in anhydrous THF (3 mL) was then added dropwise. The reaction mixture was allowed to warm to RT and left stirring overnight. The solution was poured onto brine and extracted with diethyl ether (5 x 70 mL). The organic layers were combined, washed with H_2O (4 x 100 mL) and dried over $MgSO_4$. The solvent was removed *in vacuo* to afford the monomer as a green oil (0.28 g, 0.31 mmol, 91%). ^{1}H-NMR (400 MHz, $CDCl_3$): (δ_H/ppm) 8.53 (d, 2H, *J* = 3.53 Hz), 7.34 (d, 2H, *J* = 3.49 Hz), 4.13 (t, 4H, *J* = 6.96 Hz), 1.98 – 1.89 (m, 4H), 1.52 – 1.42 (m, 4H), 1.40 – 1.26 (m, 16H), 0.91 (t, 6H, *J* = 6.90 Hz). ^{13}C-NMR (400 MHz, $CDCl_3$): (δ_C/ppm)151.94, 151.03, 134.82, 131.33, 127.17, 126.7, 117.63, 74.3, 31.85, 30.39, 29.57, 29.27, 26.05, 22.67, 14.08, -8.1. GC-MS: mass calculated for $C_{36}H_{56}N_2O_2S_3Sn$, 882.15. Found, 882.1. Elem. Anal. Calculated for $C_{36}H_{56}N_2O_2S_3Sn$: C, 49.00; H, 6.40; N, 3.17; S, 10.90 Found: C, 51.58; H, 6.62; N, 3.02; S, 10.47.

*5,6-Bis(octyloxy)-4,7-bis(5'-(trimethylstannyl)-[2,2'-bithiophen]-5-yl)benzo[c][1,2,5]thiadiazole (**M3**):*

Under an inert atmosphere, 4,7-bis(5'-bromo-[2,2'-bithiophen]-5-yl)-5,6-bis(octyloxy)benzo[c][1,2,5]thiadiazole (**2**) (0.20 g, 0.23 mmol) was dissolved in dry THF (20 mL). The solution was cooled to -78 °C and *n*-BuLi (2.5 M in hexane, 0.29 mL, 0.72 mmol) was added dropwise. The mixture was stirred for 3 hours at -78 °C. Trimethyltin chloride (0.14 g, 0.71 mmol) in THF (3 mL) was then added dropwise. Upon complete addition, the reaction mixture was gradually warmed to RT and stirred overnight. The solution was poured into brine and extracted with diethyl ether (5 x 50 mL). The organic layers were combined, washed with H_2O (3 x 100 mL) and dried over $MgSO_4$. The solvent was removed *in vacuo* to produce the final monomer as a red oil (0.23 g, 0.22 mmol, 97%). ^{1}H-NMR (400 MHz, $CDCl_3$): (δ_H/ppm) 8.52 (d, 2H, *J* = 3.93 Hz), 7.42 (d, 2H, *J* = 3.18 Hz), 7.31 (d, 2H, *J* = 3.80 Hz), 7.16 (d, 2H, *J* = 3.15 Hz), 4.18 (t, 4H, *J* = 6.91 Hz), 2.06-1.95 (m, 4H), 1.57–1.21 (br, 20H), 0.90 (t, 6H, J = 6.54 Hz), 0.43 (s, 18H). ^{13}C-NMR (400 MHz, $CDCl_3$): (δ_C/ppm) 151.55, 150.83, 138.99, 137.90, 132.97, 131.66, 127.96, 123.77, 117.24, 111.26, 74.62, 31.84, 31.86, 30.45, 29.59, 29.37, 26.09, 22.37, 14.14. GC-MS: mass calculated for $C_{44}H_{60}N_2O_2S_5Sn_2$: 1046.70; found 1045.9**.** Elem. Anal. Calculated for $C_{44}H_{60}N_2O_2S_5Sn_2$: C, 50.49; H, 5.78; N, 2.68; S, 15.32. Found: C, 52.90; H, 6.12; N, 2.56; S, 14.20.

*Poly{4,5,9,10-tetrakis[(2-ethylhexyl)oxy]pyrene-alt-5,6-bis(octyloxy)-4,7-di(thiophene-2yl)benzo[c][1,2,5]thiadiazole} (**PP$_{EH}$-DTBT-8**):*

A mixture of **M1** (0.140 g, 0.160 mmol), **M2** (0.141 g, 0.160 mmol), $Pd(OAc)_2$ (2.00 mg, 11 µmol) and tri(*o*-toly)phosphine (7.00 mg, 23 µmol) were placed in a one neck round bottom flask, degassed and placed under an argon atmosphere. Anhydrous toluene (5 mL) was added to the mixture. The solution was heated to 100 °C over 72 hours. Upon completion, the solution was cooled to room temperature and 2-(tributylstannyl)-thiophene (11.7 µL, 0.12 mmol) added. The mixture was degassed and refluxed for one hour. Upon completion, the solution was cooled to room temperature and 2-bromothiophene (45 mg, 0.12 mmol was added. The mixture was degassed and refluxed for a further one hour. Upon completion the solution was cooled to room temperature and added to chloroform (250 mL). An ammonium hydroxide solution (28% in H_2O, 40 mL) was then added and the mixture was stirred at 60 °C for 3 hours. Upon completion, the mixture was cooled down to room temperature and the organic phase separated and washed with water (3 x 150 mL). The organic phase was concentrated *in vacuo* to ~ 40 mL and precipitated in methanol (300 mL). The resulting solid was collected *via* filtration and subject to Soxhlet extraction with methanol, acetone, hexane and toluene. The hexane fraction was concentrated *in vacuo* and precipitated in methanol. The solid was filtered and the polymer was obtained as a dark red solid (50 mg, 0.04 mmol, 25%). GPC hexane fraction: M_n = 4,700 Da; M_w = 7,000 Da; PDI =

1.49. ^{1}H-NMR (500 MHz, $C_2D_2Cl_4$, 100 °C): (δ_H/ppm) 8.85 (br.s, 4H), 8.63 (br.d, 2H), 7.83 (br.d, 2H), 4.40-4.14 (m, 12H), 2.13-1.95 (m, 8H), 1.95-1.20 (m, 52H), 1.13 (br.t, 12H), 0.95 (br.t, 12H), 0.80 (br.t, 6H). Elem. Anal. Calculated for $C_{78}H_{110}N_2O_6S_3$: C, 73.89; H, 8.74; N, 2.21; S, 7.59. Found: C, 72.73; H, 8.53; N, 2.22; S, 7.33.

*Poly[4,5,9,10-tetrakis((2-ethylhexyl)oxy)pyren-alt-4,7-di([2,2'-bithiophen]-5-yl)-5,6-bis(octyloxy)benzo[c][1,2,5]thiadiazole (**PP$_{EH}$-DT2BT-8**):*

PP$_{EH}$-DT2BT-8 was synthesised according to the polymerisation method outlined for **PP$_{EH}$-DTBT-8**, using a mixture of **M1** (0.117 g, 0.134 mmol), **M3** (0.140 g, 0.134 mmol), $Pd(OAc)_2$ (2.00 mg, 11 µmol) and tri(*o*-toly)phosphine (7.00 mg, 23 µmol) in toluene (5 mL). However, the main fraction of the polymer was extracted with toluene. The polymer was obtained as a dark purple solid (0.130 mg, 0.09 mmol, 68%). GPC toluene fraction: M_n = 11,200 Da; M_w = 20,900 Da; PDI = 1.87. ^{1}H-NMR (500 MHz, $C_2D_2Cl_4$, 100 °C): (δ_H/ppm) 8.70 (br.s, 4H), 8.50 (br.d, 2H), 7.56 (br.d, 2H), 7.40 (br.d, 4H), 4.33-4.10 (m, 12H), 2.10-1.90 (m, 8H), 1.95-1.20 (m, 52H), 1.10 (br.t, 12H), 0.97 (br.t, 12H), 0.87 (br.t, 6H). Elem. Anal. Calculated for $C_{86}H_{114}N_2O_6S_5$: C, 72.12; H, 8.02; N, 1.96; S 11.19. Found: C, 70.51; H, 7.70; N, 2.01; S, 10.88.

Results and Discussions

In a previous work, the preparation of pyrene-*alt*-benzothiadiazole D-A copolymers has been reported [24]. When blended with $PC_{70}BM$ and fabricated into BHJ solar cells the resulting devices displayed modest power conversion efficiencies. In order to explore the potential of pyrene-*alt*-benzothiadiazole copolymers we have investigated the impact of replacing hydrogen atoms at the 5,6-positions of benzothiadiazole with octyloxy substituents. Additionally, we have also investigated in this work, the effect of replacing thiophene spacers between pyrene and benzothiadiazole alternating units with bithiophene spacers to probe the impact of this substitution on the properties of the resulting polymer.

Monomer preparation is depicted in Scheme 1. The syntheses of the subsequent copolymers are outlined in Scheme 2. Compound **1** and **2** were prepared according to literature procedures. Metal-halogen exchange on **1** and **2** with *n*-BuLi followed by reaction with trimethyltin chloride enabled the formation of 5,6-bis(octyloxy)-4,7-bis(5-(trimethylstannyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole (**M2**) and 5,6-bis(octyloxy)-4,7-bis(5'-(trimethylstannyl)-[2,2'-bithiophen]-5-yl)benzo[c][1,2,5]thiadiazole (**M3**), respectively (Scheme 1). Stille coupling of 2,7-dibromo-4,5,9,10-tetrakis(2-ethylhexyloxy)-pyrene (**M1**) with **M2**, and with **M3** afforded **PP$_{EH}$-DTBT-8** and **PP$_{EH}$-DT2BT-8**, respectively, in yields of 25 and 68%, respectively (Scheme 2).

The structures of the two polymers were verified by ^{1}H-NMR and elemental analysis. Both polymerisations were deemed complete after 72 hours. **PP$_{EH}$-DTBT-8** and **PP$_{EH}$-DT2BT-8** were purified *via* Soxhlet extraction using in succession methanol, acetone, hexane and toluene. The majority of **PP$_{EH}$-DTBT-8** was collected in the hexane fraction. In contrast, the bulk of **PP$_{EH}$-DT2BT-8** was collected in the toluene fraction. It is speculated that the low degree of polymerisation of **PP$_{EH}$-DTBT-8** is a consequence of steric hindrance during the coupling reaction upon repulsion between octyloxy substituents on **M2** and monomer **M1**. It is probable that these interactions also reduce the planarity of the polymer backbone increasing its solubility in hexane. Gel permeation chromatography (GPC) was used to estimate the number-average molecular weights (M_n) and weight-average molecular weights (M_w) of the two polymers against polystyrene standards. The results are outlined in Table 1. **PP$_{EH}$-DTBT-8** was estimated to have a weight average molecular weight of 7,000 Da, which is lower than its analogous polymer, **PP$_{EH}$-DT2BT-8**, which has a molecular weight of 20,900 Da. The higher degree of polymerisation of **PP$_{EH}$-**

DT2BT-8, is explained by lesser steric hindrance between the octyloxy substituents on **M3** and **M1** during the coupling reaction.

UV-vis absorption spectroscopy

UV-vis spectroscopy was used to study the optical properties of the two polymers in both solution and film states (Figure 1). The results are outlined in Table 1. Both polymers demonstrated two sets of absorption bands. The absorption bands positioned at shorter wavelengths correspond to π-π* transitions from the monomer repeat units, while the absorption bands located at longer wavelengths are attributed to intramolecular charge transfer (ICT) between the pyrene units flanked by thiophene or bithiophene groups as the electron donor moieties and benzothiadiazole as the electron-deficient units. In solution, the ICT band of **PP$_{EH}$-DTBT-8** and **PP$_{EH}$-DT2BT-8** are positioned at 493 and 521 nm, respectively. The ICT band of **PP$_{EH}$-DTBT-8** and **PP$_{EH}$-DT2BT-8** are red-shifted to 510 and 551 nm, respectively, when cast into films. The bathochromic shift can be ascribed to improved ordering and a more planar polymer backbone in solid state. It is perhaps worth noting that the ICT band of **PP$_{EH}$-DT2BT-8** displays a larger bathochromic shift from solution to films (30 nm), in comparison to that observed for **PP$_{EH}$-DTBT-8** (16 nm). The larger shift of **PP$_{EH}$-DT2BT-8** can be attributed to its extended conjugation. Furthermore, the large red-shift also suggests that **PP$_{EH}$-DT2BT-8** possess superior intramolecular order in two dimensional-stacking in films relative to **PP$_{EH}$-DTBT-8**. The UV-vis spectra of **PP$_{EH}$-DT2BT-8** exhibited an additional broad band at 412 nm in solution and at 427 nm in solid state. This band is totally absent in **PP$_{EH}$-DTBT-8**. This phenomenon is a consequence of substituting thiophene for bithiophene spacer units. The extended conjugation of bithiophene, and its higher electronic density, may result in more pronounced ICT. The absorption of **PP$_{EH}$-DT2BT-8** covers a greater part of the visible spectrum; a prerequisite for good photovoltaic performance in devices.

The optical band gaps ($E_{g\ opt}$) of **PP$_{EH}$-DTBT-8** and **PP$_{EH}$-DT2BT-8** were calculated from their onsets of absorption in film states and were estimated to be 2.06 and 1.87 eV, respectively. The lower optical band gap of **PP$_{EH}$-DT2BT-8** is a consequence of its extended conjugation in the solid state and also the higher electron donating ability of bithiophene spacers *vs.* thiophene spacers which improves ICT between donor and acceptor units along polymer chains.

The two polymers prepared within this report possess wider optical band gaps relative to the fluorinated and non-fluorinated benzothiadiazole-pyrene based polymers, **PP$_{EH}$-DTffBT** and **PP$_{EH}$-DTBT**, prepared by Alqurashy *et al* [24]. **PP$_{EH}$-DTffBT** and **PP$_{EH}$-DTB** possess optical band gaps of 1.81 and 1.76 eV, respectively. The wider optical band gaps of **PP$_{EH}$-DTBT-8** and **PP$_{EH}$-DT2BT-8**, relative to **PP$_{EH}$-DTffBT** and **PP$_{EH}$-DTBT**, can be attributed to the use of octyloxy substituents on BT units. Not only are these solubilising chains more sterically demanding but they are also electron donating. Consequently, incorporation of these chains 'pushes' electronic density onto the benzothiadiazole moiety resulting in wider band gap polymers.

Thermal Properties

Thermogravimetric analysis (TGA) was carried out to investigate the thermal properties of **PP$_{EH}$-DTBT-8** and **PP$_{EH}$-DT2BT-8**. Both polymers exhibited good thermal stabilities with degradation temperatures (5% weight loss) higher than 310 °C (Figure 2). **PP$_{EH}$-DTBT-8** and **PP$_{EH}$-DT2BT-8** displayed two onsets of degradation. Both polymers exhibit an initial onset at 315 °C which corresponds to the elimination of thermally labile alkyl chains from the polymer backbone. The second onset occurred at 494 and 500 °C for **PP$_{EH}$-DTBT-8** and **PP$_{EH}$-DT2BT-8**, respectively. This was attributed to the degradation of the polymer backbone.

Cyclic Voltammetry

The electrochemical properties of **PP$_{EH}$-DTBT-8** and **PP$_{EH}$-DT2BT-8** were investigated by cyclic voltammetry (CV). Measurements were performed on drop-cast polymer films in acetonitrile and tetrabutylammonium perchlorate as electrolyte with a scan rate of 100 mV s^{-1}. The HOMO and LUMO energy levels of the two polymers were measured from the onset of their oxidation and reduction curves, respectively. The HOMO and LUMO levels of the two polymers are summarised in Table 1. The redox curves of the two polymers are depicted in Figure 5. Previous literature has shown that introducing electron-withdrawing substituents such as F or CN decreases the HOMO level of the polymer. In contrast, the introduction of electron donating species has the opposite effect [9], [30], [31].

The HOMO level of **PP$_{EH}$-DTBT-8** (-5.54 eV) was slightly deeper than that of **PP$_{EH}$-DT2BT-8** (-5.50 eV); a result that could be due to the higher electron donating ability of bithiophene spacer units in **PP$_{EH}$-DT2BT-8** *vs.* thiophene units for **PP$_{EH}$-DTBT-8**. The LUMO level of **PP$_{EH}$-DT2BT-8** (-3.46 eV) is deeper than that of its analogous polymer **PP$_{EH}$-DTBT-8** (-3.27 eV). It is speculated that the lower molecular weight of **PP$_{EH}$-DTBT-8**, relative to **PP$_{EH}$-DT2BT-8**, and the higher electronic conjugation of the latter polymer is responsible of this observation. Work conducted previously has shown that increasing the molecular weight of the polymer yields a rapid decrease in the LUMO level relative to the HOMO level; a consequence of the LUMO level becoming localised on the acceptor moiety [24]. It is speculated that the low molecular weight of **PP$_{EH}$-DTBT-8** will decrease the polymer packing density resulting in poor charge transportation.

The two polymers prepared within this work, **PP$_{EH}$-DTBT-8** and **PP$_{EH}$-DT2BT-8**, exhibited deeper HOMO levels relative to analogous anthracene-benzothiadiazole based polymers **PPATBT-8** and **PPAT2BT-8** prepared by Almeataq *et al* [32]. **PPATBT-8** and **PPAT2BT-8** possess HOMO levels of -5.44 and -5.48 eV, respectively. The deeper HOMO levels of **PP$_{EH}$-DTBT-8** and **PP$_{EH}$-DT2BT-8** are attributed to a weaker electron donating ability of pyrene units relative to the 4-dodecyloxybenzene 9,10-functionalised anthracene units. The electrochemical band gaps of **PP$_{EH}$-DTBT-8** and **PP$_{EH}$-DT2BT-8** were estimated to be 2.27 and 2.04 eV, respectively. These are relatively close to the optical band gaps of the polymers.

Powder X-ray diffraction

Powder X-ray diffraction (PXRD) was used to investigate the molecular order of **PP$_{EH}$-DTBT-8** and **PP$_{EH}$-DT2BT-8** in the solid state (Figure 4). Both **PP$_{EH}$-DTBT-8** and **PP$_{EH}$-DT2BT-8** exhibited broad, poorly resolved peaks in the small angle region at 2θ values of 3.78 and 4.22°, respectively, which correspond to stacking distances of 23.34 and 20.91 Å, respectively and which correspond to distances between polymer backbones. Both **PP$_{EH}$-DTBT-8** and **PP$_{EH}$-DT2BT-8** display a broad diffuse peak in the wide angle region at 2θ values of 20.5 and 21.6°, respectively, which correspond to $\pi - \pi$ stacking distances of 4.32 and 4.11 Å, respectively. Unsurprisingly, **PP$_{EH}$-DTBT-8** displayed larger stacking distances relative to **PP$_{EH}$-DT2BT-8**; a consequence of more planar backbone in the latter polymer.

Photovoltaic Properties

Preliminary photovoltaic studies of **PP$_{EH}$-DTBT-8** and **PP$_{EH}$-DT2BT-8** were conducted on bulk heterojunction solar cells using blends of polymer:PC$_{70}$BM (1:3 w/w ratios) and chlorobenzene as the processing solvent. The general device structure was glass/ITO/PEDOT:PSS/Polymer:PC$_{70}$BM/Ca/Al. The experimental section provides in-depth information regarding device fabrication. Figure 5 displays the *J-V* curves of the most efficient devices. The results are outlined in Table 2. Devices fabricated from **PP$_{EH}$-DTBT-8** displayed a low PCE (0.33%) with a V_{oc} of 0.72 V, a J_{sc} 1.88 mA/cm^2 and a poor *FF* of 24.53%. **PP$_{EH}$-DT2BT-8** demonstrated better results with a PCE of 1.83%, a V_{oc} of 0.78 V, a J_{sc} 6.11 mA/cm^2 and *FF* of 38.25%. The higher PCE of **PP$_{EH}$-DT2BT-8** compared to **PP$_{EH}$-DTBT-8** is due to the significantly higher J_{sc} and *FF* values. It is hypothesised that the low J_{sc} and FF values of devices made from **PP$_{EH}$-DTBT-8** are a consequence of its lower molecular weight relative to **PP$_{EH}$-DT2BT-8**, and poor packing of polymer chains in polymer:PC$_{70}$BM blends. Further work is being conducted to determine if these hypotheses are correct.

Conclusions

In this contribution, 2-ethylhexyloxy-functionalised pyrene based donor-acceptor alternating copolymers were prepared through Stille coupling polymerisation. Reactions of 2,7-dibromo-4,5,9,10-tetrakis(2-ethylhexyloxy)-pyrene and *5,6-bis(octyloxy)-4,7-bis(5-(trimethylstannyl) thiophen-2yl) benzo[c][1,2,5]thiadiazole* or 5,6-bis(octyloxy)-4,7-bis(5'-(trimethylstannyl)-[2,2'-bithiophen]-5-yl)benzo[c][1,2,5]thiadiazole afforded **PP$_{EH}$-DTBT-8** and **PP$_{EH}$-DT2BT-8**, respectively. A comparative study was carried out in order to evaluate the effects of substituting thiophene for bithiophene upon the properties of the resulting conjugated polymers. The chemical structures of the two polymers were confirmed with ^{1}H-NMR and elemental analysis. The properties of the polymers were investigated by GPC, TGA, UV−vis absorption, cyclic voltammetry and XRD. GPC data revealed that **PP$_{EH}$-DTBT-8** possessed a lower molecular weight relative to its bithiophene analogue, **PP$_{EH}$-DT2BT-8**; a consequence of the steric hindrance between the octyloxy-solubilising groups on benzothiadiazole monomer **M2** and pyrene-based monomer **M1** during the coupling reaction. **PP$_{EH}$-DT2BT-8** exhibited a lower optical and electrochemical band gap relative to **PP$_{EH}$-DTBT-8**. It is believed the incorporation of bithiophene spacer units are responsible for this. These promote a more planar backbone, extending the conjugation length and yielding increased charge transfer along the polymer backbone in view the enhanced electron donating ability of bithiophene units *vs*. thiophene units. BHJ solar cells were fabricated from the two polymers. $PC_{70}BM$ was used as the electron acceptor. BHJ solar cells fabricated from **PP$_{EH}$-DTBT-8** possessed a PCE of 0.33% which is lower than that of **PP$_{EH}$-DT2BT-8** which has a PCE of 1.83%. The higher efficiency of **PP$_{EH}$-DT2BT-8** compared to that of **PP$_{EH}$-DTBT-8** is due to the significantly higher J_{sc} and *FF* values. It is hypothesised that this is a consequence of the higher molecular weight of **PP$_{EH}$-DT2BT-8**, relative to **PP$_{EH}$-DTBT-8**, and improved packing of polymer chains in polymer:$PC_{70}BM$ blends.

References

[1] P. Ding, C.C. Chu, B. Liu, B. Peng, Y. Zou, Y. He, K. Zhou, C.S. Hsu, A high-mobility low-bandgap copolymer for efficient solar cells, Macromol. Chem. Phys. 211 (2010) 2555–2561.

[2] Y. Li, Y. Chen, X. Liu, Z. Wang, X. Yang, Y. Tu, X. Zhu, Controlling blend film morphology by varying alkyl side chain in highly coplanar donor-acceptor copolymers for photovoltaic application, Macromolecules. 44 (2011) 6370–6381.

[3] L. Lu, T. Zheng, Q. Wu, A.M. Schneider, D. Zhao, L. Yu, Recent Advances in Bulk Heterojunction Polymer Solar Cells, Chem. Rev. 115 (2015) 12666–12731.

[4] C.H. Cho, H.J. Kim, H. Kang, T.J. Shin, B.J. Kim, The effect of side-chain length on regioregular poly[3-(4-n-alkyl) phenylthiophene]/PCBM and ICBA polymer solar cells, J. Mater. Chem. 22 (2012) 14236–14245.

[5] P.P. Maharjan, Q. Chen, L. Zhang, O. Adebanjo, N. Adhikari, S. Venkatesan, P. Adhikary, B. Vaagensmith, Q. Qiao, Photovoltaic devices and characterization of a dodecyloxybenzothiadiazole- based copolymer, Phys. Chem. Chem. Phys. 15 (2013) 6856–6863.

[6] L. Cartwright, A. Iraqi, Y. Zhang, T. Wang, D.G. Lidzey, Impact of fluorine substitution upon the photovoltaic properties of benzothiadiazole-fluorene alternate copolymers, RSC Adv. 5 (2015) 46386–46394.

[7] M. Wang, X. Hu, P. Liu, W. Li, X. Gong, F. Huang, Y. Cao, Donor-acceptor conjugated polymer based on naphtho[1,2- c:5,6- c]bis[1,2,5]thiadiazole for high-performance polymer solar cells, J. Am. Chem. Soc. 133 (2011) 9638–9641.

[8] M.L. Keshtov, S.A. Kuklin, D.Y. Godovsky, A.R. Khokhlov, R. Kurchania, F.C. Chen, E.N. Koukaras, G.D. Sharma, New alternating D-A1-D-A2 copolymer containing two electron-deficient moieties based on benzothiadiazole and 9-(2-Octyldodecyl)-8H-pyrrolo[3,4-b]bisthieno[2,3-f:3’,2’-h]quinoxaline-8,10(9H)-dione for efficient polymer solar cells, J. Polym. Sci. Part A Polym. Chem. 54 (2016) 155–168.

[9] N. Wang, Z. Chen, W. Wei, Z. Jiang, Fluorinated benzothiadiazole-based conjugated polymers for high-performance polymer solar cells without any processing additives or post-treatments, J. Am. Chem. Soc. 135 (2013) 17060–17068.

[10] H. Zhou, L. Yang, S. Xiao, S. Liu, W. You, Donor-acceptor polymers incorporating alkylated dithienylbenzothiadiazole for bulk heterojunction solar cells: Pronounced effect of positioning alkyl Chains, Macromolecules. 43 (2010) 811–820.

[11] Y. Chen, Y. Yan, Z. Du, X. Bao, Q. Liu, V.A.L. Roy, M. Sun, R. Yang, C.S. Lee, Two-dimensional benzodithiophene and benzothiadiazole based solution-processed small molecular organic field-effect transistors & solar cells, J. Mater. Chem. C. 2 (2014) 3921–3927.

[12] M. Chen, B. Zhao, J. Xin, Z. Cong, X. Li, L. Yang, W. Ma, W. Wei, C. Gao, Effects of solvent vapour annealing on the performances of benzo[1,2-b:4,5-b′]dithiophene and 4,7-

di(4-hexyl-thiophen-2-yl)-5,6-difluorine-2,1,3-benzothiadiazole-based alternating polymer solar cells with different configurations, Dye. Pigment. 161 (2019) 58–65.

[13] J. Sun, Y. Zhu, X. Xu, L. Lan, L. Zhang, P. Cai, J. Chen, J. Peng, Y. Cao, High efficiency and high v oc 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.

[14] H. Zhou, L. Yang, W. You, Rational design of high performance conjugated polymers for organic solar cells, Macromolecules. 45 (2012) 607–632.

[15] M. Zhou, M. Wang, L. Zhu, Z. Yang, C. Jiang, D. Cao, Q. Li, D-π-A-π-A Strategy to Design Benzothiadiazole-carbazole-based Conjugated Polymer with High Solar Cell Voltage and Enhanced Photocurrent, Macromol. Rapid Commun. 36 (2015) 2156–2161.

[16] Y. Li, Benzo[1,2 - b :4,5 - b ′]difuran-Based Donor − Acceptor Copolymers for Polymer Solar Cells, Macromolecules. 45 (2012) 6898-6905.

[17] A.A.B. Alghamdi, D.C. Watters, H. Yi, S. Al-Faifi, M.S. Almeataq, D. Coles, J. Kingsley, D.G. Lidzey, A. Iraqi, Selenophene vs. thiophene in benzothiadiazole-based low energy gap donor-acceptor polymers for photovoltaic applications, J. Mater. Chem. A. 1 (2013) 5165–5171.

[18] C. Duan, A. Furlan, J.J. Van Franeker, R.E.M. Willems, M.M. Wienk, R.A.J. Janssen, Wide-Bandgap Benzodithiophene-Benzothiadiazole Copolymers for Highly Efficient Multijunction Polymer Solar Cells, Adv. Mater. 27 (2015) 4461–4468.

[19] Z. Cong, S. Liu, B. Zhao, W. Wang, H. Liu, J. Su, Z. Guo, W. Wei, C. Gao, Z. An, High performance alternating polymers based on two-dimensional conjugated benzo[1,2-: B:4,5-b ′]dithiophene and fluorinated dithienylbenzothiadiazole for solar cells, RSC Adv. 6 (2016) 77525–77534.

[20] B.A. Alqurashy, L. Cartwright, A. Iraqi, Y. Zhang, D.G. Lidzey, Pyrene–benzothiadiazole-based copolymers for application in photovoltaic devices, Polym. Adv. Technol. 28 (2017) 193–200.

[21] D.S. Yang, K.H. Kim, M.J. Cho, J. Il Jin, D.H. Choi, Donor-acceptor alternating π-conjugated polymers containing Di(thiophen-2-yl)pyrene and 2,5-Bis(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,4(2H, 5H)-dione for organic thin-film transistors, J. Polym. Sci. Part A Polym. Chem. 51 (2013) 1457–1467.

[22] B.A. Alqurashy, A. Iraqi, Y. Zhang, D.G. Lidzey, Preparation and photovoltaic properties of pyrene-thieno[3,4-c]pyrrole-4,6-dione-based donor-acceptor polymers, Eur. Polym. J. 85 (2016) 225–235.

[23] B.A. Alqurashy, Preparation and Physical Characterization of Pyrene and Pyrrolo[3,4-c]pyrrole-1,4-dione-Based Copolymers, ChemistryOpen. 8 (2019) 429–433.

[24] C.E. Song, I.N. Kang, J.H. Kim, D.H. Hwang, J.C. Lee, T. Ahn, W.S. Shin, S.J. Moon, S.K. Lee, Photovoltaic performance enhancement using fluorene-based copolymers containing pyrene units, J. Polym. Sci. Part A Polym. Chem. 51 (2013) 1512–1519.

[25] R. Jin, K. Li, X. Han, Improving optoelectronic and charge transport properties of D–π–D type diketopyrrolopyrrole-pyrene derivatives as multifunctional materials for organic solar cell applications, RSC Adv. 9 (2019) 22597–22603.

[26] N. Wang, X. Bao, Y. Yan, D. Ouyang, M. Sun, V.A.L. Roy, C.S. Lee, R. Yang, Synthesis and photovoltaic properties of conjugated D-A copolymers based on thienyl substituted pyrene and diketopyrrolopyrrole for polymer solar cells, J. Polym. Sci. Part A Polym. Chem. 52 (2014) 3198–3204.

[27] 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) 2773–2782.

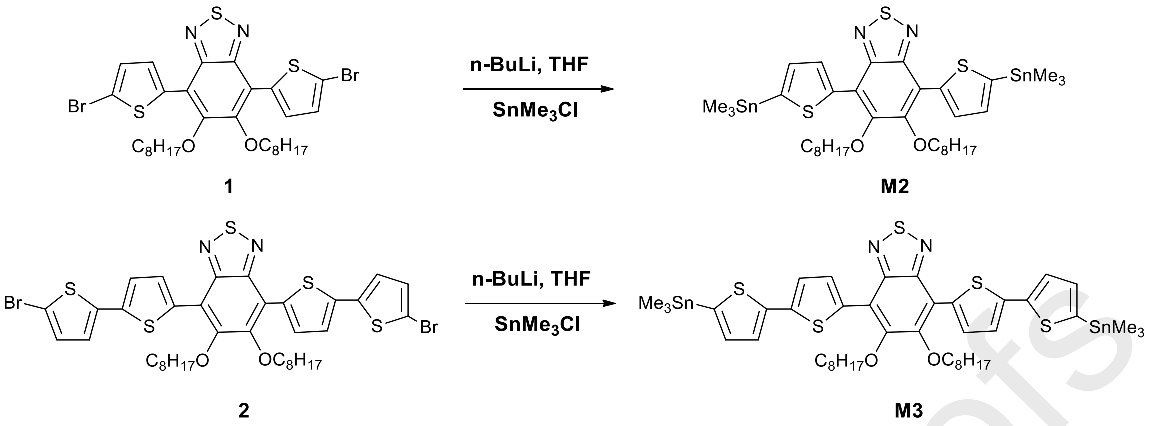
[28] M. Helgesen, S.A. Gevorgyan, F.C. Krebs, R.A.J. Janssen, Substituted 2,1,3-benzothiadiazole-and thiophene-based polymers for solar cells-introducing a new thermocleavable precursor, Chem. Mater. 21 (2009) 4669–4675.

[29] H. Yi, S. Al-Faifi, A. Iraqi, D.C. Watters, J. Kingsley, D.G. Lidzey, Carbazole and thienyl benzo[1,2,5]thiadiazole based polymers with improved open circuit voltages and processability for application in solar cells, J. Mater. Chem. 21 (2011) 13649–13656.

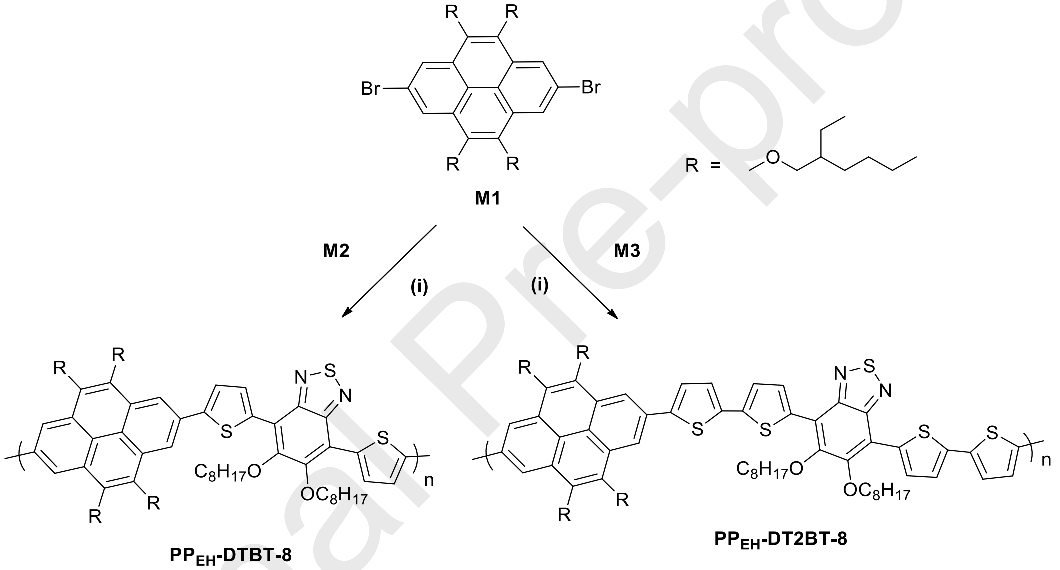
[30] A. Casey, S.D. Dimitrov, P. Shakya-Tuladhar, Z. Fei, M. Nguyen, Y. Han, T.D. Anthopoulos, J.R. Durrant, M. Heeney, Effect of Systematically Tuning Conjugated Donor Polymer Lowest Unoccupied Molecular Orbital Levels via Cyano Substitution on Organic Photovoltaic Device Performance, Chem. Mater. 28 (2016) 5110–5120.

[31] A.C. Stuart, J.R. Tumbleston, H. Zhou, W. Li, S. Liu, H. Ade, W. You, Fluorine substituents reduce charge recombination and drive structure and morphology development in polymer solar cells, J. Am. Chem. Soc. 135 (2013) 1806–1815.

[32] M.S. Almeataq, H. Yi, S. Al-Faifi, A.A.B. Alghamdi, A. Iraqi, N.W. Scarratt, T. Wang, D.G. Lidzey, Anthracene-based donor-acceptor low band gap polymers for application in solar cells, Chem. Commun. 49 (2013) 2252–2254.



***Scheme 1:** Preparation of **M2** and **M3**.*



Scheme 2: Synthetic route and chemical structures of **PP$_{EH}$-DTBT-8** and **PP$_{EH}$-DT2BT-8**: (i) Pd(OAc)$_2$, tri(*o*-tolyl)phosphine and toluene.

Table 1. GPC, UV-vis absorption and electrochemical data for **PP$_{EH}$-DTBT-8** and **PP$_{EH}$-DT2BT-8**.

Polymers	M$_n$(Da)[c]	M$_w$(Da)[c]	PDI	λ$_{max}$ (nm) Solution	λ$_{max}$ (nm) Film	ε (M^{-1} cm^{-1})[d]	E$_{g\ opt}$ (eV)[e]	HOMO (eV)[f]	LUMO (eV)[g]	E$_{g\ ele}$ (eV)[h]
PP$_{EH}$-DTBT-8[a]	4700	7000	1.49	494	510	39585	2.06	-5.54	-3.27	2.27
PP$_{EH}$-DT2BT-8[b]	11200	20900	1.87	521	551	73100	1.87	-5.50	-3.46	2.04

[a]Measurements conducted on the hexane fraction of the polymer. [b]Measurements conducted on the toluene fraction of the polymers. [c]Determined by GPC using 1,2,4-trichlorobenzene as the eluent at 140°C. [d]Extinction coefficient measured at λ$_{max}$ in CHCl$_3$. [e]Optical band gap. [f]HOMO level determined from the onset of oxidation. [g]LUMO level determined from the onset of reduction. [h]Electrochemical band gap.

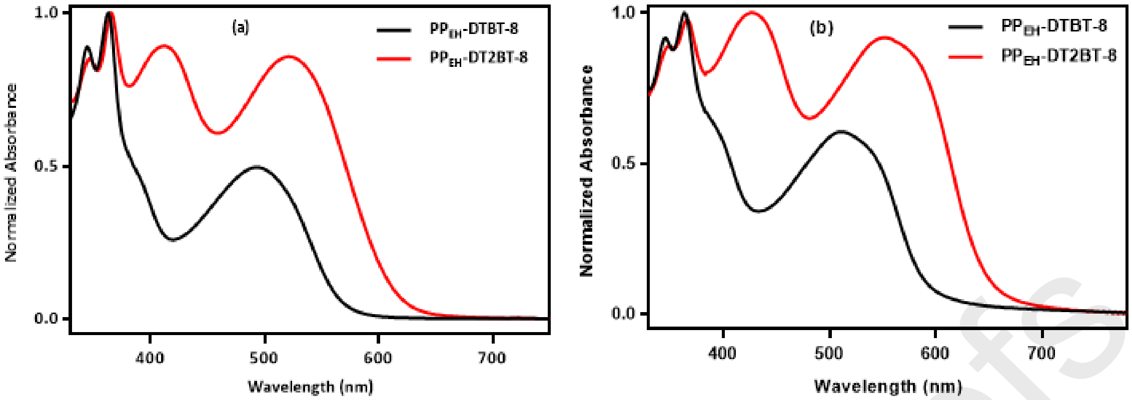


Figure 1. Normalised absorption spectra of **PP$_{EH}$-DTBT-8**, **PP$_{EH}$-DT2BT-8**, in: (*a*) chloroform solution; and (*b*) thin film.

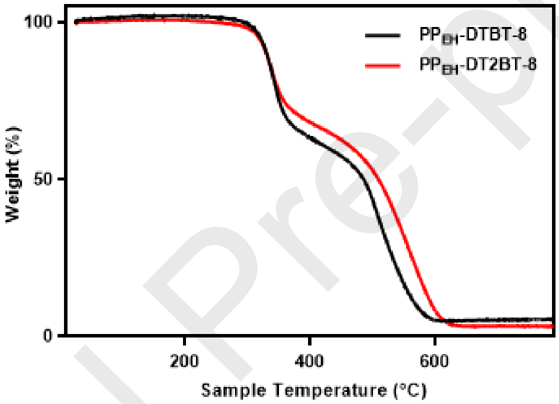


Figure 2: TGA curves of **PP$_{EH}$-DTBT-8** and **PP$_{EH}$-DT2BT-8**.

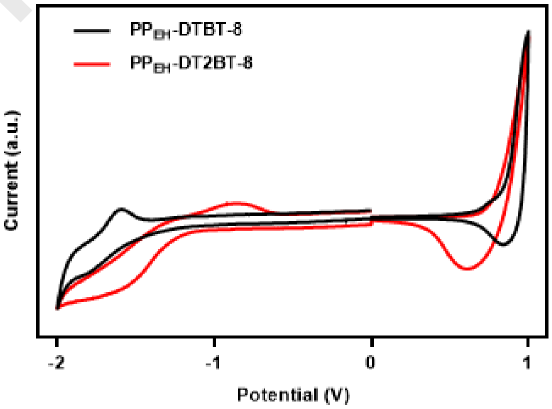


Figure 3. Cyclic voltammograms of thin films of **PP$_{EH}$-DTBT-8** and **PP$_{EH}$-DT2BT-8** on platinum disc electrodes (area 0.031 cm^2).

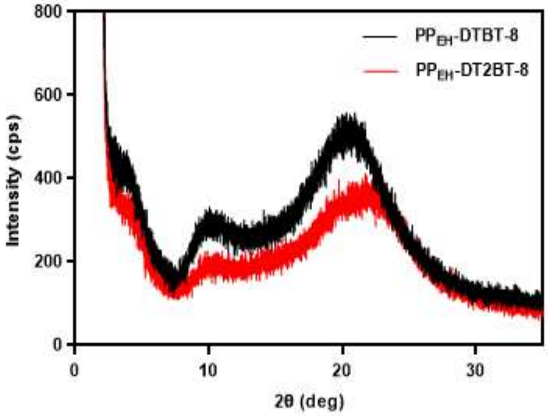


Figure 4. PXRD patterns of **PP$_{EH}$-DTBT-8** and **PP$_{EH}$-DT2BT-8**.

***Table 2**. Device Performance of the two polymers: **PP$_{EH}$-DTBT-8** and **PP$_{EH}$-DT2BT-8**.*

Polymer	J_{sc} (mA/cm^2)	V_{oc} (V)	*FF* (%)	PCE (%)
PP$_{EH}$-DTBT-8	1.88	0.72	24.53	0.33
PP$_{EH}$-DT2BT-8	6.11	0.78	38.25	1.83

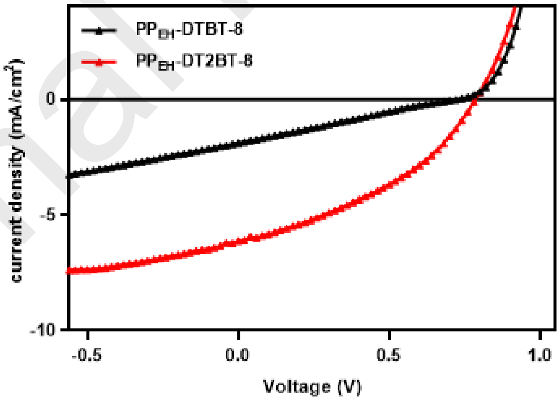


Figure 5: The J-V characteristic curves of **PP$_{EH}$-DTBT-8** and **PP$_{EH}$-DT2BT-8**.