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Synthesis, Optical and Electrochemical Properties of Naphthothiadiazole-Based Donor-Acceptor Polymers and Their Photovoltaic Applications

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The preparation and investigation of the physical properties of a series of low energy band gap alternating donor-acceptor polymers comprising 4,9-linked di-2-thienyl-2,1,3-naphthothiadiazole units and carbazole, anthracene, or fluorene units with alkoxy or alkyl substituents are presented. The influence of replacing 2,1,3-benzothiadiazole (BT) with 2,1,3-naphthothiadiazole (NT) in this series of conjugated polymers is investigated, and the optical, electrochemical with photovoltaic properties of these three polymers have examined. Photovoltaic devices with an active layer composed of thin films (65-75 nm) of polymer/$PC_{71}BM$ blends spin-coated from chlorobenzene or a mixture of carbon disulfide and acetone were analyzed. Power conversion efficiencies (PCEs) ranging from 1.74 to 2.17% are obtained with these NT-based polymer systems of PCDTNT, showing the best performance among this series of polymers.

Keywords: conjugated polymers, optoelectronic, optical properties, 2,1,3-naphthiadiazole (NT), photovoltaic properties.

1. INTRODUCTION

Currently, many studies have focused on developing polymer-based solar cells in view of their potential advantages, which include lightweight, increased flexibility, and low production costs. Great progress has been made in the field of bulk heterojunction (BHJ) solar cells [1-5]. The design of efficient polymers for use in this area requires optimal electronic and physical properties of these materials, including the energy levels of their HOMO and LUMO levels, the extent of their absorption of sunlight, as well as the optimization of the nanoscale morphology of blends of these electron-donating polymers with fullerene derivatives in order to achieve good charge extraction and efficient exciton dissociation [2, 6, 7]. The bandgap and the energy levels of frontier orbitals of the conjugated polymers used in this area have to be optimized in order to obtain good efficiencies in PSCs [8, 9]. The use of donor-acceptor alternating conjugated polymers enables the fine-tuning and adjustment of the bandgap and energy levels of these materials through control of intramolecular charge transfer along polymer chains [10-12].

The benzothiadiazole (BT) repeat unit is an excellent acceptor unit in donor-acceptor conjugated polymers, resulting in its strong electron-accepting ability. Pairing a strong electron-accepting unit such as benzothiadiazole with an alternating electron-donating unit allows to obtained low bandgap polymers, having promising photovoltaic properties [2, 13-15]. The use of even stronger electron acceptors is an attractive strategy to develop more efficient polymers for solar cell applications using fullerene-derivatives as electron acceptors. However, it should be noted to avoid lowering the LUMO energy level of the resulting polymer below −3.9 eV, as this could result in inefficient exciton dissociation [16-19]. There are many approaches to prepare conjugated polymers with narrow optical band gaps in order to broaden their absorption spectrum and thus more efficiently harvest sunlight. One such method is the replacement of benzothiadiazole (BT) units with naphthothiadiazole (NT). One report showed that replacing 2,1,3-benzothiadiazole (BT) with 2,1,3-naphthothiadiazole (NT) in poly(2,7-carbazole-alt-4,7-dithienyl-2,1,3-naphthothiadiazole) PCDTBT reduces the optical bandgap of the resulting polymer (PCDTNT)from 1.88 eV to 1.71 eV. It also red-shifts its λ_{max} position considerably (30 nm) in relation to its benzothiadiazole counterpart. Furthermore, the new naphthothiadiazole polymer possessed a high solution-processability and had suitable HOMO and LUMO energy levels for application as an electron-donor material in an organic photovoltaic (OPV) device. In spite of a high open-circuit voltage (V_{OC} = 0.81 V), the photovoltaic performance of PCDTNT in solar cells along with PCBM as an acceptor was unfortunately low as a result of poor device fill-factor (FF) [20].

Promising photovoltaic results have demonstrated using other classes of alternating copolymers comprising benzothiadiazole as the electron-accepting unit along with anthracene (PPATBT) or fluorene (PFDTBT), as the electron-donating units despite reduced solubilities and reduced molar masses of latter materials. Here, power conversion efficiencies (PCEs) of 1.93% and 5.41% were obtained respectively for PPATBT [21], and PFDTBT [22].

In this work, we present the preparation and characterization of low bandgap copolymers containing alternating naphthothiadiazole as acceptor units and 2,6-linked anthracene, or 2,7-fluorene repeat units flanked by thienyl units as the donor units. The electronic, photophysical, and photovoltaic properties of the polymers are analysed and compared to those of the corresponding donor-acceptor polymer poly(2,7-carbazole-alt-4,7-dithienyl-2,1,3-naphthothiadiazole) (PCDTNT).

2. EXPERIMENTAL

2.1 Materials

4,9-Bis(2-bromothienyl-5-yl)-2,1,3-naphthothiadiazole (4) was prepared according to previous literature procedures.[20]2,3-Diaminonaphthalene and 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (7) were purchased from Sigma Aldrich and used as received. 2,6-Bis-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-9,10-bis(4-(dodecyloxy) phenyl) anthracene (5) and 9-(heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (6) were prepared according to a modified procedure by Zhang [23] and Blouin [24] respectively. All chemicals and solvents, with the exception of those stated below, were of reagent grade quality, purchased commercially, and used without further purification unless otherwise stated. Tetrahydrofuran (THF) was distilled and dried over sodium benzophenone under an inert nitrogen atmosphere. Toluene was dried and distilled over sodium under an inert atmosphere, then stored over molecular sieves (3 Å).

2.2 Measurements

^{1}H nuclear magnetic resonance (NMR) spectra were recorded using Bruker Avance 400 (MHz) NMR spectrometers at ambient temperature using chloroform-d ($CDCl_3$) with tetramethylsilane (TMS) as an internal standard. The NMR shifts are described by using the following abbreviations: singlet (s), doublet (d), double doublet (dd), triplet (t), multiple (m), and broad (br). Moreover, coupling constants (*J*) are calculated in Hertz (Hz) and chemical shifts in part per million (ppm). CHN analyses were performed on the Perkin Elmer 2400 CHN Elemental Analyzer. In addition, the flask combustion method was used for the analysis of halides and sulfur. Mass spectra of monomers were recorded on a Perkin Elmer Turbomass Mass Spectrometer equipped with auto system XL GC. It has the ability to operate in both chemical ionization (CI) and electron ionization (EI) modes. GPC measurements were conducted on polymer solutions using chloroform as eluents at a flow rate of 1 cm^3 $minute^{-1}$. The system was calibrated against a series of narrow polystyrene standards (polymer laboratories) using a 1037 Differential Refractive Detector. UV-visible absorption spectra were performed using a Hitachi U-2010 Double Beam UV/Visible Spectrophotometer. Solution samples of polymers in $CHCl_3$ were measured by using rectangular quartz cuvettes (light path = 10 mm). Thin films of the polymers were prepared for UV-visible absorption spectra measurements by dip-coating quartz plates into approximately 1 mg cm^{-3} solutions in chloroform, then drying at room temperature. Measurements were performed under ordinary laboratory conditions. Cyclic voltammetry (CV) measurements were made using a Princeton Applied Research Model 263A Potentiostat/Galvanostat. The distributions of HOMO and LUMO levels of the compounds have determined by means of electrochemical cyclic voltammetry. The electrochemical data was conducted under an inert pure argon atmosphere in a standard three-electrode cell system using (0.1 M) tetrabutylammonium perchlorate in dry acetonitrile as the electrolyte solution. The electrode system used consists of a platinum (Pt) disk as the working electrode, Pt wire as a counter electrode, and an Ag/Ag^+ (0.01 M in dry acetonitrile) reference electrode containing silver wire inside the capillary electrode. Polymer thin films were formed by drop-casting (1.0 mg.cm^{-3}) in chloroform (HPLC graded) onto the Pt disk, and then dried in air. All three electrodes were immersed in the electrolyte solution. The experiments were calibrated with ferrocene, a reference redox system according to IUPACs recommendation [25].

2.3 Poly (9,10-bis (4-dodecyloxy) phenyl) anthracene-2,6-diyl-alt-(4,9-dithiophen-2-yl)-2,1,3-naphthothiadiazole-5,5-diyl) PPATNT

To a solution of **4** (0.186 g, 0.367 mmol) and **5** (0.35 g, 0.367 mmol) in toluene (9 ml) was added under argon a degassed aqueous solution of tetraethylammonium hydroxide (2.1 ml, 20% w/w, 2.85 mmol) and the mixture was degassed under an inert atmosphere. $Pd(OAc)_2$ (6.3 mg, 0.028 mmol) and *tri-o*-tolyl phosphine (17.2 mg, 0.056 mmol) were added to the mixture then the reaction system was degassed and heated up to 90 °C for 24 hours. After cooling to room temperature, 1-bromobenzene (0.15 g, 0.95 mmol) was added to end-cap the polymer, and the solution was heated to reflux for 1 hour before cooling down to room temperature. Phenyl boronic acid (0.15 g, 1.23 mmol) was added to the reaction mixture, and it was heated to 90 °C for 3 hours. After cooling the mixture to room temperature, the organic content was dissolved in $CHCl_3$ (200 ml) and added to an ammonium hydroxide solution (28 % in H_2O, 50 ml), followed by vigorous stirring overnight. The organic layer was separated and washed with distilled water then concentrated to about 20 ml and poured slowly into degassed methanol (300 ml) and stirred overnight. The resulting precipitate was filtered off and purified by Soxhlet extraction with the following solvents in order: methanol, acetone, hexane, toluene, chloroform, and chlorobenzene. The toluene fraction was concentrated to about 50 ml *in vacuo* and then separately poured into degassed methanol (200 ml). After stirring overnight, the precipitates were collected separately by membrane filtration and dried *in vacuo* to afford dark red-colored powders. Toluene fraction (80 mg, 32 % yield) GPC in $CHCl_3$ at 40 °C M_n =10900, M_w =23100, PDI =2.1. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.42 (br, 2H), 8.12, (br, 2H), 7.85-7.73 (br, 4H), 7.56-7.37 (br, 8H), 7.22-7.13 (br, 6H), 4.18-4.12 (br, 4H), 2.37 (s, 1H), 2.19 (s, 1H), 1.95-1.82 (br, 4H), 1.71-1.19 (br, 36H), 0.88 (t, J= 6.0, 6H). Anal. calcd for $C_{70}H_{78}N_2O_2S_3$: C, 78.17; H, 7.31; N, 2.60; S, 8.94. Found: C, 77.30; H, 6.89; N, 2.50; S, 8.10.

2.4. Poly(N-9-hepta-decanyl-2,7-carbazole-alt-5,5-(4,9-di-2-thienyl-2,1,3-naphthothiadiazole) PCDTNT.

To a mixture of monomer **4** (0.186 g, 0.367 mmol) and **6** (0.241 g, 0.367mmol) in THF (9 ml) was added a degassed aqueous solution of sodium bicarbonate (2.1 ml, 1.36 M, 2.85 mmol), and the mixture was degassed again. To this solution were added *tri-o*-tolyl phosphine (17.2 mg, 0.056 mmol) and $Pd(OAc)_2$ (6.3 mg, 0.028 mmol), and the mixture was degassed and heated to 90 °C for 48 hours. The mixture was cooled to room temperature, then 1-bromobenzene (0.15 g, 0.95 mmol) was added, degassed, and heated at 90 °C for 1 hour. The mixture was cooled to room temperature, and phenylboronic acid (0.15 g, 1.23 mmol) was added, and the mixture heated to reflux for 3 hours. The mixture was cooled down to room temperature and then added to $CHCl_3$ (200 ml). An ammonium hydroxide solution (28 % in H_2O, 50 ml) was then added to the mixture and stirred vigorously overnight. The organic layer was separated using a separating funnel and washed with distilled water, concentrated to 20 ml *in vacuo,* and poured into degassed methanol (300 ml) under stirring. The mixture was filtered then its precipitate was cleaned using Soxhlet extraction with solvents in the order; methanol, acetone, hexane, toluene, chloroform, and chlorobenzene. The chloroform fraction was concentrated (50 ml) and then poured into degassed methanol (300 ml). The resulting mixture was stirred overnight, and the solid was collected by filtration to afford the product as a dark purple powder. Chloroform fraction (210 mg, 67.7% yield) GPC in $CHCl_3$ at 40 °C M_n =23100, M_w =89600, PDI =3.8. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.56 (m, 2H), 8.18 (br, 2H), 7.95 (br, 1H), 7.78 (br, 1H), 7.68 (br, 4H), 7.60-7.51 (br, 4H), 4.70 (br, 1H), 2.42 (br, 2H), 2.02 (br, 2H), 1.4-1.10 (br, 24H), 0.83-0.77 (m, 6H). Anal. calcd for $C_{49}H_{55}N_3S_3$: C, 75.24; H, 7.09; N, 5.37; S, 12.30. Found: C, 74.58; H, 6.29; N, 5.45; S, 12.51.

2.5 Poly(2,7-(9,9-dioctyl-fluorene)-alt-5,5(4,9-di-2-thienyl-2,1,3-naphthothiadiazole) PFDTNT.

To a mixture of monomer **4** (0.186 g, 0.367 mmol) and monomer **7** (0.204 g, 0.367 mmol) in dry THF (9 ml) was added a degassed aqueous solution of sodium bicarbonate (2.1 ml, 1.36 M, 2.85 mmol) and the mixture was degassed again. The flask was charged with a mixture of *tri-o*-tolyl phosphine (17.2 mg, 0.056 mmol) and $Pd(OAc)_2$ (6.3 mg, 0.028 mmol), and the mixture was degassed again and then heated to reflux for 24 hours. After cooling to room temperature, 1-bromobenzene (0.15 g, 0.95 mmol) and dry THF (5 ml) were added and the reaction mixture was heated to 90 °C for 1 hour and then cooled to room temperature. Phenyl boronic acid (0.15 g, 1.23 mmol) was added, and the mixture was stirred at 90 °C for 3 hours. The mixture was then cooled to room temperature and poured into a mixture of $CHCl_3$ (200 ml) with an ammonium hydroxide solution (28 % in H_2O, 50 ml) and then stirred vigorously overnight. The organic layer was separated via a separating funnel and washed with water, concentrated to 20 ml *in vacuo,* and poured into degassed methanol (300 ml). The mixture was stirred overnight and then filtered through a membrane filter. The obtained solid was purified using Soxhlet extraction with organic solvents in order: methanol, acetone, hexane, toluene, chloroform, and CB. The toluene and chloroform fractions were concentrated to 50 ml and then poured into degassed methanol (200 ml) separately. The resulting mixtures were stirred overnight and the solids were collected by filtration to afford the product as a dark purple powder. Toluene fraction (70 mg, 29.1 % yield) GPC in $CHCl_3$ at 40 °C M_n = 9900, M_w = 16800, PDI = 1.7. Chloroform fraction (105 mg, 43.7% yield) GPC in $CHCl_3$ at 40 °C M_n = 41,100, M_w = 79,500, PDI =1.93. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.54 (m, 2H), 7.80 (br, 4H), 7.74 (br, 2H), 7.67 (br, 2H), 7.55 (br, 4H), 2.11 (br, 4H), 1.26- 1.06 (br, 24H), 0.85- 0.68 (m, 6H). Anal. calcd for $C_{49}H_{54}N_2S_3$: C, 76.71; H, 7.09; N, 3.65; S, 12.54. Found: C, 76.40; H, 6.27; N, 3.73; S, 12.55.

2.6 Fabrication and testing of BHJ polymer solar cells

The polymers and $PC_{71}BM$ were dissolved in different solvents and indifferent blend ratios (Table S1-Supporting information). Photovoltaic devices were fabricated onto pre-patterned ITO glass substrates (20 ohms per square) that were purchased from 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 100 nm of aluminum 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 mm^2 was placed over devices to define the test area. EQE values were determined over the wavelength range of interest by comparing the photocurrent of the OPV cell to a reference silicon photodiode having a known spectral response.

3. RESULTS AND DISCUSSION

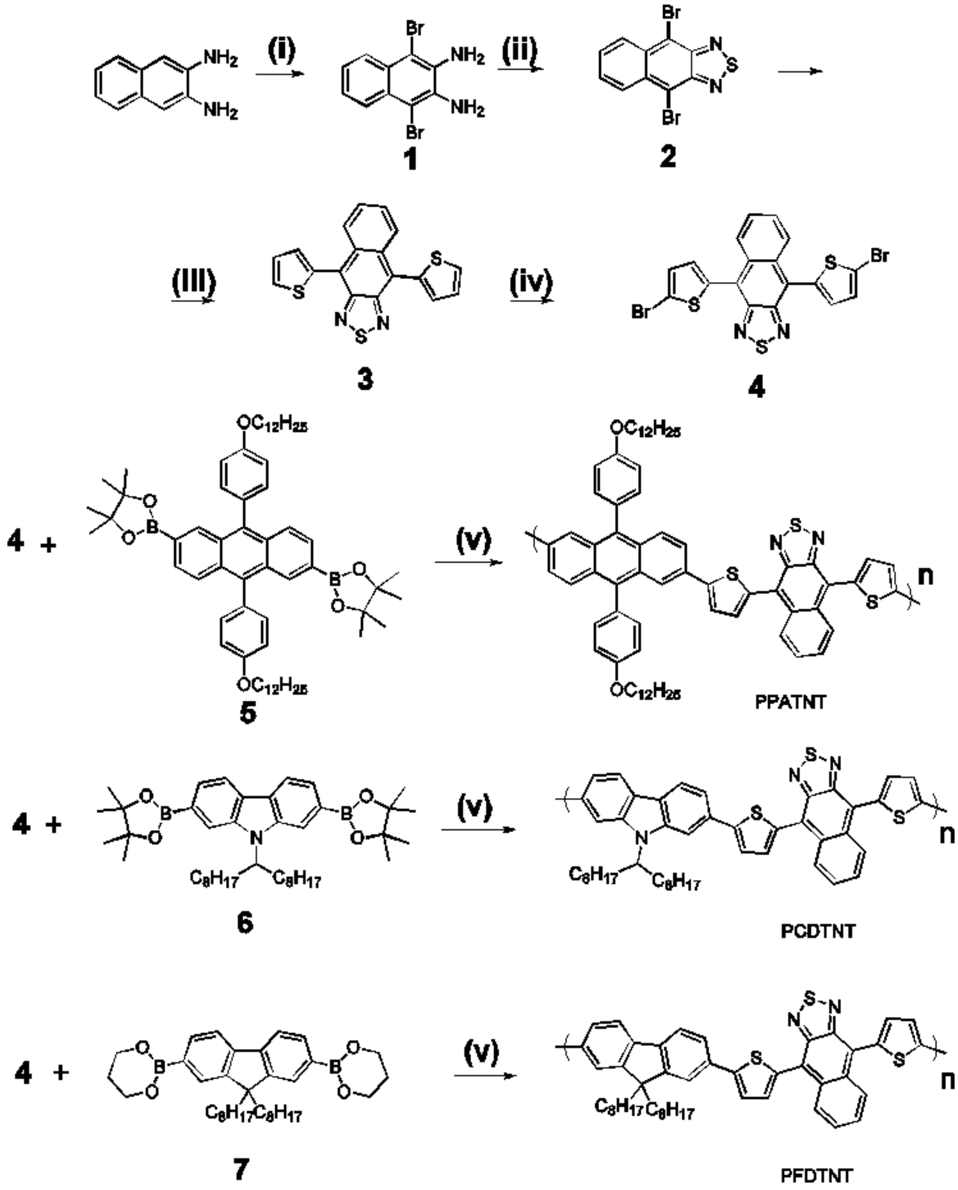
3.1 Preparation of the polymers

Scheme 1shows the preparation route to the naphthothiadiazole polymers prepared in this study. Monomer 4 was prepared according to an established literature procedure [20]. The reaction of 4 with monomers 5, 6, and 7 using Suzuki coupling reactions afforded polymers PPATNT, PFDTNT, and PCDTNT respectively. The polymers were fractionated *via* Soxhlet extraction using different organic solvents, and their toluene and/or chloroform fractions were separated. All of the polymers prepared exhibit high solubility and were easily processable in chloroform as well as in other organic solvents at ambient temperature.

Results from Gel Permeation Chromatography (GPC) analysis of these polymers have shown in .

Table 1. The analysis was carried out in chloroform as the eluent at 40 °C. Polymer PPATNT, which is the naphthothiadiazole counterpart of the known benzothiadiazole polymer PPATBT,[21] shows much greater processability. The toluene fraction of this polymer displays a number-average molecular weight M_n=10900 Da, which is three times higher than its analogous benzothiadiazole polymer (M_n=3500 Da). Similar results were obtained for naphthothiadiazole polymer PFDTNT for both of its toluene and chloroform fractions exhibit much higher values of M_n and weight-average molecular weight M_w compared to its analogous benzothiadiazole polymer PFDTBT. The Mn of the chloroform fraction of PFDTNT was 41,100 Da, while that of the PFDTBT analog, which has a much-limited solubility was M_n=5300.[22]PCDTNT, synthesized within this report showed a number-

average molecular weight (M_n = 23100 Da). This value is higher than that reported by Kim [20], for PCDTNT (M_n = 12800 Da), however, these values are not very different from those generally reported from chloroform fractions of PCDTBT[26] (M_n and M_w values of 22500 and 32600 Da, respectively). Clearly, apart from the carbazole-based polymers, the inclusion of the NT acceptor repeat units along polymer chains instead of the BT repeat unit leads to polymers have much greater processability.



Scheme 1. (i) Br$_2$, acetic acid. (ii) SOCl$_2$, pyridine, CHCl$_3$. (iii) Pd(dba$_3$)$_2$, P(o-tolyl)$_3$, 2-(tributylstannyl)thiophene, toluene, (iv) NBS, chlorobenzene. (v) Pd(OAc)$_2$, P(o-tolyl)$_3$, toluene, NEt$_4$OH

3.2 Optical Properties

Figure 1 shows the absorption spectra of the polymers, both in chloroform solution and as thin films. The values of the absorption maxima are shown in (.

Table 1) along with their optical band gaps, as determined from the onset of their absorption in films. The UV-vis spectra of the polymers display two main absorption bands for PCDTNT and PFDTNT in both chloroform solution and thin films with additional absorption bands at 413 nm in solution and around 425 nm in films for PPATNT. The UV-vis absorption spectra of polymers in films have red-shifted absorption bands relative to their solution spectra. This is due to the aggregation of polymer chains in solid-state [27-29], which increases the electronic conjugation of the polymers and improves the planarity of polymer chains. Absorption bands at high energy are attributed to π-π* transitions, while those at lower energies have attributed to intramolecular charge transfer (ICT). It can be seen in

Figure **1** that the intensity of the ICT bands is lower intensity than those of the π-π* absorption bands. This can be attributed to steric hindrance between NT repeat units and adjacent thienyl units along the conjugated polymer backbone that impedes an effective ICT between the alternating units of donors and acceptors. While PPATNT showed a slightly higher absorption maximum (584 nm *vs.* 582 and 570 nm for PCDTNT and PFDTNT, respectively). All polymers in this series showed similar optical band gaps (E_g between 1.74 and 1.76 eV), indicating similar electron-donating properties of their electron-donating segments [30-32]. Pachariyangkun [33] have reported the impact of thiophene/furan on transistor properties of arylthiadiazole based organic semiconductor. The authors have reported the (E_g value between 1.9 to 2.04 eV) for their systems.

Comparison of optical properties of the naphthothiadiazole-based polymers synthesised in this report with the benzothiadiazole analogous polymers indicates that their energy band gaps are lower than those of their counterpart polymers with BT repeat units. PPATNT has a λ_{max} of absorption at 584 nm in films while its analogue (PPATBT) has a λ_{max} at 563 nm.

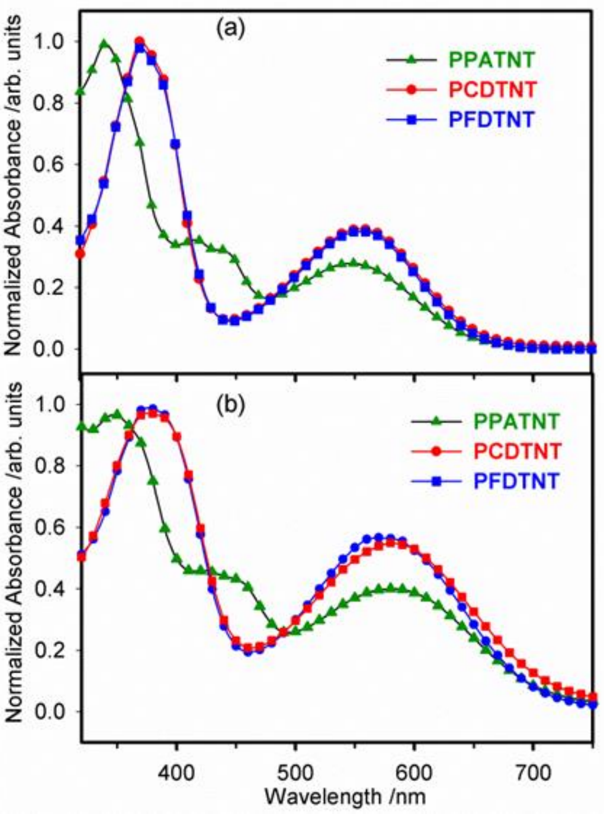


Figure 1. Normalized absorption spectra of polymers in chloroform solutions (a) and thin films (b).

The optical bandgap of PPATNT is 1.75 eV, while that of PPATBT is 1.84 eV [21]. The same comparison for PCDTNT *vs* PCDTBT indicates that the λ_{max} position for PCDTNT is red-shifted by 22 nm, resulting in a lower optical band gap of 1.74 eV for PCDTNT compared to 1.88 eV for PCDTBT.[26]PFDTNT (E_g = 1.76 eV) also displayed similar trends when compared to its benzothiadiazole equivalent PFDTBT (E_g = 1.86 eV) [22]. This decrease in band gaps for NT-based polymers has been referred to as more extended electronic delocalization on the NT unit, resulting from an additional fused benzene ring by comparison with the BT unit [20].

3.3 Electrochemical Properties

Cyclic voltammetry (CV) studies of the polymers were conducted on drop-cast films in acetonitrile with tetrabutylammonium perchlorate as the electrolyte. The CV measurements of all polymers have shown in

Figure 2 with their redox potentials, as well as their respective HOMO and LUMO levels (*vs. vacuum*) as determined from the onsets of oxidation and reduction potentials, respectively (**.**

Table 1). The results show that the HOMO levels of all NT-based polymers presented in this work are of similar values to those of the analogous polymers with BT units. The HOMO level of PPATNT at -5.40 eV (.

Table 1) is similar to that of PPATBT (-5.44 eV) [21]. The same value is observed on comparing the HOMO levels of PCDTNT to that of PCDTBT (-5.34 eV *vs.*-5.35 eV [26], respectively) and the HOMO levels of PFDTNT with its analogous polymer PFDTBT (-5.36 *v*s -5.34 eV [22] respectively). This trend suggests that a change of benzothiadiazole with naphthothiadiazole acceptor units in donor-acceptor polymers has little bearing on the position of the HOMO levels of the resulting polymers.

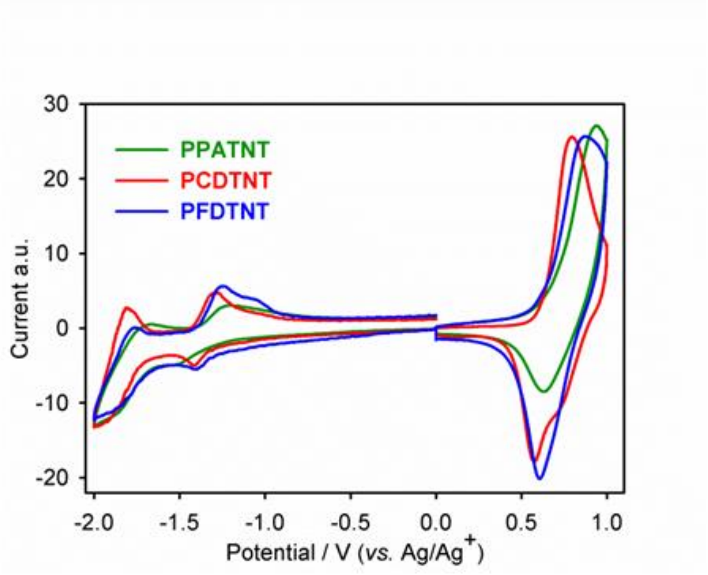


Figure 2. Cyclic voltammetry curves of thin polymer films on platinum disc electrodes (area 0.031 cm^2) at a scan rate of 100 mV s^{-1} in acetonitrile/tetrabutylammonium perchlorate (0.1 mol dm^{-3}).

The value of the LUMO level of the NT-based polymer PPATNT at -3.47 eV (**.**

Table 1) is deeper than the corresponding BT-based polymer PPATBT of (-3.21 eV) [21]. However, the values of the LUMO levels of the carbazole-based and fluorine-based NT polymers (which have both displayed two reduction waves (Fig. 2)) are very close to each other. The LUMO level of PCDTNT is at -3.44 eV, while that of PCDTBT is at -3.42 eV[26]. The LUMO of PFDTNT is at -3.50 eV, while that of the analogous BT polymer PFDTBT is at -3.44 eV [22]. The cyclic voltammetry results suggest close similarities in positions of the HOMO and LUMO levels of the NT-based polymers to those of the corresponding BT-based polymers. While it clear from the electronic spectra that the naphthothiadiazole-based polymers have relatively narrower band gaps than their corresponding benzothiadiazole analogues (~ 0.1 eV lower), the variations of the HOMO and LUMO levels of the two classes of polymers as not obvious from cyclic voltammetric studies. The deviation between optical and electrochemical band gaps might result from the presence of an energy barrier at the interface between the polymer film and the electrode surface during electrochemical measurements

3.4 Photovoltaic Device Characterisation

BHJ solar cells were fabricated using blends of the polymers as electron donors and $PC_{71}BM$ as an electron acceptor different weight ratios and in different solvents/solvent blends. The active layers were deposited by spin-casting on ITO/PEDOT:PSS anodes using a bilayer calcium/aluminum (5 nm / 100 nm) as a cathode in these devices. The best results from the photovoltaic devices obtained in these studies are summarized in **.**

Table 1, and the J–V curves are shown in **Figure 3**. **Table S1** shows OPV optimization studies on these polymers. From the table, it is evident that a polymer/fullerene weight ratio of 1/4 afforded the most efficient devices when using chlorobenzene as the casting solvent. The addition of 1,8-diiodooctane to chlorobenzene (a process which has often been described to enable improvements in device performance) [34] did not lead to an increase in the efficiency of OPV devices using the current set of polymers. The use of solvents other than chlorobenzene as casting solvents of the active layer in devices was also investigated in these studies. While the use of chloroform rather than chlorobenzene did not lead to any improvements in device efficiencies, the use of a solvent blend of carbon disulfide (CS_2) and acetone (4:1 volume ratio) which has been previously shown to have a marked impact on device efficiency,[35] was able to provide devices with higher efficiency for the higher weight average molecular weights fraction of PFDTNT (PCE = 2.02 % from films cast from CS_2/acetone *vs*. PCE = 1.78 % from films cast from chlorobenzene (table S1)). Interestingly, a comparison of the PCE values of films cast from chlorobenzene for the low and high weight average molecular weights fractions of PFDTNT showed a slightly lower PCE for the higher weight average molecular weight fraction compared to that of the lower weight average molecular weight fraction (1.78 % *vs*. 1.93 %).

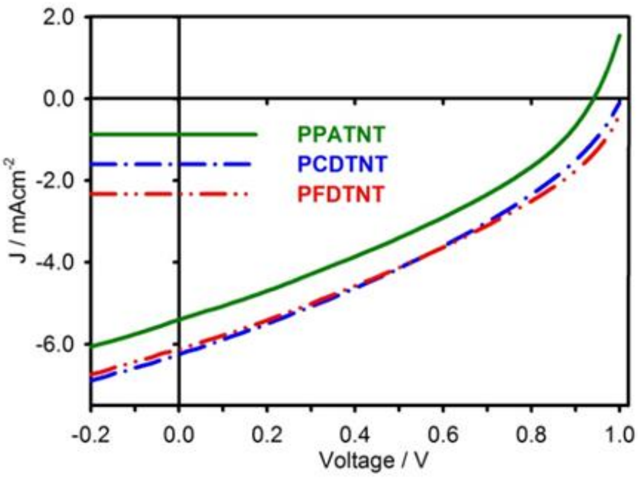


Figure 3. J–V characteristics of devices of polymers blended with $PC_{70}BM$ (1/4, w/w ratio). Device architecture: ITO / PEDOT:PSS / Active Layer / Ca (5 nm) / Al (100 nm).

As shown in **.**

Table 1, the PCDTNT and PFDTNT exhibit slightly better performances than the anthracene-based polymer PPATNT as a result of higher V_{oc} and J_{sc} values. All polymers displayed very good open-circuit voltages (V_{oc}) ranging from 0.94 to 1.02 V. In the case of the anthracene and carbazole-based polymers, V_{oc} values are higher than those observed with the analogous polymers reported in the literature with benzothiadiazole acceptor repeat units rather than naphthothiadiazole repeat units. As an example, devices using PPATNT have a V_{oc} of 0.94 V, while the PPATBT [21], which is the benzothiadiazole analogous polymer had a V_{oc} of 0.59 V. The same observation is evident on comparing the V_{oc} of PCDTNT to that of PCDTBT (1.01 V *vs.* 0.86 V [26], respectively). The electrolyte systems using phthaloyl chitosan (PhCh) based gel polymer electrolytes for DSSCs displayed the highest V_{oc} values of 0.63 V [36], and 0.52 V [37]. However, the V_{oc} of fluorine-based polymers is similar for both the naphthothiadiazole-based polymer PFDTNT and its benzothiadiazole analogous polymer PFDTBT (1.02 V *v*s. 1.03 V [22], respectively). It is well established that the V_{oc} in bulk heterojunction solar cells is generally proportional to the energy difference between the HOMO level of the electron donor and the LUMO level of the electron acceptor in the active layer [8, 38], the V_{oc} differences observed for both the anthracene and carbazole based polymers in this study (PPATNT and PCDTNT) when compared to the V_{oc} values obtained from their benzothiadiazole analogues (PPATBT and PCDTBT) are not a result of differences of the HOMO levels of the two sets of polymers. Rather, the photovoltaic performance of the NT-based polymers is lower than that of their BT analogues as a result of significantly lower FFs (even though the NT-based polymers have a lower bandgap). We speculate that such differences between the naphthothiadiazole and benzothiadiazole polymers may result from differences in the morphology when cast into a thin-film blend that may hinder the extraction of charge carriers. Further work is planned to explore this in more detail [39].

Table 1. GPC data, UV-Vis data, energy gaps of polymers and their performance in bulk heterojunction photovoltaic devices under a simulated photovoltaic light with 100 mW cm^{-2} illumination (AM1.5); cathode: 95% Ca/Al.

			λ_{max}										
polymer	M_n	M_w	Solution	Film	$E_{g\ opt}$ [c]	HOMO [d]	LUMO [e]	E_{gelec} [f]	Polymer–$PC_{71}BM$ (weight ratio)	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	PCE (%)
PPATNT [a]	10900	23100	546	584	1.75	-5.40	-3.47	1.93	1:4	-5.40	0.94	34.26	1.74
PCDTNT [b]	23100	89600	555	582	1.74	-5.34	-3.44	1.90	1:4	-6.25	1.01	34.50	2.17

PFDTNT [a]	9900	16800	554	572	1.76	-5.28	-3.49	1.79	1:4	-5.58	0.99	34.88	1.93
PFDTNT [b]	41100	79500	552	570	1.76	-5.36	-3.50	1.86	1:4	-6.12	1.02	35.14	2.02

[a] Toluene fraction. [b] Chloroform fraction. [c] Optical energy gap determined from the onset position of the absorption band. [d] HOMO position (vs. vacuum) determined from onset of oxidation. [e] LUMO position (vs. vacuum) determined from onset of reduction. [f] Electrochemical energy gap.

4. CONCLUSION

A series of low bandgap conjugated polymers comprising of 4,9-linked 2,1,3-naphthothiadiazole units as electron accepting units and 2,7-linked fluorene, 2,7-linked carbazole, or 2,6-linked anthracene alternate units flanked by thienyl units with alkoxy or alkyl substituents as donor units were successfully synthesised using the Suzuki coupling reactions. The physical, electrochemical, thermal, structural, and photovoltaic properties of the resulting polymers were examined in order to ascertain the effect of replacing 2,1,3-benzothiadiazole (BT) with 2,1,3-naphthothiadiazole (NT) in this series of conjugated polymers. UV-vis spectroscopy showed that incorporation of NT units instead of BT units results in red-shifted absorption maxima and lower bandgaps. This is explained by a more extended electronic delocalization on the NT unit in virtue of an additional fused benzene ring in comparison with the BT unit. Moreover, replacing BT moieties with NT moieties over the main chain of polymers leads to polymers with increased molecular weights and solubilities. This is believed to be attributed to the twisting of polymer chains out of planarity as a result of steric hindrance between naphthothiadiazole units and adjacent thiophene rings. The NT-based polymers display similar HOMO levels relative to their BT analogues. The LUMO levels of the NT and BT-based polymers are also comparable apart from the anthracene base polymers in which the NT-based polymer has a deeper LUMO level than its BT analogue. Photovoltaic devices with an active layer composed of thin films (65-75 nm) of polymer/$PC_{71}BM$ blends had power conversion efficiencies (PCEs) ranging from 1.74 to 2.17%. PCDTNT displayed the best performance in this series of polymers. Comparison of the photovoltaic performance of the NT-based polymers to that of their BT analogues indicated a lower performance of the NT-based polymers even though the latter polymers display lower bandgaps than the corresponding BT-counterparts a result of a significant low FF that leads to an overall low photovoltaic performance. We speculate that this may be attributed to unfavourable morphology for given polymer/fullerene systems that did not yield efficient devices. Taking the positions of energy levels and low bandgap of these polymers into account, there is the possibility to design new categories of low bandgap polymers that could be applied as effective materials in photovoltaic devices when used with fullerene derivatives**.** Further investigations into the use of these new polymers in BHJs are currently ongoing.

SUPPORTING INFORMATION

Table S1: OPV device optimisation metrics under a simulated photovoltaic light with 100 mW cm^{-2} illumination (AM1.5); Device architecture: ITO / PEDOT:PSS / Active Layer / Ca (5 nm) / Al (100 nm).

	Solvent	Polymer/Fullerene Ratio (w/w)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
PPATNT	CB [c]	1:1	0.88	-1.19	24.88	0.26
	CB	1:2	0.81	-3.16	30.06	0.77
	CB	1:3	0.87	-4.67	30.85	1.25
	CB	**1:4**	**0.94**	**-5.40**	**34.26**	**1.74**
	CB with DIO[d]	1:4	0.74	-4.02	33.16	0.98
	CF[e]	1:4	0.89	-5.29	33.40	1.58
	CS_2&Acetone	1:4	0.89	-5.16	30.65	1.41
PCDTNT	CB	1:1	0.99	-1.14	25.36	0.29
	CB	1:2	0.96	-3.05	27.17	0.79
	CB	1:3	0.94	-4.61	28.79	1.25
	CB	**1:4**	**1.01**	**-6.25**	**34.50**	**2.17**
	CB with DIO	1:4	0.95	-4.59	31.50	1.38
	CF	1:4	0.98	-4.96	35.10	1.70
	CS_2&Acetone	1:4	0.97	-5.88	33.78	1.93
PFDTNT [a]	CB	1:1	1.03	-1.49	22.63	0.35
	CB	1:2	1.02	-3.08	26.60	0.84
	CB	1:3	1.02	-4.89	31.86	1.58
	CB	**1:4**	**0.99**	**-5.58**	**34.88**	**1.93**
	CB with DIO	1:4	0.74	-4.02	33.16	0.98
	CF	1:4	0.89	-5.29	33.40	1.58
	CS_2&Acetone	1:4	0.89	-5.16	30.65	1.41
PFDTNT [b]	CB	1:1	1.05	-1.16	22.61	0.28
	CB	1:2	1.03	-3.51	28.04	1.01
	CB	1:3	0.99	-5.15	31.71	1.61
	CB	1:4	1.00	-5.41	32.96	1.78
	CB with DIO	1:4	0.97	-4.31	29.09	1.21
	CF	1:4	1.00	-5.23	32.04	1.68
	CS_2&Acetone	**1:4**	**1.02**	**-6.12**	**35.14**	**2.02**

[a] Toluene fraction of **PFDTNT**. [b] Chloroform fraction of **PFDTNT**.[c]CB =Chlorobenzene. [d] DIO = 1.8-diiodooctane additive.[e] CF = chloroform.

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References

1. B.C. Thompson, J.M.J. Fréchet, *Angew. Chemie - Int. Ed.*, 47 (2008) 58.
2. H. Zhou, L. Yang, and W. You,. *Macromolecules*, 45 (2012) 607.

3. G. Yu, J. Gao, J.C. Hummelen, F. Wudl, A.J. Heeger, *Science (80-.).*, 270 (1995) 1789.
4. C.J. Brabec, C. Winder, M.C. Scharber, N.S. Sariciftci, J.C. Hummelen, M. Svensson, M.R. Andersson, *J. Chem. Phys.*, 115 (2001) 7235.
5. S. Günes, H. Neugebauer, N.S. Sariciftci, Conjugated Polymer-Based Organic Solar Cells, (2007). *Chem. Rev.,* 107 (2007) 1324.
6. H. Shirakawa, A. MacDiarmid, A. Heeger, *Chem. Commun.* (2003) 1.
7. H. Hoppe, N.S. Sariciftci, *J. Mater. Res.*, 19 (2004) 1924.
8. M.C. Scharber, D. Mühlbacher, M. Koppe, P. Denk, C. Waldauf, A.J. Heeger, C.J. Brabec, *Adv. Mater.*, 18 (2006) 789.
9. L. Dou, Y. Liu, Z. Hong, G. Li, Y. Yang, *Chem. Rev.*, 115 (2015) 12633.
10. Y. Deng, Y. Chen, X. Zhang, H. Tian, C. Bao, D. Yan, Y. Geng, F. Wang, *Macromolecules*, 45 (2012) 8621.
11. C. Kitamura, S. Tanaka, Y. Yamashita, *Chem. Mater.*, 8 (1996) 570.
12. P.M. Beaujuge, C.M. Amb, J.R. Reynolds, *Acc. Chem. Res.*, 43 (2010) 1396.
13. H.Y. Chen, J. Hou, S. Zhang, Y. Liang, G. Yang, Y. Yang, L. Yu, Y. Wu, G. Li, *Nat. Photonics*, 3 (2009) 649.
14. P.L.T. Boudreault, A. Najari, M. Leclerc, *Chem. Mater.*, 23 (2011) 456.
15. S. Sardar, P. Kar, H. Remita, B. Liu, P. Lemmens, S.K. Pal, S. Ghosh, *Sci. Rep.*, 5 (2015) 1.
16. Y.J. Cheng, S.H. Yang, C.S. Hsu, *Chem. Rev.*, 109 (2009) 5868.
17. S.H. Park, A. Roy, S. Beaupré, S. Cho, N. Coates, J.S. Moon, D. Moses, M. Leclerc, K. Lee, A.J. Heeger, *Nat. Photonics*, 3 (2009) 297.
18. M. Wang, X. Hu, P. Liu, W. Li, X. Gong, F. Huang, Y. Cao, *J. Am. Chem. Soc.*, 133 (2011) 9638.
19. E.E. Aesumc, M. Karikomi, C. Kitamura, S. Tanaka, Y. Yamashita, *J. Am. Chem. SOC*, 117 (1995) 6791–6792.
20. J. Kim, M.H. Yun, G.H. Kim, J.Y. Kim, C. Yang, *Polym. Chem.*, 3 (2012) 3276.
21. M.S. Almeataq, H. Yi, S. Al-Faifi, A.A.B. Alghamdi, A. Iraqi, N.W. Scarratt, T. Wang, D.G. Lidzey, *Chem. Commun.*, 49 (2013) 2252.
22. A.A.B. Alghamdi, D.C. Watters, H. Yi, S. Al-Faifi, M.S. Almeataq, D. Coles, J. Kingsley, D.G. Lidzey, A. Iraqi, *J. Mater. Chem. A*, 1 (2013) 5165.
23. Z.G. Zhang, Y.L. Liu, Y. Yang, K. Hou, B. Peng, G. Zhao, M. Zhang, X. Guo, E.T. Kang, Y. Li, *Macromolecules*, 43 (2010) 9376.
24. N. Blouin, A. Michaud, M. Leclerc, *Adv. Mater.*, 19 (2007) 2295.
25. G. Gritzner. *Pure Appl. Chem.*, 62 (1990) 1839.
26. H. Yi, S. Al-Faifi, A. Iraqi, D.C. Watters, J. Kingsley, D.G. Lidzey, *J. Mater. Chem.*, 21 (2011) 13649.
27. P.J. Brown, D.S. Thomas, A. Köhler, J.S. Wilson, J.S. Kim, C.M. Ramsdale, H. Sirringhaus, R.H. Friend, *Phys. Rev. B - Condens. Matter Mater. Phys.*, 67 (2003) 1.
28. S.C. Price, A.C. Stuart, L. Yang, H. Zhou, W. You, *J. Am. Chem. Soc.*, 133 (2011) 4625.
29. P. Wei, L. Duan, D. Zhang, J. Qiao, L. Wang, R. Wang, G. Dong, Y. Qiu, *J. Mater. Chem.*, 18 (2008) 806.
30. M.M. Nofal, S.B. Aziz, J.M. Hadi, W.O. Karim, E.M.A. Dannoun, A.M. Hussein, S.A. Hussen, *Polymers*, 13 (2021) 1648.
31. S.B. Aziz, M.M. Nofal, H.O. Ghareeb, E.M.A. Dannoun, S.A. Hussen, J.M. Hadi, K.K. Ahmed, A.M. Hussein, *Polymers (Basel).*, 13 (2021) 1–23.
32. K.A. Abdalkarim, S.B. Aziz, R.T. Abdulwahid, S.M. Alshehri, T. Ahamad, J.M. Hadi, S.A. Hussein, *Arab. J. Chem.*, 14 (2021) 103215.
33. A. Pachariyangkun, M. Suda, S. Hadsadee, S. Jungsuttiwong, P. Nalaoh, P. Pattanasattayavong, T. Sudyoadsuk, H.M. Yamamoto, V. Promarak, *J. Mater. Chem. C*, 8 (2020) 17297.
34. S.J. Lou, J.M. Szarko, T. Xu, L. Yu, T.J. Marks, L.X. Chen, *J. Am. Chem. Soc.*, 133 (2011) 20661.

35. J. Griffin, A.J. Pearson, N.W. Scarratt, T. Wang, A.D.F. Dunbar, H. Yi, A. Iraqi, A.R. Buckley, D.G. Lidzey, *Org. Electron.*, 21 (2015) 216.
36. A.M. Zulkifli, N.I. Aqilah Mat Said, S.B. Aziz, E.M. Ali Dannoun, S. Hisham, S. Shah, A.A. Bakar, Z.H. Zainal, H.A. Tajuddin, J.M. Hadi, M.A. Brza, S.R. Saeed, P.O. Amin, *Molecules*, 25 (2020) 4115.
37. A.M. Zulkifli, N.I.A.M. Said, S.B. Aziz, S. Hisham, S. Shah, A.A. Bakar, Z.H.Z. Abidin, H.A. Tajuddin, L. Sulaiman, M.A. Brza, J.M. Hadi, S. Al-Zangana, *Int. J. Electrochem. Sci.*, 15 (2020) 7434.
38. N. Blouin, A. Michaud, D. Gendron, S. Wakim, E. Blair, R. Neagu-Plesu, M. Belletête, G. Durocher, Y. Tao, M. Leclerc, *J. Am. Chem. Soc.*, 130 (2008) 732.
39. M. Dolores Perez, C. Borek, S.R. Forrest, M.E. Thompson, *J. Am. Chem. Soc.*, 131 (2009) 9281