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Preparation and Photovoltaic Properties of Pyrene-Thieno[3,4-c]pyrrole-4,6-dione-Based Donor-Acceptor Polymers

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Abstract

Four new donor-acceptor conjugated copolymers, containing pyrene moieties flanked by thienyl or bithienyl groups as a donor units and thieno[3,4-c]pyrrole-4,6-dione (TPD) as acceptor units, were successfully prepared *via* a direct arylation polymerisation method. While all polymers prepared had 2-ethylhexyloxy-substituents on the pyrene repeat units, two different alkyl-substituents (octyl or 4-hexylphenyl groups) were attached to their TPD moieties. The influence of these different substituents as well as the number of thienyl units linking the pyrene and TPD units along polymer chains on the photophysical, electronic and photovoltaic properties of these materials was investigated. All polymers displayed good thermal stability up to 315°C. The optical band gap of the four polymers, **PP_{EH}DT-TPD_O**, **PP_{EH}DT-TPD_{HP}**, **PP_{EH}DT2-TPD_O** and **PP_{EH}DT2-TPD_{HP}**, were estimated to be 2.00, 2.06, 1.94 and 1.91 eV, respectively. Polymers that possessed a single thiophene unit attached to the pyrene unit, **PP_{EH}DT-TPD_O** and **PP_{EH}DT-TPD_{HP}**, displayed deeper HOMO levels compared to those with bithiophene units, **PP_{EH}DT2-TPD_O** and **PP_{EH}DT2-TPD_{HP}**. Photovoltaic devices were fabricated from all polymers. **PP_{EH}DT2-TPD_O** boasted the highest efficiency with a PCE (2.06 %), a *FF* of 53.07 %, a *J_{sc}* of 4.66 mA/cm² and a *V_{oc}* of 0.83 V.

Keywords

Pyrene; thieno[3,4-c]pyrrole-4,6-dione; conjugated polymers; BHJ solar cells.

Introduction

Solar energy has proven to be a promising alternate energy source to the finite, environmentally harmful fossil fuels that are currently used as the world's main source of energy [1]. Inorganic solar cells, based on crystalline silicon, have demonstrated efficiencies in excess of 25 % [2]. However, their manufacturing costs, high embodied energy and temperature dependant performance have restricted the widespread use of this technology [2,3]. Consequently, research into alternative photovoltaic devices has been initiated. Organic photovoltaic devices, which utilise conjugated polymers and fullerene derivatives in the active layer, have shown promise as an alternative to traditional inorganic solar cells [2,4]. Organic solar cells possess several advantages over their inorganic counterparts including: abundant materials for fabrication, can be manufactured using low-cost solution based manufacturing on flexible substrates, are lightweight and can be recycled [2,4]. However, organic solar devices have three major disadvantages: stability, lifetime and efficiency [5]. Organic solar cells exhibit efficiencies lower than traditional devices, however, power conversion efficiencies exceeding 10 % have been recorded with these cells [6]. Work continues in order to improve the stability and efficiency of organic solar cells in order to make organic photovoltaics a sustainable technology [6].

Traditional palladium-catalysed cross-coupling reactions (Suzuki or Stille) are commonly used in the preparation of conjugated polymers used in the active layer of organic photovoltaic devices [7]. These cross-coupling reactions involve the use of organo-boron or tin reagents which are expensive to prepare and toxic in the case of tin compounds [8,9]. These drawbacks have accelerated the development of alternative cross-coupling reactions. Amongst these methods, direct arylation polymerisation (DAP) has shown great promise as an alternative to traditional routes [7-9]. DAP activates the C-H bond of heteroarenes facilitating coupling to an aryl halide. This occurs without the need for organometallic reagents which minimises the number of synthetic steps [7,9].

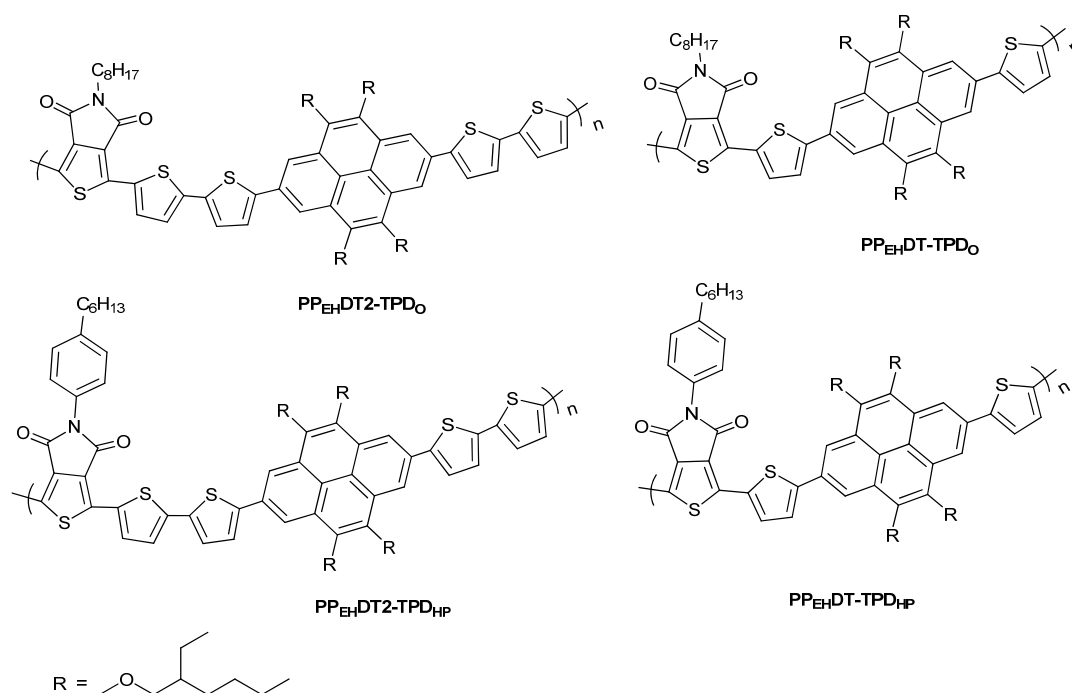
The thieno[3,4-c]pyrrole-4,6-dione (TPD) moiety has been extensively investigated for use in organic solar cells [10,11]. The TPD moiety possesses a high degree of structural symmetry and planarity, which can aid electronic delocalisation along the polymer backbone resulting in a low band gap and more efficient harvesting of sunlight. The electron deficient imide group renders the TPD moiety electron-deficient [10-12]. Thus, when polymerised with an electron-rich

monomer, the TPD unit can form a highly advantageous donor-acceptor arrangement which can improve charge transfer along the polymer backbone. Furthermore, the TPD moiety can be functionalised by attaching different solubilising groups to the nitrogen of the imide group [13]. Leclerc *et al* initiated research into the TPD moiety by copolymerising TPD with benzodithiophene (BDT). The resulting copolymer exhibited an efficiency of 5.5 % [10]. Chu and co-workers synthesised the high molecular weight **PDTSTPD-C8** copolymer which demonstrated an efficiency of 7.5 % when fabricated into BHJ photovoltaic devices [14]. Recently, Clément *et al* investigated the impact side chains have in **PBDTTPD** polymers and the influence they have on the efficiency of BHJ devices. The research group discovered that TPD moieties substituted with n-heptyl substituents exhibited devices with a power conversion efficiency up to 8.5 % and a V_{oc} of 0.97 V [15].

Pyrene as a class of polycyclic aromatic hydrocarbons (PAHs) have been used in OLED, FET and recently OPV devices [16,17]. Pyrene-based conjugated polymers have gained little interest from researchers relative to others PAH such as anthracene and naphthalene [18,19]. The main reason for the limited numbers of reports is the restricted methodology for the functionalization of the pyrene moiety. The majority of synthesis reported in the literature has investigated the substitution of pyrene at the “1,3,6,8”, “2,7” and “4,5,9,10” positions [20]. Pyrene is an electron rich, planar and symmetrical unit that should display a strong π - π stacking [21]. Liu *et al* reported the synthesis of series of pyrene-diketopyrrolopyrrole based oligomers for use in organic solar cells [17]. **Py₂Ph₂Th₄(DPP)₃** exhibited a low band gap of 1.60 eV. When fabricated into photovoltaic devices **Py₂Ph₂Th₄(DPP)₃** exhibited an efficiency of 3.71 % [17]. Recently, Wang *et al* synthesised **PDTPy-alt-DPP** which demonstrated an efficiency of 4.43 % when fabricated into BHJ solar cells using PC₇₀BM as an acceptor [21].

In this contribution, we report the synthesis and characterisation of four novel D–A polymers comprising alternate pyrene and TPD units, which were used as the electron donor and electron acceptor, respectively. Poly((2,2'-(4,5,9,10-tetrakis((2-ethylhexyl)oxy)pyrene-2,7-diyl)dithiophene)-alt-(5-octyl-thieno[3,4,c]pyrrole-4,6-dione)) (**PP_{EHDT}-TPD_O**), poly((2,2'-(4,5,9,10-tetrakis((2-ethylhexyl)oxy)pyrene-2,7-diyl)dithiophene)-alt-(5-(4-hexylphenyl)-thieno[3,4-c]pyrrole-4,6-dione)) (**PP_{EHDT}-TPD_{HP}**), poly((5,5''-(4,5,9,10-tetrakis((2-ethylhexyl)oxy)pyrene-2,7-diyl)di-2,2'-bithiophene)-alt-(5-octyl-thieno[3,4,c]pyrrole-4,6-dione))

(**PP_{EH}DT2-TPD_O**) and poly((5,5''-(4,5,9,10-tetrakis((2-ethylhexyl)oxy)pyrene-2,7-diyl)di-2,2'-bithiophene)-alt-(5-(4-hexylphenyl)-thieno[3,4-c]pyrrole-4,6-dione)) (**PP_{EH}DT2-TPD_{HP}**) were synthesised *via* a direct arylation polymerisation method (Scheme 1). Studies on the photophysical, electronic and photovoltaic properties of the four polymers are presented and discussed.



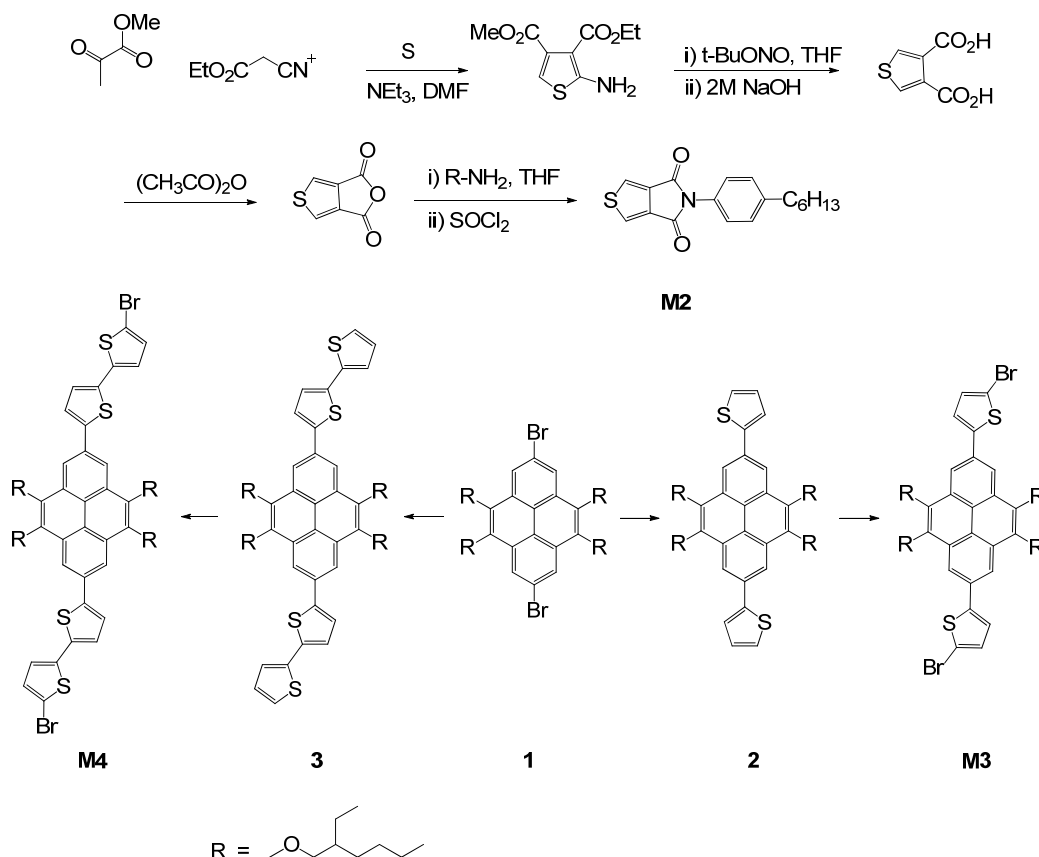
Scheme 1: Structure of **PP_{EH}DT-TPD_O**, **PP_{EH}DT-TPD_{HP}**, **PP_{EH}DT2-TPD_O** and **PP_{EH}DT2-TPD_{HP}**.

Results and Discussions

Monomer synthesis

5-octyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (**M1**) was prepared according to literature procedures [22]. The synthesis of 5-(4-hexylphenyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (**M2**), 5,5''-(4,5,9,10-tetrakis((2-ethylhexyl)oxy)pyrene-2,7-diyl)bis(2-bromothiophene) (**M3**) and 5,5''-(4,5,9,10-tetrakis((2-ethylhexyl)oxy)pyrene-2,7-diyl)bis(5-bromo-2,2'-bithiophene) (**M4**) are depicted in Scheme 2. Stille coupling of 2,7-dibromo-4,5,9,10-tetrakis((2-ethylhexyl)oxy)pyrene (**1**) with 2-tributylstannylthiophene and with 2,2'-bithiophen-5-yl-trimethylstannane produced intermediates **2** and **3**, respectively, in a yield of 89 % for **2** and 71

% for **3**. Bromination of **2** and **3** using N-bromosuccinimide (NBS) yielded the target monomers, **M3** and **M4**. These were obtained in a yield of 84 and 95 %, respectively.



Scheme 2: Synthetic route towards monomers **M2**, **M3** and **M4**.

Polymer synthesis

The four polymers were prepared *via* direct arylation polymerization. PdCl₂(MeCN)₂ and P(C₆H₄-o-OMe)₃ were used as the catalyst and cesium carbonate (Cs₂CO₃) as the base. Pivalic acid (PivOH) was used as the carboxylate source and THF as the solvent. Previous literature has shown that a carboxylate source is essential for direct arylation [23]. The carboxylate source generates a palladium carboxylate, which breaks the C-H bond of heteroarenes facilitating the cross coupling reaction. The polymerisations of **PP_{EH}DT-TPD_O** and **PP_{EH}DT-TPD_{HP}** were left for 48 hours. In contrast, the polymerisation of **PP_{EH}DT2-TPD_O** and **PP_{EH}DT2-TPD_{HP}** were left for 2 and 5 hours respectively, as in the preparation of the latter two polymers, large quantities of materials formed precipitates at the early stages of the reactions. The crude polymers were

purified *via* Soxhlet extraction using methanol, acetone and hexane to remove catalytic residues and oligomers. Toluene and chloroform were then used in succession to extract the polymers. **PP_{EH}DT-TPD_{HP}** provided most of its high molecular weight fraction from the toluene fraction while for **PP_{EH}DT-TPD_O**, **PP_{EH}DT2-TPD_O** and **PP_{EH}DT2-TPD_{HP}**, the chloroform fractions extracted the desired fractions of the polymers.

The chemical structures of **PP_{EH}DT-TPD_O**, **PP_{EH}DT-TPD_{HP}**, **PP_{EH}DT2-TPD_O** and **PP_{EH}DT2-TPD_{HP}** were confirmed by ¹H-NMR and elemental analysis. The number average molecular weight (M_n) and weight average molecular weight (M_w) of all polymers were estimated from high temperature (140°C) gel permeation chromatography (GPC) analysis using a series of polystyrene standards, and 1,2,4-trichlorobenzene (TCB) as the eluent. The data is summarized in Table 1. Polymers that are substituted with the aromatic 4-hexylphenyl groups displayed lower molecular weights relative to their counterparts with octyl substituents. It is speculated that the planar aromatic ring attached to the TPD moieties in these polymers promotes planarity and aggregation of polymer backbones, which impedes the extent of their degree of polymerisation. Polymers that incorporate bithiophene units between the pyrene and TPD units (**PP_{EH}DT2-TPD_O** and **PP_{EH}DT2-TPD_{HP}**) exhibited lower molecular weights relative to their counterparts which possess a single thiophene unit. When compared to thiophene, the bithiophene unit possesses an extended π -conjugation, which promotes aggregation of polymer chains and a reduced molecular weight.

Table 1: GPC, optical and electrochemical data for **PP_{EH}DT-TPD_O**, **PP_{EH}DT-TPD_{HP}**, **PP_{EH}DT2-TPD_O** and **PP_{EH}DT2-TPD_{HP}**

Polymers	M_n (Da) ^c	M_w (Da) ^c	PDI	λ_{max} (nm)		$E_{g\ opt}$ (eV) ^d	HOMO (eV) ^e	LUMO (eV) ^f	E_g^{ele} (eV) ^g
				Solution	Film				
PP _{EH} DT-TPD _O ^a	19700	38400	1.95	474	529	2.00	-5.57	-3.59	1.98
PP _{EH} DT-TPD _{HP} ^b	5700	8700	1.53	469	489	2.06	-5.55	-3.54	2.01
PP _{EH} DT2-TPD _O ^a	9100	12700	1.40	517	564	1.94	-5.50	-3.52	1.98
PP _{EH} DT2-TPD _{HP} ^a	5500	9200	1.67	499	532	1.91	-5.46	-3.51	1.95

^aMeasurements conducted on the chloroform fraction of the polymers. ^bMeasurements conducted on the toluene fraction of the polymers. ^cDetermined by GPC in 1,2,4-trichlorobenzene at 140°C. ^dOptical band gap. ^eHOMO level determined from the onset of oxidation. ^fLUMO level determined from the onset of reduction. ^gElectrochemical band gap.

UV-vis absorption spectroscopy

The UV-vis absorption spectra of **PP_{EH}DT-TPD_O**, **PP_{EH}DT-TPD_{HP}**, **PP_{EH}DT2-TPD_O** and **PP_{EH}DT2-TPD_{HP}** were recorded in chloroform solution (Figure 1a) and thin film (Figure 1b). The results are summarized in Table 1. All polymers displayed absorption bands in the range of 300-450 nm and 450-750 nm. The bands located at short wavelengths can be attributed to the π - π^* transitions of the conjugated backbone, while those located at long wavelengths correspond to intramolecular charge transfer (ICT) bands along the conjugated polymer backbone from the electron rich unit (the pyrene moieties flanked by thienyl or dithienyl units) to the electron deficient unit (the TPD moiety). In dilute chloroform solutions, the ICT band of **PP_{EH}DT-TPD_O**, **PP_{EH}DT-TPD_{HP}**, **PP_{EH}DT2-TPD_O** and **PP_{EH}DT2-TPD_{HP}** are positioned at 474, 469, 517 and 499 nm, respectively. In thin film this was red-shifted to 529, 489, 564 and 532 nm for **PP_{EH}DT-TPD_O**, **PP_{EH}DT-TPD_{HP}**, **PP_{EH}DT2-TPD_O** and **PP_{EH}DT2-TPD_{HP}**, respectively. The red-shifts indicate that the polymers adopt more ordered, planar structures in the solid state.

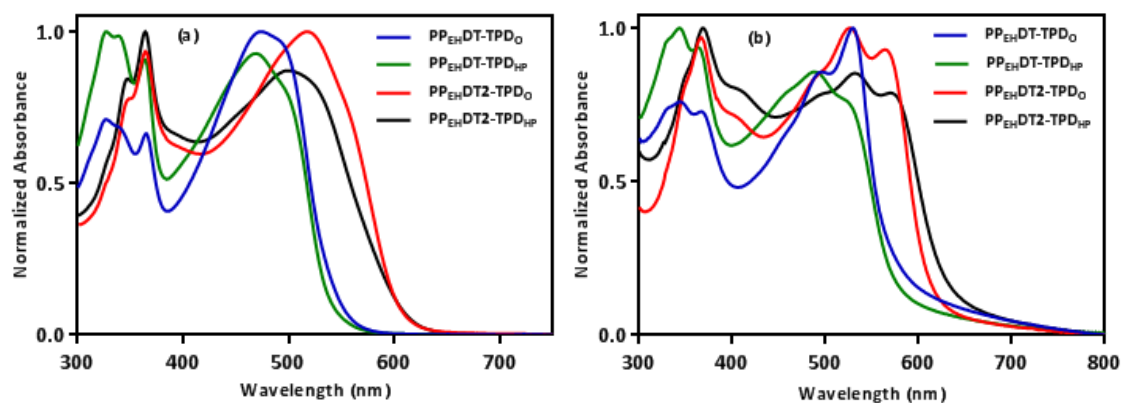


Figure 1: Normalised UV-vis absorption spectra of **PP_{EH}DT-TPD_O**, **PP_{EH}DT-TPD_{HP}**, **PP_{EH}DT2-TPD_O** and **PP_{EH}DT2-TPD_{HP}** in: (a) chloroform solutions; and (b) thin films.

Shoulder peaks appeared in the solid state, at longer wavelengths for all polymers. Interestingly, these shoulder peaks are not very prominent in solution. This phenomenon can be attributed to more ordered structures of polymer backbones in the solid state and is believed to arise from a pronounced stacking and aggregation of polymer chains in films. **PP_{EH}DT2-TPD_O** and **PP_{EH}DT2-TPD_{HP}**, which possess bithiophene spacer units, display red shifted absorption maxima, relative to their analogous polymers that contain single thiophene units. This can be

attributed to the extended conjugation length of the bithiophene unit, which yields a more planar conformation. Furthermore, the electron donating properties of the bithiophene units are higher than those of a single thiophene unit leading to more pronounced intramolecular charge transfer between the donor and acceptor units. The optical band gaps of **PP_{EH}DT-TPD_O**, **PP_{EH}DT-TPD_{HP}**, **PP_{EH}DT2-TPD_O** and **PP_{EH}DT2-TPD_{HP}** were estimated to be 2.00, 2.06, 1.94 and 1.91 eV, respectively. **PP_{EH}DT2-TPD_O** and **PP_{EH}DT2-TPD_{HP}** exhibited narrower optical band gaps relative to **PP_{EH}DT-TPD_O** and **PP_{EH}DT-TPD_{HP}**. The bithiophene unit enhances intramolecular charge transfer along the polymer backbone, increasing the electron delocalization leading to a lower optical band gap.

PP_{EH}DT-TPD_O, **PP_{EH}DT-TPD_{HP}**, **PP_{EH}DT2-TPD_O** and **PP_{EH}DT2-TPD_{HP}** are similar polymers to anthracene-TPD based polymers prepared by Cartwright *et al* [24]. TIPS-functionalized anthracene was used as an electron donor instead of pyrene moiety [24]. **PTATPD(O)**, **PTATPD(DMO)**, and **PTATPD(BP)** were synthesised with optical band gaps of 2.16, 2.14, and 2.12 eV, respectively. The pyrene-TPD based copolymers synthesised in this contribution exhibited lower optical band gaps relative to those prepared by Cartwright *et al* [24]. This can be ascribed to the additional benzene ring in the pyrene moiety which increases the conjugation length, producing higher coplanar polymer structures that increases π - π stacking in the thin film. However, it should be noted that the anthracene-TPD based copolymers did not possess any thiophene spacer units [24]. The authors speculated that the lack of a spacer unit yield large amounts of intramolecular steric repulsion between solubilising groups along polymer chains which reduces the planarity and decreased the electronic conjugation [24]. Work conducted within this contribution suggests that the incorporation of spacer units, thiophene or bithiophene, minimises these intramolecular steric repulsions facilitating the formation of more planar polymer backbones with lower optical band gaps.

Thermal properties

The thermal characteristics of all polymers were investigated *via* thermogravimetric analysis (TGA). The analysis was conducted in an inert nitrogen atmosphere using a heating rate of 10°C min⁻¹. All polymers showed good thermal stabilities with degradation temperatures (5 % weight loss) in excess of 300°C (Figure 2). **PP_{EH}DT-TPD_O**, **PP_{EH}DT-TPD_{HP}**, **PP_{EH}DT2-TPD_O** and **PP_{EH}DT2-TPD_{HP}** showed two decomposition temperatures occurring at 321/516, 320/472,

330/513 and 316/500 °C, respectively. The initial weight-loss corresponds to the loss of the alkyl chains from the pyrene unit. The second decomposition phase can be attributed to degradation of the residual polymer backbone.

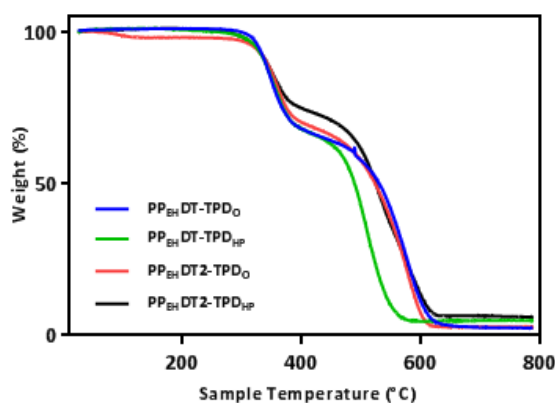


Figure 2: TGA curves of **PP_{EH}DT-TPD_O**, **PP_{EH}DT-TPD_{HP}**, **PP_{EH}DT2-TPD_O** and **PP_{EH}DT2-TPD_{HP}**.

Cyclic Voltammetry

The electrochemical properties of **PP_{EH}DT-TPD_O**, **PP_{EH}DT-TPD_{HP}**, **PP_{EH}DT2-TPD_O** and **PP_{EH}DT2-TPD_{HP}** were analysed using cyclic voltammetry (CV) (Figure 3). The CV measurements were performed under an inert atmosphere of argon on drop-cast polymer thin films with a scan rate of 100 mV s⁻¹. The analysis was conducted in a tetrabutylammonium perchlorate electrolyte solution. The HOMO and LUMO energy levels were calculated from the onset of the oxidation and reduction, respectively. The data is summarised in Table 1. The HOMO/LUMO energy levels of **PP_{EH}DT-TPD_O**, **PP_{EH}DT-TPD_{HP}**, **PP_{EH}DT2-TPD_O** and **PP_{EH}DT2-TPD_{HP}** were estimated to be -5.57/-3.59, -5.55/-3.54, -5.50/-3.52 and -5.46/-3.51 eV, respectively. Polymers that possess a single thiophene spacer unit, **PP_{EH}DT-TPD_O** and **PP_{EH}DT-TPD_{HP}**, displayed deeper HOMO levels relative to those with bithiophene units, **PP_{EH}DT2-TPD_O** and **PP_{EH}DT2-TPD_{HP}**. The shallower HOMO levels of polymers incorporating bithiophene units is a consequence of increased intermolecular charge transfer along the polymer backbone; a finding consistent with the lower optical band gaps of **PP_{EH}DT2-TPD_O** and **PP_{EH}DT2-TPD_{HP}** relative to **PP_{EH}DT-TPD_O** and **PP_{EH}DT-TPD_{HP}**.

Both of **PP_{EH}DT-TPD_{HP}** and **PP_{EH}DT2-TPD_{HP}** which have 4-hexylphenyl substituents on their TPD units have exhibited slightly shallower HOMO levels relative to their analogous polymers

PP_{EH}DT-TPD_O and **PP_{EH}DT2-TPD_O** which have octyl substituents on their TPD units. This can be attributed to the higher electron donating properties of the 4-hexylphenyl substituents when compared to those of octyl chains. This as a result reduces the electron accepting properties of the TPD units which in turn reduces the intramolecular charge transfer between donor and acceptor units along polymer chains and provides slightly shallower HOMO levels as well as LUMO levels that are slightly closer to the vacuum level. The LUMO values of all polymers are higher than the LUMO level of PC₇₀BM (-3.90 eV) [25]. Previous literature has shown that a minimum energy offset of 0.3 eV between the LUMO of the p-type material (conjugated polymer) and the n-type material (fullerene derivative) is enough to facilitate efficient exciton dissociation [10]. All polymers synthesised in this contribution display an energy offset in excess of this 0.3 eV minimum. Therefore, all polymers should display efficient exciton dissociation when fabricated into BHJ photovoltaic devices. The electrochemical band gaps (E_g^{elc}) of **PP_{EH}DT-TPD_O**, **PP_{EH}DT-TPD_{HP}**, **PP_{EH}DT2-TPD_O** and **PP_{EH}DT2-TPD_{HP}** were estimated to be 1.98, 2.01, 1.98 and 1.95 eV, respectively. The E_g^{elc} of the four polymers are comparable to their optical band gaps.

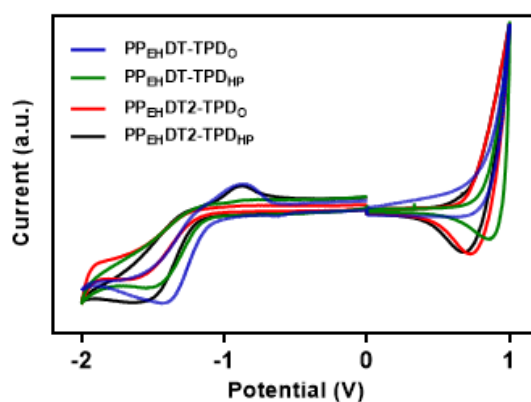


Figure 3: Cyclic voltammograms of **PP_{EH}DT-TPD_O**, **PP_{EH}DT-TPD_{HP}**, **PP_{EH}DT2-TPD_O** and **PP_{EH}DT2-TPD_{HP}**.

Powder X-ray diffraction (PXRD)

The molecular organization and crystallinity of **PP_{EH}DT-TPD_O**, **PP_{EH}DT-TPD_{HP}**, **PP_{EH}DT2-TPD_O** and **PP_{EH}DT2-TPD_{HP}** in solid state were investigated by powder X-ray diffraction (PXRD) (Figure 4). For efficient charge transport and high performance BHJ devices, polymer

chains need to display well-ordered structures in the solid-state [26]. **PP_{EH}DT-TPD_O** and **PP_{EH}DT-TPD_{HP}** both demonstrated small peaks in the small angle region at 2θ values of 3.85° and 3.62° , respectively, which correspond to lamellar stacking distances of 22.9 and 24.4 Å, respectively. **PP_{EH}DT-TPD_O** and **PP_{EH}DT-TPD_{HP}** also display a broad diffuse peak in the wide angle at a 2θ value of 21.0° , which corresponds to a $\pi - \pi$ stacking distance of 4.22 Å. **PP_{EH}DT-TPD_{HP}** exhibited a larger lamellar stacking distance relative to **PP_{EH}DT-TPD_O**, which can be attributed to the sterically bulky 4-hexylphenyl group attached to the TPD moiety. The same phenomenon is observed when comparing **PP_{EH}DT2-TPD_O** and **PP_{EH}DT2-TPD_{HP}**. They also revealed a similar lamellar distance to **PP_{EH}DT-TPD_O** and **PP_{EH}DT-TPD_{HP}** with lamellar stacking distances of 22.9 and 24.4 Å, respectively. Both **PP_{EH}DT2-TPD_O** and **PP_{EH}DT2-TPD_{HP}** displayed a reduced $\pi - \pi$ stacking distance of 3.61 Å relative to **PP_{EH}DT-TPD_O** and **PP_{EH}DT-TPD_{HP}**. The results suggest that polymers containing bithiophene spacer units adopt a more defined arrangement in solid state. A consequence the extended electronic conjugation brought about by the incorporation of bithiophene spacer units.

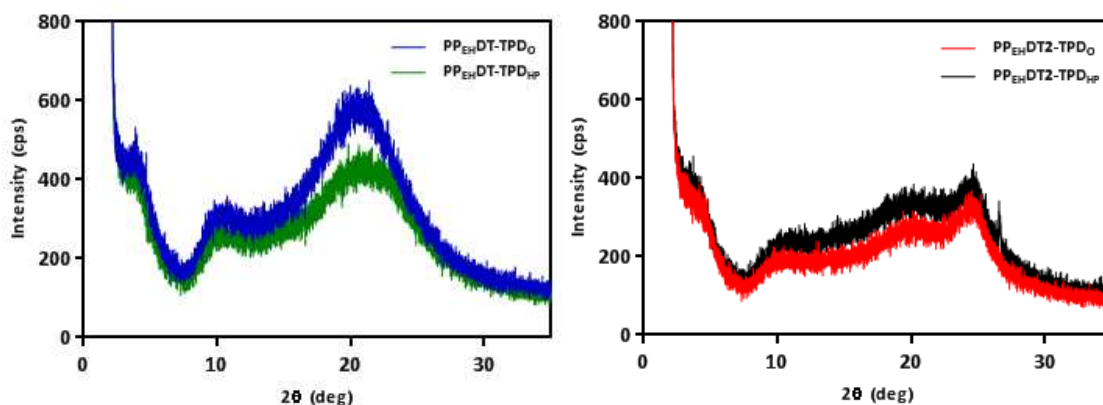


Figure 4: PXR D patterns of **PP_{EH}DT-TPD_O**, **PP_{EH}DT-TPD_{HP}**, **PP_{EH}DT2-TPD_O** and **PP_{EH}DT2-TPD_{HP}**.

Photovoltaic Properties

Preliminary photovoltaic measurements of **PP_{EH}DT-TPD_O**, **PP_{EH}DT-TPD_{HP}**, **PP_{EH}DT2-TPD_O** and **PP_{EH}DT2-TPD_{HP}** were conducted on a series of Glass/ITO/PEDOT:PSS/Polymer:PC₇₀BM/Ca/Al devices using blends of polymer:PC₇₀BM in

weight ratios 1:3. Chlorobenzene was used as the processing solvent. The J - V characteristic curves of the highest performance devices are shown in Figure 5. The results are summarised in Table 2. **PP_{EH}DT-TPD_O** exhibited the highest open circuit voltage in this series of polymers with a V_{oc} value of 0.92 V. This finding is in agreement with the deep HOMO level of the polymer in comparison to the other polymers. However, the power conversion efficiency (PCE) of devices made with **PP_{EH}DT-TPD_O** are only 0.33 % as a result of the poor short-circuit currents observed ($J_{sc} = 0.84 \text{ mA/cm}^2$). A similar PCE of 0.33 % was observed from **PP_{EH}DT-TPD_{HP}** which was also chiefly as a result of a low J_{sc} value (1.09 mA/cm^2).

The photovoltaic results suggest that polymers which incorporate a bithiophene spacer unit display higher efficiencies when compared to those which incorporate single thiophene spacers. Photovoltaic devices fabricated from **PP_{EH}DT2-TPD_O** displayed the highest PCE with a value of 2.06 %. The device demonstrated a FF of 53.07 %, a J_{sc} 4.66 mA/cm^2 and a V_{oc} of 0.83 V. In contrast, **PP_{EH}DT2-TPD_{HP}** displayed a lower PCE (1.46 %) with a FF of 46.74 %, J_{sc} 3.69 mA/cm^2 and a V_{oc} of 0.85 V. It is hypothesised that the higher efficiency of **PP_{EH}DT2-TPD_O**, relative to **PP_{EH}DT2-TPD_{HP}**, as well as to **PPEHDT-TPD_{HP}** and **PP_{EH}DT-TPD_O**, is a result of improved packing of polymer chains in polymer : PC₇₀BM blends. This yields improved charge mobility and extraction of photo-generated charge carriers. However, atomic force microscopy images and external quantum efficiency measurements are required to confirm this hypothesis.

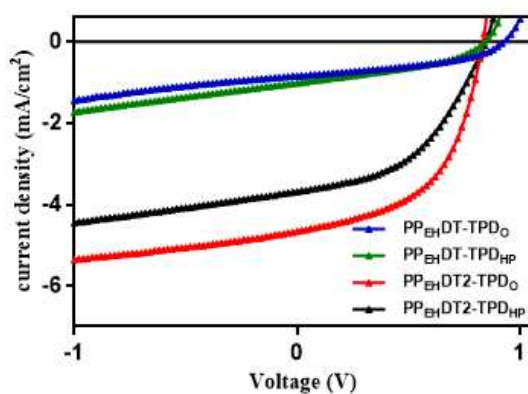


Figure 5: The J - V characteristic curves of **PP_{EH}DT-TPD_O**, **PP_{EH}DT-TPD_{HP}**, **PP_{EH}DT2-TPD_O** and **PP_{EH}DT2-TPD_{HP}**.

Table 2: Device Performance of **PP_{EH}DT-TPD_O**, **PP_{EH}DT-TPD_{HP}**, **PP_{EH}DT2-TPD_O** and **PP_{EH}DT2-TPD_{HP}**.

Polymer	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
PP _{EH} DT-TPD _O	0.84	0.92	42.20	0.33
PP _{EH} DT-TPD _{HP}	1.09	0.84	38.47	0.33
PP _{EH} DT2-TPD _O	4.66	0.83	53.07	2.06
PP _{EH} DT2-TPD _{HP}	3.69	0.85	46.74	1.46

Conclusion

Four novel pyrene-alt-thieno[3,4-c]pyrrole-4,6-dione copolymers were prepared *via* direct arylation polymerisation. Either octyl or 4-hexylphenyl substituents were attached to the TPD moieties along polymer chains in order to evaluate the influence of these substituents on the photophysical, electronic and photovoltaic properties of the resulting polymers. Polymers that possess 4-hexylphenyl substituents, **PP_{EH}DT-TPD_{HP}** and **PP_{EH}DT2-TPD_{HP}**, exhibited lower molecular weights relative to their octyl analogues, **PP_{EH}DT-TPD_O** and **PP_{EH}DT2-TPD_O**. It is speculated that the planar phenyl ring on the 4-hexylphenyl substituents promote backbone planarity resulting in aggregation of polymer chains. This phenomenon prevents the formation of high molecular weight materials. **PP_{EH}DT2-TPD_O** and **PP_{EH}DT2-TPD_{HP}** displayed lower optical band gaps when compared to **PP_{EH}DT-TPD_O** and **PP_{EH}DT-TPD_{HP}**, a consequence of incorporating bithiophene spacers along the polymer backbone which promote improved intramolecular charge transfer. PXRD suggested that polymers with bithiophene units, **PP_{EH}DT2-TPD_O** and **PP_{EH}DT2-TPD_{HP}**, possessed smaller π - π stacking distances relative to polymers with a single thiophene unit, **PP_{EH}DT-TPD_O** and **PP_{EH}DT-TPD_{HP}**. BHJ photovoltaic devices fabricated from **PP_{EH}DT2-TPD_O** and **PP_{EH}DT2-TPD_{HP}** displayed modest efficiencies of 2.06 and 1.46 %, respectively. The higher PCE value of **PP_{EH}DT2-TPD_O** was a result of a higher FF and J_{sc} values. Both **PP_{EH}DT-TPD_{HP}** and **PP_{EH}DT-TPD_O** displayed poor efficiencies with values not exceeding 0.33 %. These preliminary results have shown that the use of pyrene-TPD copolymers display promise as a p-type materials in BHJ photovoltaic cells. Further work is being conducted into the use of these novel polymers in BHJ photovoltaic devices.

Experimental

Materials: All chemicals and solvents 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 inert argon with molecular sieves (3 Å). 5-octyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione [22] and [2,2'-bithiophen]-5-yltrimethylstannane [27] were synthesised according to previous literature procedures.

Measurements: ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV 250 (250 MHz) or Bruker AV 400 (400 MHz) using chloroform-d (CDCl_3) or acetone (acetone-d_6). ^1H -NMR of the polymers were recorded on Bruker Avance III HD 500 (500 MHz) spectrometer at 100°C using 1,2-dideuterotetrachloroethane ($\text{C}_2\text{D}_2\text{Cl}_4$). Coupling constants are given in Hertz (Hz). Elemental analysis was performed on a Perkin Elmer 2400 series 11 CHNS/O analyser. The Schöniger flask combustion method was used to analyse halides. GPC analysis was performed using 1,2,4-trichlorobenzene at 140°C . Polymer samples were spiked with toluene as a reference. UV-visible absorption spectra were recorded using a Hitachi U-2010 Double Beam UV/Visible Spectrophotometer. Polymer solutions were made using chloroform and measured using quartz cuvettes (path length = 1×10^{-2} m). TGA's were obtained using a Perkin Elmer TGA-1 Thermogravimetric Analyser at a scan rate of $10^\circ\text{C min}^{-1}$ under an inert nitrogen atmosphere. Cyclic voltammograms were recorded using a Princeton Applied Research Model 263A Potentiostat/Galvanostat. A three electrode system was used including a Pt disc as the working electrode, platinum wire as the counter electrode and Ag/AgCl as the reference electrode. Measurements were carried out in a solution of tetrabutylammonium perchlorate in acetonitrile (0.1 mol dm^{-3}) on polymer films that were prepared by drop casting polymer solution. Ferrocene was employed as the reference redox system; in accordance with IUPAC's recommendations. The energy level of Fc/Fc^+ was assumed at -4.8 eV to vacuum. The half-wave potential of Fc/Fc^+ redox couple was found to be 0.08 V vs. Ag/Ag^+ reference electrode. Powder X-ray diffraction (PXRD) samples were recorded on a Bruker D8 advance diffractometer with a $\text{CuK}\alpha$ radiation source (1.54 \AA , rated as 1.6 kW). The scanning angle was conducted over the range $2\text{-}40^\circ$.

Fabrication and testing of BHJ polymer solar cells: The polymers and PC₇₀BM were dissolved in chlorobenzene, and were then put on a hot plate held at 70 °C overnight with stirring to allow dissolution. The polymer:fullerene blend ratios were 1:3. Photovoltaic devices were fabricated onto pre-patterned ITO glass substrates (20 ohms per square) that were supplied by Ossila Limited. The ITO/glass substrates were first cleaned by sonication in dilute NaOH followed by IPA. A 30 nm thick PEDOT:PSS layer was spin-coated onto the ITO/glass substrates. These were then transferred to a hot-plate held at 120 °C for 10 minutes before being transferred to a nitrogen glove-box. All active layers were spin cast onto the glass/ITO/PEDOT:PSS substrate. The devices were then transferred into a thermal evaporator for deposition of a cathode (5 nm of calcium followed by a 100 nm of aluminium evaporated at a base pressure of $\sim 10^{-7}$ mbar). The cathode was deposited through a shadow-mask producing a series of independent pixels. Devices were encapsulated using a glass slide and epoxy glue before testing. PCEs were determined using a Newport 92251A-1000 AM 1.5 solar simulator. An NREL calibrated silicon cell was used to calibrate the power output to 100 mW cm⁻² at 25 °C. An aperture mask having an area of 2.06 mm² was placed over devices to define the test area.

5-(4-Hexylphenyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (M2):

4-Hexylaniline (0.66 g, 0.72 ml, 3.73 mmol) was added dropwise to a solution of thieno[3,4-c]furan-1,3-dione (0.5 g, 3.24 mmol), in anhydrous THF (5 mL) under inert argon atmosphere. The mixture was left to stir for 3 h at 50 °C. Upon completion, the mixture was cooled to room temperature and thionyl chloride (4.1 g, 2.5 ml, 34 mmol) was then added dropwise. The reaction mixture was stirred at 50 °C overnight. Upon completion of the reaction, the crude material was precipitated in a H₂O:CH₃OH mixture (60 mL: 30 mL). The crude material was filtered off and purified *via* silica gel column chromatography using CHCl₃ as the eluent. to afford the monomer as a white powder (0.80 g, 2.55 mmol, 79 %). *M.p.* = 188 – 192 °C. ¹H NMR (400 MHz, CDCl₃) (δ_{H} /ppm): 7.97 (s, 2H), 7.31 (dd, *J* = 13.47 and 8.06 Hz, 4H), 2.66 (t, *J* = 7.74 Hz, 2H), 1.70-1.61 (br, 4H), 1.43–1.30 (br, 4H), 0.91 (t, *J* = 6.88 Hz, 3H). ¹³C NMR (400 MHz, CDCl₃) (δ_{C} /ppm): 161.73, 143.40, 136.25, 129.36, 129.12, 126.50, 35.71, 31.73, 31.30, 29.04, 22.62, 14.3. GC-MS: mass calcd. for C₁₈H₁₉NO₂S 313.11; Found 313.1. Elem. Anal. Calcd. for C₁₈H₁₉NO₂S: C, 68.98; H, 6.11; N, 4.47; S, 10.23. Found: C, 68.84; H, 6.09; N, 4.38 S, 10.00.

2,7-Di(thien-2-yl)-4,5,9,10-tetrakis(2-ethylhexyloxy)-pyrene (2)

2,7-Dibromo-4,5,9,10-tetrakis(2-ethylhexyloxy)-pyrene (**1**) (600 mg, 0.687 mmol), tri-*o*-tolylphosphine (67 mg, 0.02 mmol) and Pd₂dba₃ (25 mg, 0.03 mmol) were placed in a one neck round bottom flask and placed under an inert argon atmosphere. Anhydrous toluene (15 mL) and 2-tributylstannylthiophene (0.57 ml, 1.78 mmol) were added to the reaction mixture. The reaction mixture was refluxed for 16 hours. The solvent was removed and the crude product was purified by silica gel column chromatography using petroleum:CHCl₃ (5:1) as the eluent. The title product was collected as a yellow oil (0.54 g, 0.61 mmol, 89 %). ¹H NMR (400 MHz, CDCl₃) (δ_H/ppm): 8.71 (s, 4H), 7.65 (dd, *J* = 3.60 and 1.09 Hz, 2H), 7.42 (dd, *J* = 5.09 and 1.03 Hz, 2H), 7.22 (dd, *J* = 5.03 and 3.61 Hz, 2H), 4.27 (d, *J* = 5.08 Hz, 8H), 2.06-1.95 (m, 4H), 1.88-1.37 (m, 32H), 1.09 (t, *J* = 7.48 Hz, 12H), 0.95 (t, *J* = 7.08 Hz, 12H). ¹³C NMR (400 MHz, CDCl₃) (δ_C/ppm): 145.57, 144.68, 132.10, 129.21, 128.31, 125.38, 123.55, 120.17, 116.28, 40.92, 30.81, 29.41, 23.99, 23.26, 14.18, 11.35. GC-MS: mass calcd. for C₅₆H₇₈O₄S₂ 878.53; Found 878.4. Elem. Anal. Calcd. for C₅₆H₇₈O₄S₂: C, 76.49; H, 8.94; S, 7.01. Found: C, 76.42; H, 8.83; S, 7.01.

2,7-Bis(5-bromo-thien-2-yl)-4,5,9,10-tetrakis(2-ethylhexyloxy)-pyrene (M3)

2,7-Di(thien-2-yl)-4,5,9,10-tetrakis(2-ethylhexyloxy)-pyrene (**2**) (513 mg, 0.584 mmol) was dissolved in glacial acetic acid (15 ml) and CHCl₃ (15 ml). N-Bromosuccinimide (NBS) (208 mg, 1.17 mmol) was added and the reaction mixture was left to stir in the dark, at room temperature, for 20 hours. Upon completion of the reaction, the solvent was removed *in vacuo* and the crude material was purified *via* silica gel column chromatography using petroleum ether:CHCl₃ (10:3) as the eluent. The title product (**M3**) was obtained as a yellow solid (511 mg, 0.50 mmol, 84 %). *M.p.* = 69 – 73 °C. ¹H-NMR (400 MHz, CDCl₃) (δ_H/ppm): 8.60 (s, 4H), 7.37 (d, *J* = 3.08 Hz, 2H), 7.17 (d, *J* = 3.79 Hz, 2H), 4.25 (d, *J* = 5.92 Hz, 8H), 2.04-1.93 (m, 4H), 1.85-1.37 (m, 32H), 1.08 (t, *J* = 7.56 Hz, 12H), 0.96 (t, *J* = 7.07 Hz, 12H). ¹³C NMR (400 MHz, CDCl₃) (δ_C/ppm): 146.96, 144.65, 131.40, 131.16, 129.34, 123.68, 120.17, 115.93, 112.04, 40.91, 30.84, 29.38, 23.97, 23.25, 14.14, 11.32. GC-MS mass calcd. for C₅₆H₇₆Br₂O₄S 1036.35; Found 1036.20. Elem. Anal. Calcd. for C₅₆H₇₆Br₂O₄S₂: C, 64.85; H, 7.39; Br, 15.41; S, 5.92. Found: C, 64.40; H, 7.24; Br, 15.79; S, 5.92.

2,7-Di(2,2'-bithiophen-5-yl)-4,5,9,10-tetrakis(2-ethylhexyloxy)-pyrene (3)

2,7-Dibromo-4,5,9,10-tetrakis(2-ethylhexyloxy)-pyrene (**1**) (454 mg, 0.52 mmol), tri-*o*-tolylphosphine (67 mg, 0.02 mmol) and Pd₂dba₃ (25 mg, 0.03 mmol) were placed in a one neck round bottom flask and placed under an inert argon atmosphere. The mixture was dissolved in anhydrous toluene (15 mL) and 2,2'-bithiophen-5-yltrimethylstannane (444 mg, 1.35 mmol) was added. The reaction mixture was refluxed overnight. Upon completion, the solvent was removed *in vacuo* and the crude product was purified by silica gel column chromatography using petroleum ether:CHCl₃ (5:1) as the eluent. The title product was obtained as a yellow oil (382 mg, 0.36 mmol, 71 %). ¹H NMR (400 MHz, CDCl₃) (δ_H/ppm): 8.70 (s, 4H), 7.56 (d, *J* = 3.82 Hz, 2H), 7.30 (dd, *J* = 4.56 and 3.29 Hz, 6H), 7.10 (dd, *J* = 5.11 and 3.62 Hz, 2H), 4.27 (d, *J* = 5.08 Hz, 8H), 2.06-1.95 (m, 4H), 1.88-1.37 (m, 32H), 1.09 (t, *J* = 7.48 Hz, 12H), 0.95 (t, *J* = 7.08 Hz, 12H). ¹³C NMR (CDCl₃) (δ_C/ppm): 144.68, 144.24, 137.60, 137.30, 131.77, 129.26, 127.92, 124.93, 124.47, 124.20, 123.66, 120.20, 115.94, 40.93, 30.90, 29.44, 24.00, 23.32, 14.22, 11.40. GC-MS: mass calcd. for C₆₄H₈₂O₄S₄ 1042.5; Found 1042.6. Elem. Anal. Calcd. for C₆₄H₈₂O₄S₄: C, 73.66; H, 7.92; S, 12.29. Found: C, 73.57; H, 7.82; S, 10.25.

2,7-Bis-(5'-bromo-[2,2']bithiophenyl-5-yl)-4,5,9,10-tetrakis(2-ethylhexyloxy)-pyrene (M4):

2,7-Di(2,2'-bithiophen-5-yl)-4,5,9,10-tetrakis(2-ethylhexyloxy)-pyrene (**3**) (170 mg, 0.14 mmol) was dissolved in anhydrous chlorobenzene (10 mL). NBS (58.04 mg, 3.26 mmol) was added and the reaction mixture was left to stir in the dark, overnight at 50°C. Once this time had elapsed, the temperature was raised to 100°C and the reaction was stirred for a further 15 minutes. The solvent was removed *in vacuo* and the crude product was dissolved in diethyl ether (5 mL) and precipitated in methanol (25 mL) and separated by filtration to produce the title product, **M4**, as a yellow solid (185 mg, 0.13 mmol, 95 %). *M.p.* = 109 – 112 °C. ¹H NMR (400 MHz, CDCl₃) (δ_H/ppm): 8.67 (s, 4H), 7.54 (d, *J* = 3.78 Hz, 2H), 7.22 (d, *J* = 3.73 Hz, 2H), 7.04 (dd, *J* = 9.12 and 3.87 Hz, 4H), 4.27 (d, *J* = 5.08 Hz, 8H), 2.06-1.95 (m, 4H), 1.88-1.37 (m, 32H), 1.09 (t, *J* = 7.48 Hz, 12H), 0.95 (t, *J* = 7.08 Hz, 12H). ¹³C NMR (CDCl₃) (δ_C/ppm): 144.74, 144.67, 139.04, 136.17, 131.57, 130.73, 129.30, 125.16, 124.23, 123.67, 120.22, 116.00, 111.04, 40.92, 30.90, 29.44, 24.00, 23.333, 14.22, 11.40. GC-MS: mass calcd. for C₆₄H₈₀Br₂O₄S₄ 1200.3; Found 1200.4. Elem. Anal. Calcd. for C₆₄H₈₀Br₂O₄S₄: C, 63.98; H, 6.71; Br, 13.30; S, 10.68. Found: C, 62.16; H, 6.60; Br, 13.41; S, 9.85.

Poly(4,5,9,10-tetrakis(2-ethylhexyloxy)-2,7-pyrene-alt-1,3-di(thiophene)-(5-octyl-thieno[3,4,c]pyrrole-4,6-dione)) (PP_{EHDT}-TPD_O)

A mixture of **M3** (170 mg, 0.16 mmol), 5-octyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (**M1**) (43.48 mg, 0.164 mmol), PdCl₂(MeCN)₂ (1.3 mg, 5.00 μmol), P(C₆H₄-o-OMe)₃ (1.8 mg, 5.00 μmol), Cs₂CO₃ (160 mg, 0.5 mmol) and PivOH (16.7 mg, 0.16 mmol) were put in a Schlenk tube and placed under an inert argon atmosphere. Anhydrous THF (1 mL) was added to the mixture. The reaction mixture was stirred at room temperature for 30 minutes and then at 100°C for 48 h. The solution was cooled down to room temperature and washed with water (3 x 150 mL). The organic phases were combined, concentrated *in vacuo* and precipitated in methanol. The resulting solid was collected *via* filtration and subject to Soxhlet extraction with methanol, acetone, hexane, toluene and chloroform. The chloroform fraction was concentrated *in vacuo* and precipitated in methanol. The solid was filtered by a membrane filter and the polymer was obtained as a dark red solid (44 mg, 0.038 mmol, 24 %). GPC chloroform fraction: $M_n = 19,700$ Da; $M_w = 38,400$ Da; PDI = 1.95. ¹H NMR (500 MHz, C₂D₂Cl₄, 100°C) (δ_H/ppm): 8.75 (s, 4H), 8.60 (d, 2H), 8.30 (d, 2H), 4.3 (d, 8H), 3.80 (t, 2H), 2.10-1.20 (br, 48H), 1.20-0.85 (br, 27H). Elem. Anal. Calcd. for C₇₀H₉₃NO₆S₅: C, 73.71; H, 8.22; N, 1.23; S, 8.43; Found: C, 73.32; H, 8.56; N, 1.00; S, 7.37.

Poly(4,5,9,10-tetrakis(2-ethylhexyloxy)-2,7-pyrene-alt-1,3-di(thiophene)-(5-(4-hexylphenyl)-thieno[3,4,c]pyrrole-4,6-dione)) (PP_{EHDT}-TPD_{HP})

PP_{EHDT}-TPD_{HP} was synthesised according to the polymerisation method outlined for **PP_{EHDT}-TPD_O**. The polymerisation reaction was left running for 48 h and the product was obtained as a dark red solid (28 mg, 0.023 mmol, 18 %). GPC toluene fraction: $M_n = 5,700$; $M_w = 8700$; PDI = 1.53. ¹H NMR (500 MHz, C₂D₂Cl₄, 100°C) (δ_H/ppm): 8.80-8.65 (br, 4H), 8.60 (d, 2H), 8.30 (d, 2H), 7.45-7.30 (q, 4H), 4.30 (d, 8H), 2.66 (t, 2H), 2.10-1.93 (br, 4H), 1.90-1.20 (br, 40H), 1.20-0.85 (br, 27H). Elem. Anal. Calcd. for C₇₄H₉₃NO₆S₅: C, 74.77; H, 7.89; N, 1.18; S, 8.09. Found: C, 75.08; H, 11.00; N, 0.80; S, 6.90.

Poly(4,5,9,10-tetrakis(2-ethylhexyloxy)-2,7-pyrene-alt-1,3-bis(2,2'-bithiophene)-(5-octyl-thieno[3,4,c]pyrrole-4,6-dione)) (PP_{EHDT2}-TPD_O)

PP_{EH}DT2-TPD_O was synthesised according to the polymerisation method outlined for **PP_{EH}DT-TPD_O**. The polymerisation reaction was left running for only 2 h as a result of formation of polymer precipitates at an early stage of the reaction. The polymer was obtained as a dark red solid (42 mg, 0.032 mmol, 24 %). GPC chloroform fraction: $M_n = 9,100$, $M_w = 12,700$, PDI = 1.40. ¹H NMR (500 MHz, C₂D₂Cl₄, 100°C) (δ_H /ppm): 8.70-8.55(br, 4H), 7.46 (d, 2H), 7.35 (dd, 2H), 7.20 (dd, 4H), 4.3 (d, 8H), 3.70 (t, 2H), 2.20-0.70 (br, 75H). Elem. Anal. Calcd. for C₇₈H₉₇NO₆S₅: C, 71.79; H, 7.49; N, 1.07; S, 12.29. Found: C, 67.00; H, 7.00; N, 1.00; S, 11.10.

Poly(4,5,9,10-tetrakis(2-ethylhexyloxy)-2,7-pyrene-alt-1,3-bis(2,2'-bithiophene)-(5-(4-hexylphenyl)-thieno[3,4,c]pyrrole-4,6-dione)) (PP_{EH}DT2-TPD_{HP})

PP_{EH}DT2-TPD_{HP} was synthesised according to the polymerisation method outlined for **PP_{EH}DT-TPD_O**. The polymerisation reaction was left running for 5 h as a result of formation of polymer precipitates at an early stage of the reaction. The polymer was obtained as a black solid (55 mg, 0.040 mmol, 44 %). GPC chloroform fraction: $M_n = 5,500$, $M_w = 9,200$, PDI = 1.66. ¹H NMR (500 MHz, C₂D₂Cl₄, 100°C) (δ_H /ppm): 8.80-8.65 (br, 4H), 8.60 (d, 2H), 8.30 (d, 2H), 7.45-7.30 (q, 4H), 4.30 (d, 8H), 2.66 (t, 2H), 2.10-1.93 (br, 4H), 1.90-1.20 (br, 44H), 1.20-0.85 (br, 27H). Elem. Anal. Calcd. for C₈₂H₉₇NO₆S₅: C, 72.79; H, 7.23; N, 1.04; S, 11.85. Found: C, 69.00; H, 6.81; N, 0.90; S, 10.42.

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References

- [1] Q. Ye, C. Chi, Conjugated polymers for organic solar cells, Solar Cells—New Aspects and Solutions, Kosyachenko LA (ed.). InTech: Rijeka (2011) 453-476.
- [2] 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(57) (2015) 46386-46394.

- [3] G. Li, R. Zhu, Y. Yang, Polymer solar cells, *Nat. Photonics* 6(3) (2012) 153-161.
- [4] T.M. Clarke, J.R. Durrant, Charge photogeneration in organic solar cells, *Chem. Rev.* 110(11) (2010) 6736-6767.
- [5] S.A. Gevorgyan, M.V. Madsen, B. Roth, M. Corazza, M. Hösel, R.R. Søndergaard, M. Jørgensen, F.C. Krebs, Lifetime of organic photovoltaics: status and predictions, *Adv. Energy Mater.* 6(2) (2016) 1-17.
- [6] T. Ameri, P. Khoram, J. Min, C.J. Brabec, Organic ternary solar cells: a review, *Adv. Mater.* 25(31) (2013) 4245-4266.
- [7] K. Wang, M. Wang, Direct Arylation Polymerization: A Green, Streamlining Synthetic Approach to π -conjugated Polymers, *Curr. Org. Chem.* 17(9) (2013) 999-1012.
- [8] P.-O. Morin, T. Bura, B. Sun, S.I. Gorelsky, Y. Li, M. Leclerc, Conjugated Polymers à la Carte from Time-Controlled Direct (Hetero) Arylation Polymerization, *ACS Macro Lett.* 4(1) (2014) 21-24.
- [9] E. Iizuka, M. Wakioka, F. Ozawa, Mixed-Ligand Approach to Palladium-Catalyzed Direct Arylation Polymerization: Synthesis of Donor–Acceptor Polymers with Dithienosilole (DTS) and Thienopyrroledione (TPD) Units, *Macromolecules* 48(9) (2015) 2989-2993.
- [10] H. Zhou, L. Yang, W. You, Rational design of high performance conjugated polymers for organic solar cells, *Macromolecules* 45(2) (2012) 607-632.
- [11] P. Berrouard, S.p. Dufresne, A. Pron, J. Veilleux, M. Leclerc, Low-cost synthesis and physical characterization of thieno [3, 4-c] pyrrole-4, 6-dione-based polymers, *J. Org. Chem.* 77(18) (2012) 8167-8173.
- [12] J.W. Rumer, C.K. Hor, I. Meager, C.P. Yau, Z. Huang, C.B. Nielsen, S.E. Watkins, H. Bronstein, I. McCulloch, Alkyl side-chain branching point effects in thieno [3, 4-c] pyrrole-4, 6-dione copolymers, *J. Org. Semicond.* 1(1) (2013) 30-35.
- [13] L. Lu, T. Zheng, Q. Wu, A.M. Schneider, D. Zhao, L. Yu, Recent advances in bulk heterojunction polymer solar cells, *Chem. Rev.* 115(23) (2015) 12666-12731.
- [14] T.Y. Chu, J. Lu, S. Beaupré, Y. Zhang, J.R. Pouliot, J. Zhou, A. Najari, M. Leclerc, Y. Tao, Effects of the Molecular Weight and the Side-Chain Length on the Photovoltaic Performance of Dithienosilole/Thienopyrroledione Copolymers, *Adv. Funct. Mater.* 22(11) (2012) 2345-2351.
- [15] C.m. Cabanetos, A. El Labban, J.A. Bartelt, J.D. Douglas, W.R. Mateker, J.M. Fréchet, M.D. McGehee, P.M. Beaujuge, Linear side chains in benzo [1, 2-b: 4, 5-b'] dithiophene–thieno

- [3, 4-c] pyrrole-4, 6-dione polymers direct self-assembly and solar cell performance, *J. Am. Chem. Soc.* 135(12) (2013) 4656-4659.
- [16] L. Zöphel, D. Beckmann, V. Enkelmann, D. Chercka, R. Rieger, K. Müllen, Asymmetric pyrene derivatives for organic field-effect transistors, *Chem. Commun.* 47(24) (2011) 6960-6962.
- [17] S.-Y. Liu, W.-Q. Liu, J.-Q. Xu, C.-C. Fan, W.-F. Fu, J. Ling, J.-Y. Wu, M.-M. Shi, A.K.-Y. Jen, H.-Z. Chen, Pyrene and diketopyrrolopyrrole-based oligomers synthesized via direct arylation for OSC applications, *ACS appl. mater. interfaces* 6(9) (2014) 6765-6775.
- [18] M.S. Almeataq, H. Yi, S. Al-Faifi, A.A. 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(22) (2013) 2252-2254.
- [19] M. Zhao, K. Hashimoto, K. Tajima, Synthesis of copolymer based on naphthalene diimide connected with a non-conjugated flexible linker, *Synth. Met.* 175 (2013) 9-14.
- [20] T.M. Figueira-Duarte, K. Müllen, Pyrene-based materials for organic electronics, *Chem. Rev.* 111(11) (2011) 7260-7314.
- [21] N. Wang, X. Bao, Y. Yan, D. Ouyang, M. Sun, V. 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(22) (2014) 3198-3204.
- [22] J. Warnan, C. Cabanetos, A.E. Labban, M.R. Hansen, C. Tassone, M.F. Toney, P.M. Beaujuge, Ordering Effects in Benzo [1, 2-b: 4, 5-b'] difuran-thieno [3, 4-c] pyrrole-4, 6-dione Polymers with > 7% Solar Cell Efficiency, *Adv. Mater.* 26(25) (2014) 4357-4362.
- [23] M. Wakioka, N. Ichihara, Y. Kitano, F. Ozawa, A highly efficient catalyst for the synthesis of alternating copolymers with thieno [3, 4-c] pyrrole-4, 6-dione units via direct arylation polymerization, *Macromolecules* 47(2) (2014) 626-631.
- [24] L. Cartwright, T.J. Neal, N.J. Rutland, A. Iraqi, Anthracene-thieno [3, 4-c] pyrrole-4, 6-dione based donor–acceptor conjugated copolymers for applications in optoelectronic devices, *Polym. Adv. Technol.* 27(4) (2016) 525-531.
- [25] Y. He, J. You, L. Dou, C.-C. Chen, E. Richard, K.C. Cha, Y. Wu, G. Li, Y. Yang, High performance low band gap polymer solar cells with a non-conventional acceptor, *Chem. Commun.* 48(61) (2012) 7616-7618.

[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(9) (2013) 2773-2782.

[27] K. Parab, K. Venkatasubbaiah, F. Jäkle, Luminescent triarylborane-functionalized polystyrene: synthesis, photophysical characterization, and anion-binding studies, *J. Am. Chem. Soc.* 128(39) (2006) 12879-12885.