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Article

PHOTOPHYSICAL, THERMAL AND STRUCTURAL PROPERTIES OF THIOPHENE AND BENZODITHIOPHENE-BASED COPOLYMERS SYNTHESIZED BY DIRECT ARYLATION POLYCONDENSATION METHOD

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Abstract: Three low band gap copolymers based on isoindigo acceptor units were designed and successfully synthesized by direct arylation polycondensation method. Two of them were benzodithiophene(BDT)-isoindigo copolymers (**PBDTI-OD** and **PBDTI-DT**) with 2-octlydodecyl(OD) and 2-decyltetradecyl (DT) substituted isoindigo units, respectively. Thiophene donor and DT-substituted isoindigo acceptor units were copolymerized to synthesize **PTI-DT**. The copolymers have broad absorption range that extends to over 760 nm with a band gap $\approx$ 1.5 eV. The photophysical property studies showed the BDT based copolymers have non-polar ground states. Their emission exhibited the population of intramolecular charge transfer (ICT) state in polar solvents and tightly bound excitonic state in non-polar solvents due to self-aggregation. On the contrary, the emission from the thiophene based copolymers was only from the tightly bound excitonic state. The thermal decomposition temperature of the copolymers was above 380 ^{o}C. The X-ray diffraction pattern of the three copolymers showed a halo due $\pi - \pi$ stacking. A second sharper peak was observed in the BDT-based copolymer with longer side chain on the isoindigo unit (**PBDTI-DT**) and the thiophene based copolymers with **PTI-DT** exhibiting a better structural order.

Keywords: Intramolecular charge transfer; copolymers; $\pi - \pi$ stacking; direct arylation polycondensation; and

1. Introduction

The introduction of π-conjuageted polymers to the fast growing solar cell technology has brought forth new features of flexibility and solution processabiltiy in the so called organic solar cells (OSCs) devices. OSCs have shown a leap in efficiency in the past five years to above 18% in single junction [1] and over 17% in multi-junction [2] devices. This tremendous improvement is mainly attributed to the introduction of new donor/acceptor polymers that can harvest the broad solar spectrum with appropriate energetics in the active layer. A vast number of polymers have been synthesized and characterized to enrich the structure-property relation recipe for efficient OSCs. Alternating donor-acceptor (D-A) copolymers are commonly synthesized to get low band gap polymers with good solar harvest that extends to near infra-red region. Some important parameters that needs to be addressed during the synthesis of the D-A copolymers include that the HOMO level should be lower-lying, with their LUMO lying in the region for efficient exciton dissociation. The synthesis of low band gap polymers using a simple and economically viable technique has gained attention of researchers due to its potential for industrialization of the OSC technology. Direct arylation polycondensation method (DAP) has by far shortened the synthesis route compared to the commonly used Suzuki and Negasaki cross coupling techniques. In this reaction, the unsubstituted arylene monomers are directly coupled with dihaloarylene units with the help of transition metals usually palladium acetate. The by-product at each of the synthesis steps is therefore drastically reduced making the DAP method more environmental friendly and economically viable. The mass production of OSCs will need an enormous amount of donor and acceptor organic materials. An easy and fast synthesis method such as DAP is undoubtedly important to realize the commercialization of OSCs technology. Despite its many interesting merits, the method has a drawback that its selectivity between C-H bonds for some monomers is poor. Consequently, the method is more commonly used to synthesize homopolymers like poly-3-hexylthiophene(P3HT) and benzodithiophene (BDT)[3–5]. However, DAP synthesized the D-A copolymers are limited. Recently, our group and others have reported the successful synthesis of D-A copolymers using DAP method [6–9].

The choice of D and A units in the synthesis of D-A copolymers determines their electrical, optical and structural properties that will subsequently determine the performance of the OSC the materials are used for. Isoindigo is one of the highly used acceptor unit due to its good electron withdrawing properties. The fused ring benzo[1,2-b:4,5-b']dithiophene (BDTs) and thiophene units are most commonly used donor units in the synthesis of D-A copolymers that produced high PCE of over 11% in OSCs[10]. These polymers are usually aloxy or alkyl substituted to enhance their solubility. A basic understanding of the polymers structure-property relation is vital for the optimization of their structure for higher power conversion efficiency of OSCs. The optical property, intra/inter-chain interactions in the polymers, and their morphology in the films are some of the parameters that play important roles in charge photogeneration processes in OSCs. In addition, their thermal properties determine their life time in harsh environmental condition and also their application in flexible OSCs application that is normally processed at temperature below 150 ^{o}C.

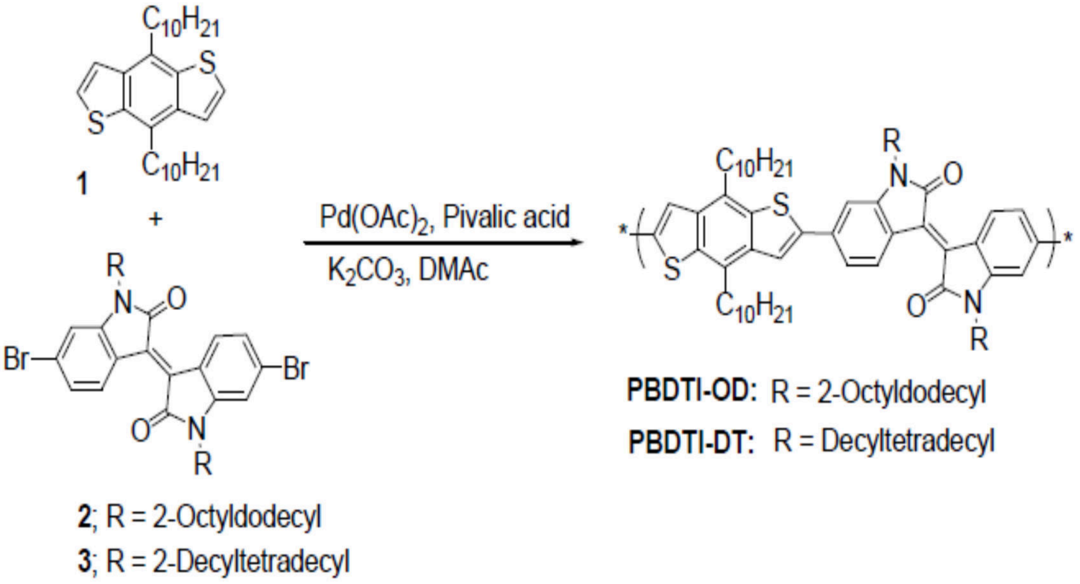
In this work, we report the synthesis of three D-A copolymers based on an isoindigo acceptor unit. The two copolymers have alkyl substituted BDT (**PBDTI-OD** and **PBDTI-DT**) donor units while in the third copolymer (**PTI-DT**) an alkyl substituted thiophene unit is used. The structures of the BDT based copolymers were systematically tailored by increasing the side chain length in the isoindigo units from 2-octyldodecyl (OD) to 2-decyltetradecyl (DT) while keeping the backbone structure the same in **PBDTI-OD** and **PBDTI-DT**, respectively. The third copolymer was synthesized to see the effect of electron donating groups by changing the donor units from BDT to thiophene in **PTI-DT**. The structural difference in the three copolymers allowed us to investigate the effect of backbone structure on their photo-physics, thermal and structural properties. We found two relaxation channels in BDT based copolymers while a one channel relaxation was found in **PTI-DT**. The copolymers showed excellent thermal stability with decomposition temperature (T^{D} = 5% mass loss) above 380 ^{o}C. The X-ray diffraction pattern of the copolymers suggested a better structural ordering was found in the thiophene based copolymer.

2. Materials and Methods

2.1. Materials and Synthesis

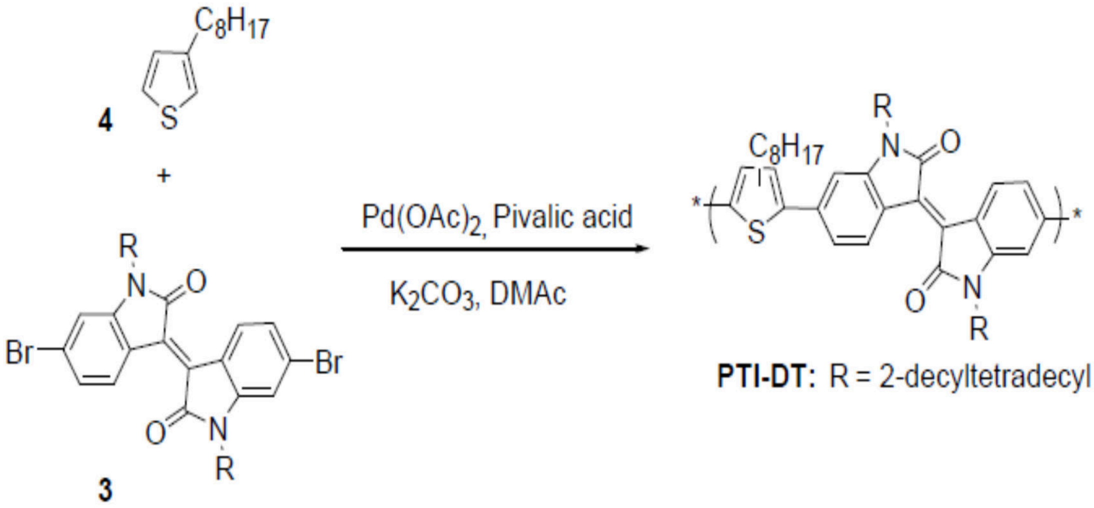
Three copolymers based on isoindigo acceptor were designed and synthesized using direct heteroarylation polymerization (DAP) method for the first time. The two copolymers were synthesized by copolymerization of 4,8-bis(decyl)benzo[1,2-b;4,5-b']dithiophene (BDT) (**1**) donor unit and isoindigo acceptor unit. A 2-octyldodecyl (OD) and 2-decyltetradecyl (DT) branched side chains were attached on N of the isoididigo unit (**2** and **3**) to synthesize **PBDTI-OD** and **PBDTI-DT**, respectively as shown in Scheme-1. In the synthesis of **PBDTI-OD**/**PBDTI-D**, a 1:1 ratio of BDT(**1**) (0.5 mmol) and isoindigo (**2/3**)(0.5 mmol) was copolymerized using palladium acetate, (0.01 mmol), pivalic acid (0.15 mmol) and potassium carbonate (1.3 mmol) as catalyst, acidic additive and base, respectively. The polymerization reaction took place in an inert atomsphere at a temperature of 100 ^{o}C using anhydrous dimethylacetamide (DMAc) for **PBDTI-DT** and a mixture of DMAc and Toluene as the reaction solvents for **PBDTI-OT**. The heating was stopped after 7 and 19 h for **PBDTI-OD** and **PBDTI-DT**, respectively and the solutions were left to cool down to room temperature. The copolymers were precipitated in methanol and filtered. The crude copolymers were dissolved in chloroform (CF) and washed with aqueous solution ethylene-diaminetatraacetic acid (pH=8) to remove trace metals, followed by 0.1 N HCl and distilled water. **PBDTI-OD** was Soxhlet extracted with methanol, hexane, diethylether and chloroform while **PBDTI-DT** was extracted with methanol, acetone, ethyl-acetate, hexane, diethylether and chloroform. Note here that due to the high solubility of **PBDTI-OD** in hexane the extraction was discontinued before a clear solution was obtained. The CF extract of **PBDTI-OD** was concentrated and precipitated in acetone. After drying the filtered polymer at 40 ^{0}C in a vacuum oven for 24 h, a 0.41 g solid was obtained. The solid obtained was further stirred in hexane overnight to compensate for the time it was discontinued during extraction. Subsequently, the copolymer was filter to get a 0.36 g blue-black copolymer with a yield of 56%. Similarly, the CF extract of **PBDTI-DT** was concentrated and precipitated in methanol. The filtered copolymer was dried in an oven at 40 ^{0}C for 24 h and a 0.32 g dark brown solid with a yield above 43% was obtained.

PTI-DT was synthesized in a similar reaction condition like the above two copolymers by copolymerizing a thiophene (0.5 mmol) donor monomer (**4**) with isoidigo acceptor unit with 2-decyltetradecyl branched side chain (**3**) as shown in Scheme-2. The polymerization was done in an anhydrous DMAc reaction solvent for 3.5 h. Following the same procedure, the crude polymer was extracted. **PTI-DT** was Soxhlet extraction in methanol, acetone and ethylacetate and CF which afforded a 0.37 g dark-brown solid with a 66% yield after drying in an oven at 40^{o}C overnight. Note here that the long side chains attached both on the donor and acceptor units of the copolymers increased their solubility in chlorinated solvents like CF and 1,2-dichlorobenzene (oDCB). Comparing the three copolymers, **PBDTI-OD** was found to be less soluble in the chlorinated solvents like CF and oDCB. On the other hand, introduction of the long side chains might create steric hindrance in their backbone that might twist the copolymers. However, BDT has a planar structure that is expected to make the backbone **PBDTI-OD** and **PBDTI-DT** less twisted and have longer conjugation length over the thiophene based copolymer, **PTI-DT**.



Scheme 1. Syntheses scheme of **PBDTI-OD** and **PBDTI-DT**: A BDT unit (**1**) donor units is coupled with isoindigo (**2** and **3**) acceptor units with OD and DT side chains to synthesize low band gap copolymers **PBDTI-OD** and **PBDTI-DT**, respectively

Size exclusion chromatography was done using Waters Alliance GPVC2000 with a refractive index detector. The columns used are Waters Stragel®HMW 6EX2 and Waters Stragel®HT 6EX1. The measurements were taken in 1,2 4-trichlorobenzene at a temperature of 135 ^{o}C. The relative molecular mass was measured against polystyrene standards. The average molecular weight (M_w) of **PBDTI-OD**, **PBDTI-DT** and **PTI-DT** were found to be 53,461, 71,234 and 23,574 g/mol, respectively. The high M_w of the copolymers is due to the long alkyl side chains appended both in the donor and acceptors units. The calculated poly-dispersity index (PDI = M_w/M_n) of the three copolymers shows that **PTI-DT** has a more uniform molecular weight distribution. The molecular weight and yield data is summarized in Table 1.



Scheme 2. Synthesis scheme of **PTI-DT**: A thiophene (**4**) donor unit is coupled with isoindigo (**3**) acceptor unit to synthesize a low band gap copolymer – **PTI-DT**

Table 1. Molecular weight and yield data of **PBDTI-OD**, P**BDTI-DT** and **PTI-DT**

Copolymer	Yield (%)	M$_n$ (g/mol)	M$_w$(g/mol)	PDI
PBDTI-OD	56.25	16,932	53,461	3.2
PBDTI-DT	43.71	17,974	71,234	4.0
PTI-DT	66.07	12,537	23,574	1.9

2.2. *Absorption and Photoluminescence Spectroscopy*

The absorption spectra of **PBDTI-OD**, **PBDTI-DT** and **PTI-DT** both in solutions and spin coated films were taken using Perkin Elmer Lambda 19, UV/Vis/NIR spectrophotometer. Similarity, their photo-luminescence (PL) spectra were recorded both in solutions and spin coated films using JY Horiba, model 'Fluoromax'-4 fluoro-spectrometer. The absorption and PL spectra in solutions were taken in three solvents to see spectral change due to polarity of the solvents: CF, o-DCB, and cyclohexane (Chex) with polarity index of 4.1, 2.7 and 0.2, respectively. The PL spectra of the copolymers in solutions and films were taken at excitations matching their longer wavelength electronic transition. The solutions for PL measurement absorb only 0.05 at the maxima to avoid self absorption.

2.3. *X-ray Diffraction*

X-ray diffraction (XRD) pattern of the copolymers were taken in drop casted films on glass substrate using X-ray diffractometer 7000S of Shimadzu Scientific Instruments with a copper target, Cu-Kα-radiation with 40 kV X 40 mA power. The XRD patterns were recorded for 2θ values from 2 to 40^0. The interlayer spacing between the planes(d) was calculated using Bragg's equation (eq-1).

$$n\lambda = dsin(\theta) \tag{1}$$

,where n, λ and θ are order of diffraction (1), wavelength of the x-ray (0.154 nm) and angle of diffraction, respectively.

2.4. *Thermogravimetric Analysis*

The thermal properties of the copolymers determines their stability in harsh environment. Hence, their thermal behaviours were investigates using DTG-60H thermogravimetric analyser (TGA) in platinum crucibles under nitrogen atmosphere flowing at rate of 50 ml/min.

2.5. *Electrochemistry*

Squarewave voltammetry (SWV) was done to measure the frontier energy orbital of the copolyers in a three-electrode setup. Platinium electrodes were used both as working and counter electrodes while Ag/AgCl was used as a reference electrode which was calibrated against ferocene/ferrocyne (Fc/Fc$^+$). The redox potential of Fc/Fc$^+$ was found to be 0.44 eV versus the reference electrode taking its energy level to be 4.8 eV below the vacumm. The copolymers films were drop casted on the Pt disc working electrode and a 0.1 M solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in anyhdrous acetonitrile served as supporting electrolyte. The higherst occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were determined from the onset of oxidation and reduction potentials , respectively using eq 2[11].

$$E_{HOMO/LUMO} = e(E_{ox/red} + 4.36)eV \tag{2}$$

3. Results and Discussion

3.1. Optical and Electrochemical Properties of ***PBDTI-OD****,* ***PBDTI-DT*** *and* ***PTI-DT***

The absorption spectra of **PBDTI-OD**, **PBDTI-DT** and **PTI-DT** were taken both in CF solutions and films as shown in Figure 1a and b. The absorption spectra of **PBDTI-OD** and **PBDTI-DT** in CF solutions are characterized by one dominant transition peaking at 631 and 628 nm, respectively and two peaks below 450 nm. The absorption spectra of **PTI-DT** is quite different from the BDT based copolymers. A dominant one transition in solution that peaks at 615 nm and a modest peak at 450 nm is observed. The two energy band profile exhibited in **PBDTI-OD**, **PBDTI-DT** and **PTI-DT** is common in push-pull copolymers. The low energy band is the $S_0 \rightarrow S_1$ transition usually with an intra-molecular charge transfer (ICT) characteristics due to the charge transfer between the donor and acceptors moieties in the copolymers. On the other hand, the high energy band is due to the $\pi - \pi^*$ transition which is common in the π-conjugated polymers due to the alternating single and double bonds in their backbone [12]. The presumably assigned ICT state transition in **PBDTI-OD** and **PBDTI-DT** is red shifted by more than 11 nm with respect to **PTI-DT** suggesting a better electron donating property of the BDT[13]. This also can be due to the long alkyl side chains on the thiophene and isoindigo units of **PTI-DT** that can sterically intract leading to a twisting in the backbone of the copolymer. A computaion work on a similar BDT based copolymer showed that the copolymers are likely to adopt planar structure [13] which facilitates ICT in **PBDTI-OD** and **PBDTI-DT** chains.

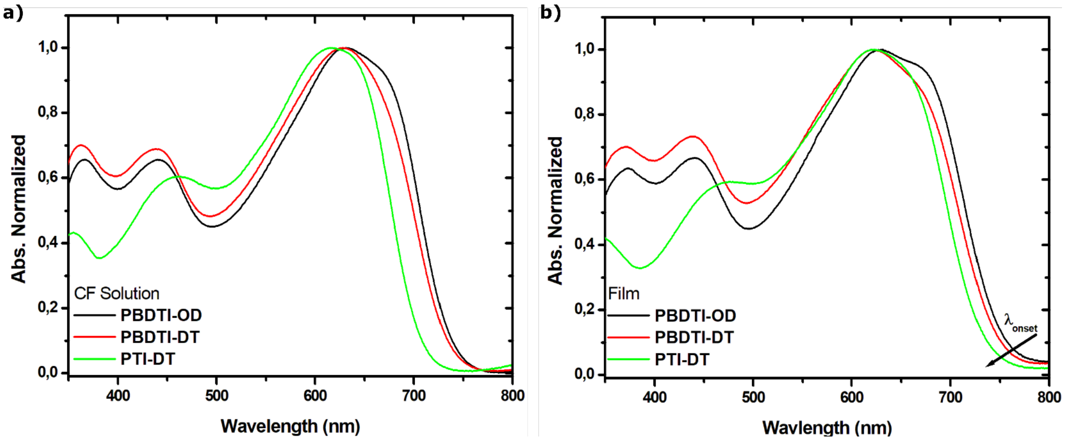


Figure 1. Absorption spectra of **PBDTI-OD** (black) , **PBDTI-DT**(red) and **PTI-DT**(green) in a) CF solutions and b) spin coated films

The absorption spectra of the copolymers taken in spin coated films were found to be red shifted by 30, 25 and 40 nm from their solution spectra in **PBDTI-OD**, **PBDTI-DT** and **PTI-DT**, respectively. The red shift in absorbance upon solidification shows a better interchain interaction in the films due to $\pi - \pi$ stacking which is beneficial for charge transport when the copolymers are used in OSCs. The larger red shift in absorbance of **PTI-DT** upon solidification indicates a different intra and intermolecular interaction from the DBT based copolymer exists in the copolymer due to the thiophene donor unit. One of the reasons can be that **PTI-DT** is twisted in the absence of strong intermolecular interaction in dilute solution. However, the stronger inter-molecular force in the solid films pushes the copolymer into a palnar conformation resulting in a siginicant red shift of absrotpion onset [14,15]. Similarly, the smaller absorption onset shift in the films of **PBDTI-DT** compared to **PBDTI-OD** shows the more planar structure of **PBDTI-OD** due to the shorter side chain on the isoindigo unit [16]. The optical band gap (E_g) of the three copolymers was calculated from the onset of absorption in films and were found to be 1.53, 1.54 and 1.56 eV for **PBDTI-OD**, **PBDTI-DT**, and **PTI-DT**, respectively. The copolymers have similar bandgap that is suitable to harvest a substantial solar irradiation in the high solar flux region[17]. The backbone structures of the copolymers has a negligible effect on their band gap. The optical properties of the copolymers are summarized in Table 2.

The PL spectra of the thin films were taken by exciting at their absorption maxima in the longer wavelength region and were found to be Stokes shifted by 179, 189 and 185 nm in **PBDTI-OD**, **PBDTI-DT** and **PTI-DT**, respectively (see Figure 3). The large Stokes shift inhibits interchain excitation energy transfer via Förster resonance energy transfer (FRET) in the copolymers. However, the large Stokes shift also shows multiple processes have taken place to stabilize the first excited state. Since ICT formation in solid films is not efficient, the emission from the first excited state ($S_0 \leftarrow S_1$) is ascribed to tightly bound intrachain excitons relaxation. The strong $\pi - \pi$ interaction upon solidfication of the copolymers enables efficient interchain charge transfer interaction that dominates over intrachain charge transfer (i.e. ICT population). Our work on three similar copolymer with two and three thiophene donor units coupled with isoindgo acceptor unit showed similar results [6,7].

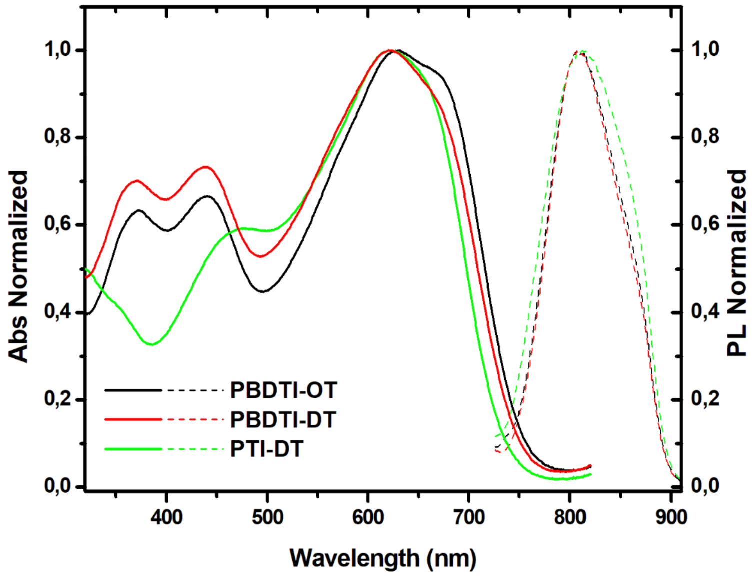


Figure 2. Absorption (solid line) and PL (broken line) spectra of **PBDTI-OD** (black) , **PBDTI-DT**(red) and **PTI-DT**(green).

The HOMO and LUMO energy levels of the copolymers were determined using SWV from the onsets of their oxidation and reduction potentials as shown in Figure 4. The HOMOs and LUMOs of the copolymers are summarized in Table-2. The difference in the HOMOs between the copolymers with the same donor units (**PBDTI-OD** and **PBDTI-DT**) was 0.2 eV whereas, the difference is only 0.1 eV between **PBDTI-DT** and **PTI-DT** (having the same acceptor unit). The highest LUMO was found in **PBDTI-OD** followed by **PBDTI-OD** then **PTI-DT**. The π-electron density in the copolymers is not expected to be significantly affected by the alky side chains[18]. The reason for the difference in HOMOs between **PBDTI-OD** and **PBDTI-DT** should therefore be due to the effect of the length of the alkyl side chains on the reorganization of the copolymers in the drop casted films [7,16]. This is expected due to the relatively lower solubility of **PBDTI-OD**.

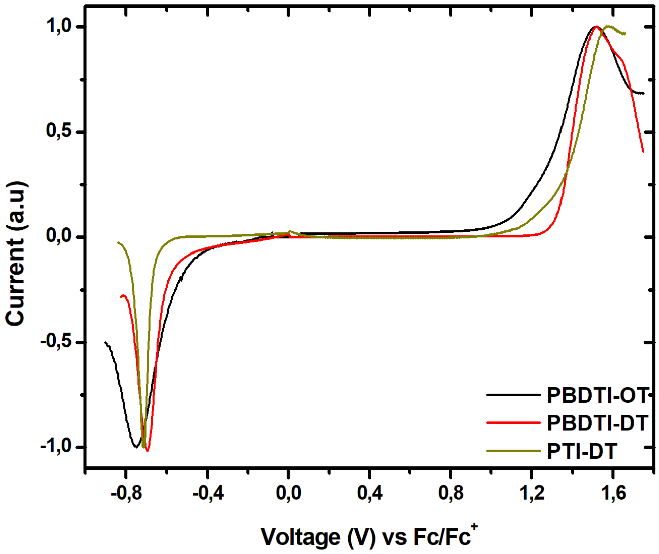


Figure 3. SWV of **PBDTI-OD** (black), **PBDTI-DT** (red) and **PTI-DT** (dark yellow): the copolymers exhibited distinct oxidation and reduction onsets and peaks

However, the difference in the energetics of **PBDTI-DT** and **PTI-DT** is significantly dependent on the electron donating strength of BDT vesus thiophene units, respectively. The stronger electron donating property of BDT would enhance the ICT in **PBDTI-DT** which will stabilize its LUMO level compared to **PTI-DT** in which the donor unit is a thiophene[19]. Note here that the reorganization of the copolymers in the casted films also plays a role. The medium lying HOMO level of the copolymers is beneficial for attaining high open circuit voltage when they are used in OSCs as donor mateials since $V_{OC} = e(E_{LUMO}^{Acceptor} - E_{HOMO}^{Donor})$, where e is the elementary charge [20]. The LUMO offset of the copolymers with a fullerene acceptor should be around 0.3 eV for efficient exciton disscociation at the donor/acceptor interface[20,21]. The LUMO offset of the **PBDTI-OD**, **PBDTI-DT** and **PTI-DT** with respect to the commonly used fullerene acceptor, $PC_{71}BM$ (LUMO = 4.0 eV) are 0.1, 0.2 and 0.3 eV, respectively. The LUMO offsets in the BDT based copolymers are below the recommended value which is detrimental to exciton dissociation in fullerene based OSCs while efficient exciton dissociation is expected in **PTI-DT** based OSCs. Hence, **PBDTI-OD** and **PBDTI-DT** would work better when blended with non-fullerene acceptors.

Table 2. Electrochemical and Optical Properties of **PBDTI-OT**, **PBDTI-DT** and **PTI-DT**

Name	λ_{max}Soln (nm)		λ_{max}Film (nm)		$^1Shift(nm)$		$^2E_g^{Opt}$	E_{HOMO}	E_{LUMO}
	λ_{max1}	λ_{max2}	λ_{max1}	λ_{max2}	$\Delta\lambda_{max1}$	$\Delta\lambda_{max1}$	eV	eV	eV
PBDTI-OD	366, 440	631	374, 440	631	8, 0	0	1.53	-5.5	-3.9
PBDTI-OT	363, 437	628	370, 438	623	7, 4	-5	1.54	-5.7	-3.8
PTI-DT	—, 457	615	—,461	623	-, 4	8	1.56	-5.6	-3.7

[1] Abs peak shift from solution to film [2] $E_g = 1200/\lambda_{onset}$

3.2. *Photophysical properties of the copolymers*

To further understand the photo-physics of the copolymers their absorption and PL spectra were taken in CF, oDCB and Chex solution in a concentration range from 125 - 5.7 μg/ml. The absorbance of all the copolymers in the three solvents showed negligible shift with concentration gradient which indicates the absence of aggregation in the solutions. The absorption spectra of the copolymers remained the same with increasing solvent polarity as shown in Figure 5a-c(solid line). This confirms that the ground states (S_0) of the copolymers are non-polar. The PL spectra of **PBDTI-OD** showed a red shift of 18 nm as the solvent polarity increases from 2.7 (oDCB) to 4.2 (CF). The Stokes shift of **PBDTI-OD** in Chex is higher than both oDCB and CF despite its low polarity index of 0.2. Similarly, a 29 nm red shift in PL of **PBDTI-DT** is found with increasing solvent polairty from 2.7 (oDCB) to 4.2 (CF). An ever larger Stokes shift in was observed when Chex was used as a solvent. However, the PL spectra of **PTI-DT** showed negligible shift in the three solvents.

The red shift in PL of of **PBDTI-OD** and **PBDTI-DT** with increasing solvent while their absorption remained the same confirms the higher dipole moments of their first excited states (S_1). This is consistent with our assumption that the long wavelength region transitions in the copolymers have ICT character. Hence, their electronic structure changes from the non-polar $D - A$ to the dipolar $D^+ = A-$ configuration[12]. The larger Stokes shift observed in Chex solutions of **PBDTI-OD** and **PBDTI-DT** shows the population of a different state other than ICT. Consequently, the electron in the first excited state of the copolymers have two channels; one is the ICT state and the other is the tightly bound excitonic state. The later is populated when there is a significant interchain interaction either in films or solutions. A poor solvent like Chex is expected to form aggregates that induce interchain interaction in the solutions resulting in a red shifted PL. Thus, the emission in the non-polar solvent could be explained by the tightly bound interchain exciton model instead of the commonly used ICT model[22,23]. However, the Uv-Vis absorbance of **PBDTI-OD** and **PBDTI-DT** taken in solutions of a concentration range that the PL measurements were taken confirmed the absence of aggregation. Therefore, the aggregation effect observed in the Chex solutions should be a self-aggregation causing the copolymers chains to form tight coils. As a result, the excited electron can be transferred to the other part of the chain acting as an interchain exciton [6,24]. Consequently, the PL spectra will be red shifted despite the low polarity of the solvent.

The photophysics of **PTI-DT** is quite different that both its ground and exited states are both not influenced by the polarity of the solvents. The similar Stokes shift both in polar (CF and oDCB) and the non-polar (Chex) solvents shows that the self-aggregation of the copolymer chain exists in all solvents. The copolymer showed a large absorption onset shift as well as peak shift while the BDT based copolymers showed no peak shift upon solidification (see Table 2). This was attributed to the twisting of the thiophene based copolymer in dilute solution in the absence of strong intermolecular interaction. The twisting in the backbone of **PTI-DT** favours self-aggregation effect in any solvent. The ICT population from the first excited state of **PTI-DT** is dominated by the excitonic state making the emitting state insensitive to polarity of the environment.

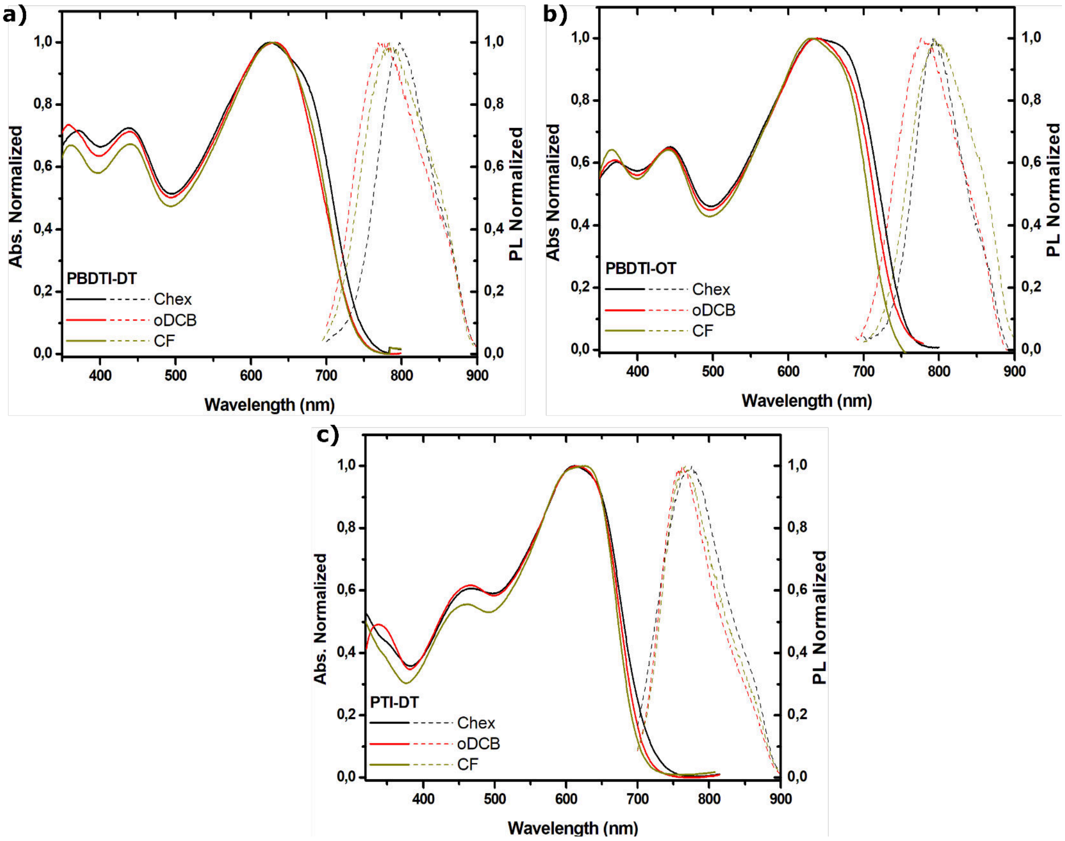


Figure 4. Absorption (solid line) and PL (broken line) of a) **PBDTI-OT**, b)**PBDTI-DT** and c) **PTI-DT** in Chex (black), oDCB (red) and CF (dark yellow) solutions

In summary, the BDT based copolymers have a bi-relaxation channel that can be modulated with the solvents while **PTI-DT** has a quasi-one relaxation channel. The population of ICT and tightly bound excitonic states were found in BDT-based copolymers while only the later was found in **PTI-DT**. The results suggest the importance of donor units in the synthesis of D-A copolymers for efficient ICT processes.

3.3. *Thermal Properties of **PBDTI-OT**, **PBDTI-DT** and **PTI-DT***

The thermal properties of **PBDTI-OT**, **PBDTI-DT** and **PTI-DT** were studied using TGA as shown in Figure 6. The three copolymers have a good thermal stability with decomposition temperature (T^D = 5% weight loss) above 380 ^{o}C. The thermal degradation in these materials follows a two step degradation: one around 380 ^{o}C and the other above 550 ^{o}C. The first degradation accounts for the chopping of the side chains. The shorter side chain in the isoindigo unit of **PBDTI-OT** has slightly increased its thermal stability compared to **PBDTI-DT**despite its lower molecular weight. The second thermal degradation is due to the decomposition of the backbone structure of the copolymers. The slight increase in the degradation temperature in **PBDTI-OT** also shows the strong bonding in its backbone structure compared to **PBDTI-DT** and **PTI-DT**. In general, the thermal stability of the copolymers makes them applicable to flexible organic solar cells which normally are processed below 150 ^{o}C.

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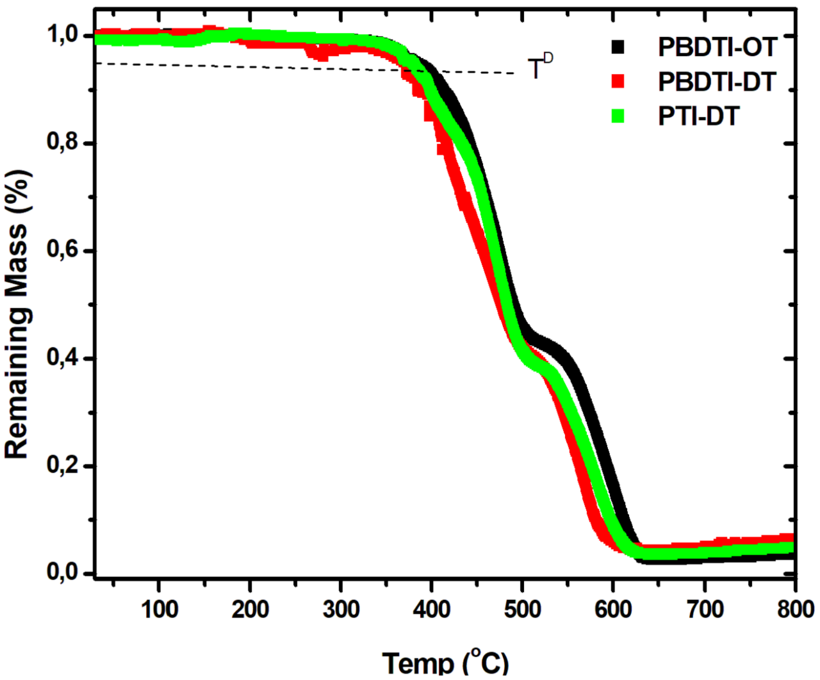

Figure 5. TGA measurement of **PBDTI-OT**(black), **PBDTI-DT**(red) and **PTI-DT**(green)

*3.4. Structural properties of **PBDTI-OT**, **PBDTI-DT** and **PTI-DT** films*

The structures of the copolymers were studied by powder XRD in drop casted thin films and the result is shown in Figure 7. The XRD patterns of the three copolymers exhibit a broad peak (010) centered around $2\theta = 22^o$ due to the $\pi - \pi$ stacking. The calculated $\pi - \pi$ stacking distance using Bragg's equation (eq-1) are 0.38, 0.41 and 0.41 nm in **PBDTI-OT**, **PBDTI-DT** and **PTI-DT** films, repectively confirming the precence of strong intermolecular interaction in the copolymers backbones [25]. **PBDT-DT** and **PTI-DT** exhibit a (100) diffraction peak at $2\theta = 3.82$ and 3.60^o corresponding to lammelar spacings of 2.3 and 2.5 nm, respectively. The inter-lammelar spacing in **PTI-DT** (2.5) nm) is higher than the well studied thiophene based homopolymer, poly-3-hexylthiophne (P3HT) (d= 1.63) [26]. This is due to the longer side chains both in the thiophene and isoindIgo units of **PTI-DT** compared to P3HT. Note here that the (100) plane diffraction peak is sharper in **PTI-DT** indicating its slightly higher crystallinity over the BDT based copolymer. On the other hand, the benzodithiophene based copolymer with shorter side chain on the isoindigo unit (**PBDT-OT**) is fully amorphous. The higher crystallity of thiophene based copolymer is beneficial for improved charge transport.

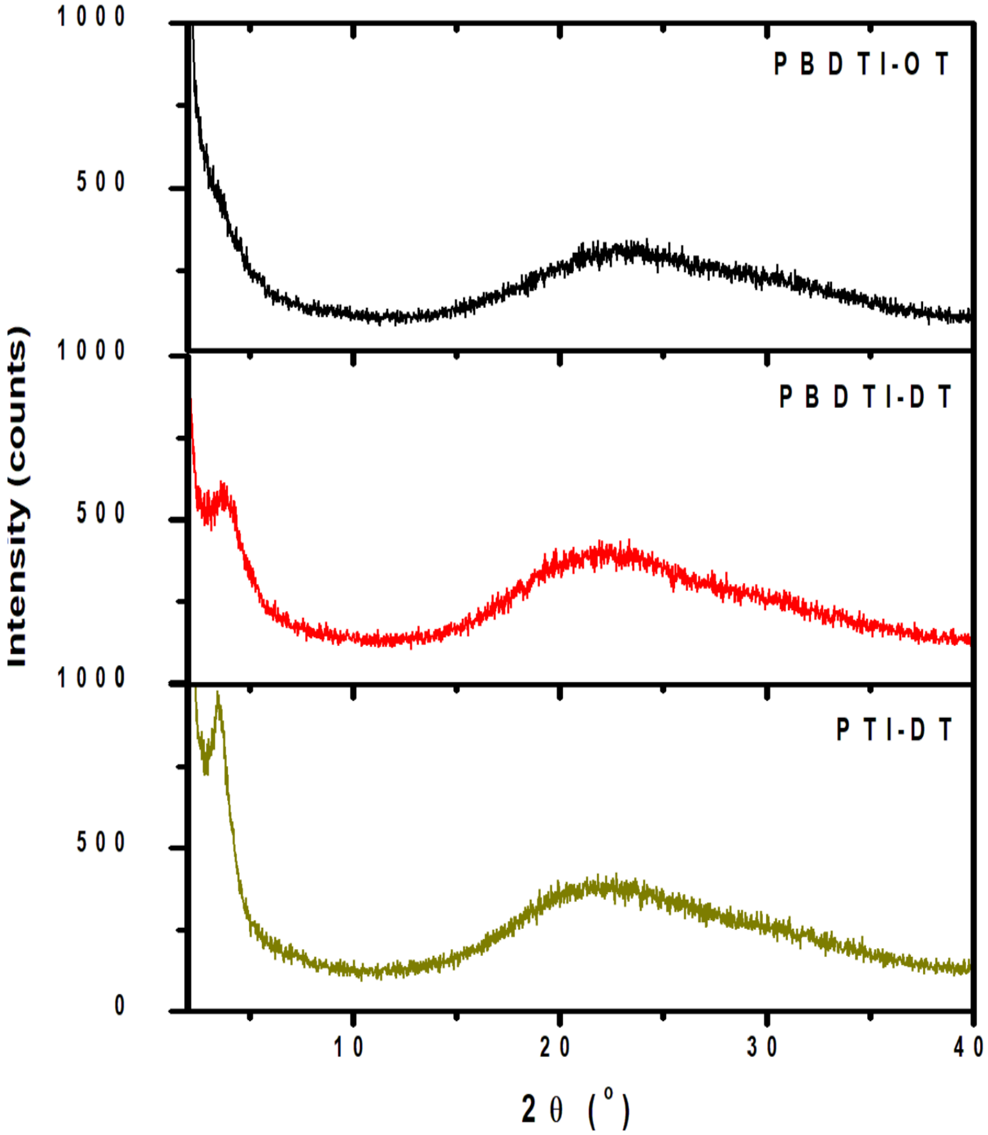

Figure 6. XRD patterns **PBDTI-OT** (black), **PBDTI-DT**(red) and **PTI-DT**(dark yellow) in drop casted films.

4. Conclusions

Three copolymers with BDT (**PBDTI-OD** and **PBDTI-DT**) and thiophene (**PTI-DT**)donor units and isoindigo acceptor units were designed and synthesized using DAP method. The molecular weight of the BDT based copolymers was more than two fold higher than **PTI-DT**. The copolymers absorb in a wide range from from 300 to above 760 nm in thin films making them low band gap polymer with $E_g \approx 1.5$ eV. The photophysical properties of the copolymers were studied both in films and solutions. Solvent polarity dependent spectroscopy studies on **PBDTI-OD** and **PBDTI-DT** show that the ground state is not sensitive to polarity of the environment while the excited state is. This leads us to conclude that the ground states of the BDT-based copolymers are non-polar. The PL spectra of the BDT-based copolymers were red shifted with increasing solvent polarity of chlorinated solvents confirming the dipolar characteristics of their first excited state. Therefore, the first excited state has an ICT characteristics. However, the Stokes shift of **PBDTI-OD** and **PBDTI-DT** in the non-polar solvent, Chex, was not blue shifted as expected from its low polarity index. Self-aggregation of the copolymers in the poor solvent was found to favour population of a tightly bound excitonic state thereby inhibiting the generation of ICT state. The absorption and PL spectra of the thiophene based copolymer were not influenced by solvent polarity. This leads us to conclude that self-aggregation in the thiophene based copolymers is induced despite the solvent polarity. Therefore, ICT state population in **PTI-DT** is not efficient. The copolymers showed excellent thermal stability with decomposition temperature above 380 ^{o}C. The XRD patterns of the three copolymers showed a halo from (010) plane due to $\pi - \pi$ stacking. A second diffraction peak was observed in **PBDTI-DT** and **PTI-DT** confirming a better crystallinity in these copolymers.

Author Contributions: ZA and WM have synthesized the copolymer and write up the synthesis part. NT characterized the remaining part of the work and write it up.

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