

A Review of the Modification of PCDTBT Structure Used in the Polymeric Solar Cells

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Review Article

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ABSTRACT

This paper is a review about the modification of poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) structure over the last few years. This manuscript presents the various carbazole, benzothiadiazole, and π -bridge modified units in PCDTBT. These modifications include fluorination, π -bridge alteration, ladderization of donor unit, substitution of selenium, and architecture of donor-acceptor arrangement along the polymeric backbone, such as D- π -A₁- π -A₂- π and et cetera. All the resulting PCDTBT derivatives were studied for the purpose to enhance the photovoltaic performance of the resulting polymeric solar cell. Although the power conversion efficiency of these modified PCDTBTs has yet surpassed 10%, PCDTBT-based copolymers still remain as one of the significant polymers in the research of the polymeric solar cell.

INTRODUCTION

Recently, the power conversion efficiency (PCE) of the polymeric solar cell (PSC) already surpassed 10%^[1-4]. There are various options for both donor and acceptor units to synthesize the excellent photovoltaic (PV) performance of conjugated copolymer. Amongst the synthesized donor-acceptor (D-A) copolymers, PCDTBT is one of the D-A copolymers which has been extensively studied by researchers in the laboratory and under real-world conditions^[5,6]. Hence, the focus point of this review paper is on the incorporation of electron-donating carbazole (Cz) unit with the electron-accepting benzothiadiazole (BT) unit through heterocyclic π -bridges.

The donor moiety along the PCDTBT backbone is carbazole, also known as 9-azafluorene, which is structurally analogous to the fluorene (**Figure 1**)^[7-9]. The only difference between fluorene and carbazole is that the carbon atom at the 9th-position of fluorene was replaced by a nitrogen atom to form carbazole. According to Cheng et al., this replacement forestalls the ketone formation at the 9th-position as oxidation is not possible to the nitrogen atom present in the carbazole structure. Besides that, desirable solubility nature of carbazole can be obtained by functionalized the 9th-positioned nitrogen with suitable alkyl chains. Moreover, carbazole units can be presented in the form of stable radical cation as they exhibit good photochemical and thermal stability for both. These characteristics enable the carbazole to be applied as p-type semiconductors^[9].

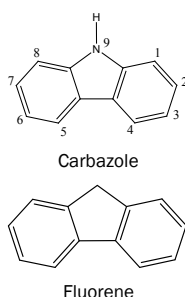


Figure 1. Chemical structure of carbazole and fluorene.

Carbazole monomers can undergo polymerization by linked with each other at either 3,6-position or 2,7-position to form

poly(3,6-carbazole) or poly(2,7-carbazole) respectively^[9]. It was found that the *meta*-linkages of phenylene present in poly(3,6-carbazole) have restricted conjugation. For the 2,7-linked polycarbazole, the *para*-linkage result in longer effective conjugation length^[9,10]. Researchers discovered that the poly(2,7-carbazole) is more favorable to be used as donor moieties in PSC than poly(3,6-carbazole). This is because of the charges able to diffuse along the 2,7-linked conjugated carbazole backbones better than the 3,6-linkage carbazole PSC^[9].

In the year 2009, three researchers from Japan successfully synthesized poly(1,8-carbazole). This study also reported that the alkyne-linked poly(1,8-carbazole) exhibits better thermal stability as compared to the poly(1,8-carbazole) without alkyne linkage^[11]. Besides that, the efficiency of carbazole connectivity increased from poly(3,6-carbazolyene)<poly(1,8-carbazolyene)<poly(2,7-carbazolyene)^[12]. In addition, carbazole monomers can also be polymerized through 2,9-position and 3,9-position^[13-16]. Furthermore, there is some research applied the ladderized carbazole as the donor moiety, which will be further elaborated in Section 6.

During the past few decades, intensive study has been done by incorporating various kinds of carbazole derivatives with different types of acceptor units, which is denoted as X in **Figure 2**. Some examples for X are quinoxaline, pyrido[3,4-b]pyrazine, benzoxadiazole, thienopyrazine, benzothiadiazole, and etcetera^[17]. This review paper focuses on the PCDTBT and its derivatives, which the X is benzothiadiazole. The introduction of various types of alkyl chains on carbazole unit and alkoxy substitutions on the benzothiadiazole unit help to obtain reasonable and desirable solubility of the resulting copolymers during the solution processing. Besides that, the alkoxy substitutions also enhance the planarity of the polymers^[18]. After comparison, the octyl and octyloxy substituents are found to be the most promising side chains for the PCDTBT derivatives.

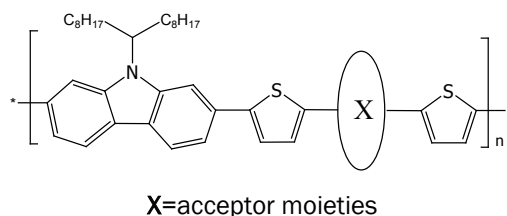


Figure 2. Carbazole-based polymers.

PCDTBT

During the past two decades, poly[N-9'-heptadecanyl 2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) (**Figure 3**) was discovered to be a promising donor material which possesses impressive stability and low HOMO level for the solar cell^[19-21]. Hence, intensive study and various modifications have been done on PCDTBT in order to improve the existing features and efficiency^[22]. The initial PCE achieved by PCDTBT-based polymeric solar cell (PSC) is 3.6%^[23]. However, this PCE value has been surmounting by replacing the PC₆₁BM with PC₇₀BM acceptors in bulk heterojunction (BHJ) of PSC, and the resulting PCE value is c.a. 6.1% with internal quantum efficiency (IQE) up to 100%^[24-26].

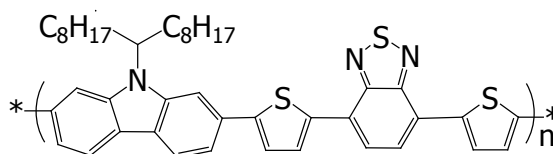


Figure 3. Chemical structure of PCDTBT.

Recently, the PCE value reported by Wang et al. in 2013 have achieved up to 7.5% by employing graphene oxide as the electron-transporting layer of PCDTBT: PC₇₁BM-based BHJ PSC^[25,27]. Even though the recent highest PCE for PCDTBT-based PSC is yet to surpass 10% PCE, PCDTBT copolymers have still remained as a remarkable conjugated copolymer^[22,24,25,27,28]. Various types of PCDTBT derivatives have been synthesized via ladderization, fluorination, or substitution with analogous compounds, such as selenophene, naphthothiadiazole and excreta to optimize the existing PV properties^[29].

Spectacularly, it was found that the PCE of PCDTBT-based PSC can be further improved by the addition of small amount of silver nanoparticles into the active layer^[30].

Modification of BT Unit

Ding et al. developed an analogous poly (N -90-heptadecanyl -2,7- carbazole -alt -5,5- (40,70-di-2-thienyl -50, 60-bis (octyloxy)-2, 1, 3-benzothiadiazole), PCDOTBT by incorporated two octyloxy chains on the benzothiadiazole unit^[31]. These two octyloxy side chains on the benzothiadiazole unit induce the S-O molecular interaction, which enhances the solubility in common organic solvent and increases the planarity of the resulting copolymers^[31,32].

The optical and electrochemical properties of the PCDOTBT are summarized in **Table 1**. The highest PCE value achieved

by the PCDDTBT-based PSC device is 1.44% with the 2.5% of DIO additive in DCB processing solvent^[31]. In addition, Ding et al. also reported a copolymer with impressive PCE, i.e., 4.02%, which used benzodithiophene instead of carbazole as donor moieties. Neither additives nor annealing is applied during the fabrication of this polymer-based PV device^[33].

Table 1. The experimental data for PCDTBT and its derivatives.

Characteristics Polymer	Copolymers							BHJ PSC							Ref	
	M _n ^a (kDa)	M _w ^a (kDa)	T _d ^b (°C)	HOMO ^c (eV)	LUMO ^c (eV)	PDI	E _g ^d (eV)	E _g ^e film ^e (eV)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF	μ _h ^f (cm ² /Vs)	μ _e ^f (cm ² /Vs)	PCE (%)		
PCDTBT	PC ₆₁ BM	37	73	430	-5.5	-3.6	1.97	1.87	1.88	0.89	6.92	0.63	1 × 10 ⁻³	n.a.	3.6	[17,23]
	PC ₇₀ BM							n.a.	n.a.	0.88	10.6	0.66	n.a.	n.a.	6.2	[24]
PCDDOTBT	64.8	25.1	327	-5.11	-3.29	2.58	1.82	1.82	0.72	5.63	0.36	2.03 × 10 ⁻⁴	n.a.	1.44	[31]	
PCDDOTBT-12	24.6	50.5	n.a.	-5.6	-3.61	2.05	1.99	1.99	0.97	10.68	0.58	1.8 × 10 ⁻³	n.a.	6.04	[34]	
PCDTNT	12.8	36.4	425	-5.37	-3.63	1.67	1.74	1.71	0.81	4.98	0.33	2.0 × 10 ⁻⁶	n.a.	1.31	[38]	
HXS-1	DCB	16.6	51.4	300	-5.21	-3.35	3.1	1.86	n.a.	0.85	8.3	0.51	3 × 10 ⁻⁵	1 × 10 ⁻³	3.6	[32,40]
	DCB/DIO							1.86	1.95	0.81	9.8	0.69	1 × 10 ⁻⁴	3 × 10 ⁻⁴	5.4	[39]

^aMeasurement conducted by differential refractive index(DRI) detection. ^bOnset of degradation temperature obtained from TGA with 5% of weight loss. ^cHOMO and LUMO energy level determined from the onset of oxidation and reduction, respectively. ^dElectrochemical energy gap= $|LUMO-HOMO|$ (eV). ^eOptical energy gap of the copolymeric thin film, E_g^{opt}. ^fμ_h represent hole mobility while μ_e represent electron mobility (cm²/Vs).

When the octyloxy side chains of BT were replaced with dodecyloxy groups, PCDDOTBT-12 is formed. These two dodecyloxy chains result in slight enlargement of band gap by down-shift c.a. 0.1 eV HOMO energy level of PCDDOTBT-12 as compared with the PCDTBT. From **Table 1**, it can be noticed that the band gap of PCDDOTBT-12 is largest. The annealed (60 °C, 20 min) PCDDOTBT-12: PC₇₁BM blend film (1:4 w/w) PSC possesses relatively high hole mobility than the other copolymers PSC in **Table 1**^[34,35]. The blend film was incorporated in an inverted solar cell, which achieved PCE value up to 6.04% when organic poly(diethyl-6-(2,7-carbazol-9-yl)hexylphosphonate), PC-P interlayer was applied in the PV device^[34,36].

In addition, Casey et al. reported an experiment about the substitution of thioalkyl (-SR) onto the BT unit of PCDDOTBT, known as PCSDTBT. Both -SR and -OR (alkoxy) group possess different effects on the polymeric conformation and the electronic properties of the copolymers. This research compares both PCDDOTBT and PCSDTBT. The -SR group was found to result in extremely large Stokes shifts and high V_{oc} value (i.e., >1.0 V). The PCE value for PCDDOTBT in this study is c.a. 4%, which is double the PCE of PCSDTBT1 and PCSDTBT2, c.a. 2%. The alteration of -SR chain length does not have great influence on PV performance of the PSC^[37].

When the BT in PCDTBT was replaced with 2,1,3-naphthothiadiazole (NT), the extended aromatic π-conjugation in the acceptor unit has successfully narrowed the optical band gap of PCDTNT (**Figure 4**) as compared to the PCDTBT (1.87 eV). The result tabulated in the BHJ PSC column for PCDTNT is obtained from PCDTNT:PC₇₁BM blend which contains 1.0 v/v% 1,8-octanedithiol (ODT) additive, which enhance the PV performance of PCDTNT-based PSC to 1.31% PCE value. The PCE value of PCDTNT-based PSC without additive only achieve 0.42%. These low PCE values can be explained from the relatively low FF value obtained by PCDTNT than the other PSC in **Table 1**, which limited the PV performance of PCDTNT-based PSC. The low FF value is due to the relatively low molecular weight (M_w), low hole mobility, and the bulky NT units result in unfavourable morphology^[38].

HXS-1

Poly(2-(5-(5,6-bis(octyloxy)-4-(thiophene-2-yl)benzo[c][1,2,5]thiadiazole-7-yl)thiophene-2-yl)-9-octyl-9H-carbazole), HXS-1 (**Figure 5**) was firstly reported by Qin and co-workers in 2009, and further studied by many other research teams. According to Qin et al., HXS-1 was designed for a more planar configuration in order to enhance the charge transport ability of the copolymers in solar cell application. The result shows that the HXS-1-based PSC prepared by using DCB: DIO as solvent possesses high FF and J_{sc} value, i.e., 69% and 9.6 mA/cm², respectively. These values indicate that a balanced charge transport have been achieved and the FF of 0.69 was the highest value amongst the PSC that achieved >5% on that time. Besides that, HXS-1 exhibits wide absorption in the visible region and possesses promising solubility in both chloroform and dichlorobenzene (DCB)^[39].

In addition, Li et al. studied the effect of 1,8-diiodooctane (DIO) additive on the PV performance of HXS-1 -based PSC. The results show that the present of DIO helps to enhance the charge transport and reduce the recombination of charge carrier in the blend films. The external quantum efficiency (EQEs) of PSCs spin-coated without DIO was found to be much lower than the PSCs with DIO. All in all, the addition of DIO additive as the solvent in the HXS-1: PC₇₁BM based PSC enhanced the photovoltaic performance of the cells^[40]. The PCE of the PSC increased from 3.6%^[32,40] to 5.4%^[39,40] by using DIO as the solvent additive.

Furthermore, HXS-2 and HXS-3 are produced when two and three carbazole donor units are linked together before copolymerized with the acceptor moieties^[39,41]. The torsion angle of the copolymeric backbone increased when the carbazole units increased. The PCE value of HXS-2 and HXS-3 are 0.43% and 0.23%, which experienced dramHXS-1^[41].

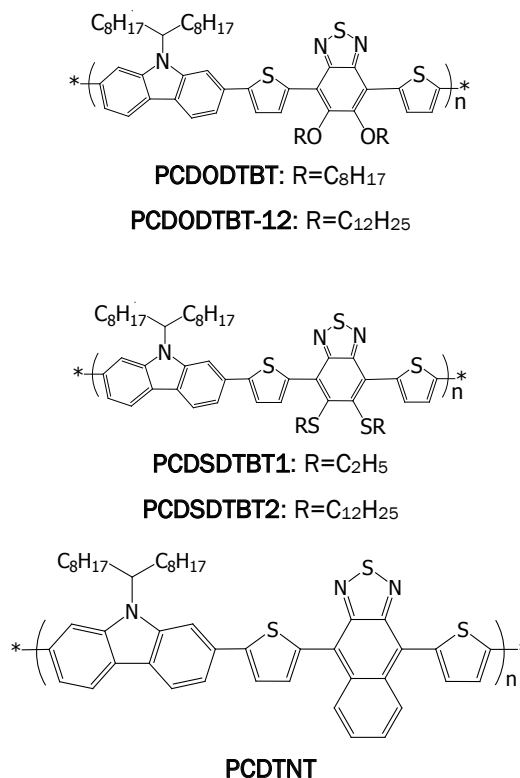


Figure 4. Incorporation of alkoxy and thioalkyl groups in BT unit and replacement of BT by NT unit.

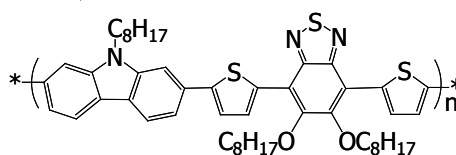


Figure 5. Chemical structure of **HXS-1**.

EFFECT OF FLUORINATION

Fluorination of the polymeric backbone was found to be a promising pathway to enhance the PV performance of BHJ polymeric solar cells^[42]. An introduction of fluorine atoms into the conjugated backbone enable the energy levels to be effectively tuned by lowering HOMO and LUMO without causing significant alteration in the energy band gaps. Besides that, fluorine atoms also enhance the charge transport, molecular arrangement, and the optical properties of the resulting conjugated polymers^[29]. The incorporation of these fluorine atoms needs to be done before functionalization^[29,42].

Interestingly, it was found that non-covalent Coulomb interaction (**Figure 6**) exists between fluorinated BT with the thiophene π -bridges through S...F, CH...F, CH...N interactions^[43]. Hence, many researchers start to grow interest in the fluorinated acceptor units^[44,45].

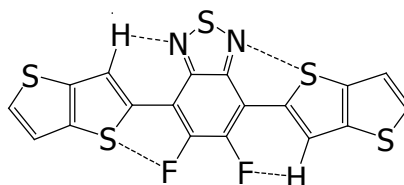


Figure 6. The non-covalent Coulomb interaction.

Umeyama et al. were the first to synthesize P1 for the study of fluorination effect on the physical and chemical properties of PCDTBT. P2 with extra hexylthiophene units was then synthesized to surmount the poor solubility of the former P1. The electron-withdrawing fluorine atoms tend to reduce the HOMO energy level of the copolymer, yet this fluorination effect can be offset by the addition of electron donating hexylthiophene units, which in turn lead to a higher HOMO level than the PCDTBT. Moreover, the optical band gap of the P2 film (1.82 eV) was found to be smaller than the PCDTBT (1.89 eV). On the contrary, the optical band gap for the P1 film is 1.96 eV, which is higher than PCDTBT. This high band gap was caused by the low molecular weight of P1 film due to the meagre solubility. Besides that, several factors result in the PCE values for 1:4 w/w, P1:PC₇₀BM (1.29%) and P2:PC₇₀BM (1.98%) blended based PSC devices were found to be much lower than the analogous PCDTBT (6.16%)^[46].

One year later, a research paper regarding the singly and doubly fluorination on the benzothiadiazole of PCDTBT was published by Kim et al. The experimental details of these two P3 and P4 derivatives were tabulated in **Table 2**. Based on the data obtained, P4 with two substituted fluorine atoms was found to have lower HOMO and LUMO energy levels relative to the singly fluorinated P3, and yet both P3 and P4 exhibit similar band gap. Besides that, the hole mobility for the P3 and P4-based organic thin film transistors (OTFT) c.a. $3.03 \times 10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and $9.50 \times 10^{-5} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ respectively [29].

Table 2. A summary of experimental and characterization data for **P1-P11**.

Characteristics Polymer	Copolymers						BHJ PSC								Ref.
	M_n^a (kDa)	M_w^a (kDa)	T_d^b ($^{\circ}\text{C}$)	HOMO ^{cv} (eV)	LUMO ^c (eV)	PDI	$E_g^{\text{elec d}}$ (eV)	$E_g^{\text{opt film}^e}$ (eV)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	μ_h^f (cm ² /Vs)	μ_e^f (cm ² /Vs)	PCE (%)	
P1	4	n.a.	409	-5.54	-3.58	1.5	1.96	1.96	0.82	4.93	0.32	n.a.	n.a.	1.29	[46]
P2	13	n.a.	407	-5.44	-3.62	2	1.82	1.82	0.88	6.56	0.34	n.a.	n.a.	1.98	
P3	11	n.a.	450	-5.54	-3.71	1.39	1.83	1.82	0.95	9.04	0.46	2.87×10^{-4}	1.64×10^{-4}	3.96	[29]
P4	31.5	n.a.	437	-5.67	-3.83	2.05	1.84	1.82	0.88	6.94	0.34	3.49×10^{-5}	7.27×10^{-5}	2.07	
P5	11.4	20.6	390	-5.23	-3.12	1.81	2.11	1.82	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	
P6	7.7	11.9	367	-5.44	-3.45	1.55	1.99	1.86	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	[22]
P7	6.1	8.9	351	-5.24	-3.11	1.46	2.13	1.88	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	
P8	9.1	23.9	328	-5.23	-3.48	2.63	1.75	n.a.	0.91	9.5	0.55	3.1×10^{-3}	n.a.	4.8	[32]
P9	31.1	57.2	n.a.	-5.2	-3.3	1.84	1.9	1.95	0.88	8.7	0.52	3.5×10^{-3}	n.a.	4.1	[54]
P10	18.6	48	n.a.	-5.3	-3.5	2.58	1.8	1.89	0.9	9.6	0.47	3.1×10^{-3}	n.a.	4.5	
P11	16.2	48.6	388	-5.47	-3.39	3	2.08	1.84	0.83	9.44	0.43	1.23×10^{-4}	n.a.	3.4	[18]

^aMeasurement conducted by differential refractive index(DRI) detection. ^bOnset of degradation temperature obtained from TGA with 5% of weight loss.

^cHOMO and LUMO energy level determined from the onset of oxidation and reduction, respectively. ^dElectrochemical energy gap=LUMO-HOMO I (eV).

^eOptical energy gap of the copolymeric thin film, E_g^{opt} . ^f μ_h represent hole mobility while μ_e represent electron mobility (cm²/Vs).

Later on, Cartwright et al. have investigated and compared the optical, electrochemical, thermal, and molecular arrangement of the three different type of fluorinated PCDTBT (**Figure 7**), i.e., PCffDTBT (P5), PCDTffBT (P6), and PCffDTffBT (P7). From **Table 2**, P5 was found to exhibit highest molecular weight than the other two counterparts, which was speculated to result in the highest decomposition temperature. Both copolymers with fluorinated carbazole unit (i.e., P5 and P7) were found to have higher HOMO and LUMO energy level as compared with the non-fluorinated carbazole-based copolymer, P6. However, the electrochemical bandgap achieved by P6 is the lowest amongst these three fluorinated PCDTBTs. Meanwhile, P5 has the lowest optical bandgap which enables the P5-based copolymer to harvest more photons from the solar spectrum. Besides that, the XRD study discovered that the copolymers with fluorinated benzothiadiazole unit (i.e., P6 and P7) have the ability to promote the π - π stacking of the solid state copolymeric backbones, which in turn improve the molecular ordering of the copolymer [22].

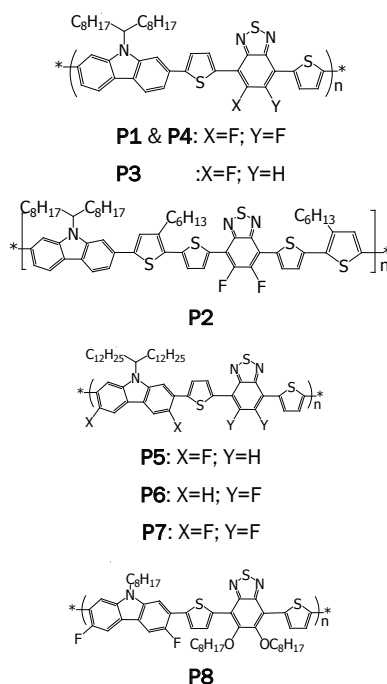


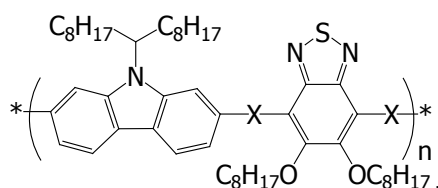
Figure 7. Fluorinated PCDTBT derivatives.

Fluorination of HXS-1 on 3,6-position of the carbazole donor unit produces the copolymer, P8, which was studied by Du et al. This study shows that the substitution of two fluorine atoms on the carbazole result in lower HOMO and LUMO energy levels. In comparison with the non-fluorinated HXS-1, P8 possesses smaller bandgap, higher V_{oc} , and J_{sc} , which manifest that P8 is a good donor material for PSC with PCE value up to 4.8%. Besides that, the thermal and electrochemical stability of the P8-based copolymer were found to be better than the HXS-1-based copolymer. This outcome is likely due to the fluorination of carbazole moiety which in turn protects the highly active 3,6-positions. DIO additive was used during the fabrication of HXS-1-based PSC to enhance the PV performance. On the other hand, the addition of DIO in the processing solvent during fabrication of P8-based PSC does not result in any positive impact on the PV performances but 1-chloronaphthalene (CN) can. The best PCE value, i.e., 4.80% was obtained from the PSC that fabricated by using trichlorobenzene (TCB) processing solvent which consists of 10% of CN^[32].

THE π -BRIDGES

There are a few studies about the π -bridges between donor and acceptor moieties along the polymeric backbones. It was found that the π -bridges enhance the π - π interaction which in turn facilitate the charge mobility of the copolymers^[47-52]. The π -bridges have a great impact on the optoelectronic properties and molecular architecture of the copolymers^[52]. Generally, the π -bridges are five-membered heterocycles which contain group 16 element, such as furan, thiophene, selenophene, and tellurophene^[48]. The most commonly used π -bridges are thiophene, and its derivatives, e.g. thienothiophene (TT), dithiophene (2T), or oligothiophenes. According to Wang et al., TT exhibits much superior PV performance than the furan and thiophene^[52,53].

In 2014, Pearson et al. reported the study of linker group effect of TT or 2T as the π -bridges of the copolymer donor material. This study found that there is a slight improvement in PCE value of P10-based PSC than the P9-based PSC (**Figure 8**). This is because the J_{sc} value of the P10-based blend OPVs is higher than the P9-based OPVs. The improvement of J_{sc} value without suppression of V_{oc} value, which results in small augment in PCE value of P10-based PSC as compared with the P9 PSC. Moreover, relatively red-shifted onset absorption and much narrow band gap have been obtained for P10 as compared to P9^[54]. Furthermore, by referring to the PCE value (1.44%) obtained by the PCDOTBT-based PSC, both P9 and P10-based PSC have achieved a huge leap in the PV efficiency. This can be concluded that the π -bridge conjugation increased from thiophene<2T<TT for the D(Cz)-A(BT) copolymers.



P9 : X \equiv dithiophene

P10 : X \equiv thienothiophene

P11 : X \equiv thienothiophene (with $-\text{OC}_{12}\text{H}_{25}$ as BT alkoxy side chains)

Figure 8. PCDOTBT polymers with different π -bridges.

In addition, there was a paper reported a conjugated polymer, P11 with dodecyloxy-chains on the benzothiadiazole units instead of the octyloxy side chains. The highest PCE value of P11, i.e., 3.4%, which is achieved by the P11-based PSC device with blend ratio of 1:4 for P11: PC₇₁BM and processing solvent of CB/DIO (20:1 v/v)^[18].

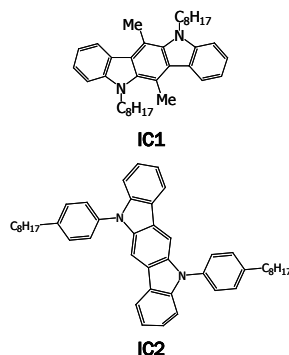
On the other hands, a group of researcher has investigated the copolymers with three different donors (i.e., fluorene, carbazole, dibenzosilole) linked directly to the BT acceptors without any π -bridges. However, the PV efficiency for all these three copolymeric PSCs is extremely low, with PCE value merely exceed 0.2%^[55].

LADDERIZATION

An electron donating indolocarbazole unit is formed when two carbazole units are fused together by sharing one benzene ring. This large rigid coplanar indolocarbazole ring improved the intermolecular π - π stacking, which enhanced the charge mobility in the PSC^[53,56,57]. The indolocarbazole can be polymerized through either 3,9-linkage or 2,8-linkage, where the former possesses more extensive conjugation along the polymeric backbone than the latter linkage^[58,59].

Moreover, there are several papers reported that the indolo[3,2-b]carbazole and its derivatives (**Figure 9**) are excellent hole transport units, which can be applied to fabricate high mobility organic thin-film transistor (OTFT)^[59-61]. For example, the hole mobility of the IC1 and IC2 OTFT is up to $10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and $0.12 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively^[62,63].

It was found that the BT exhibits similar spatial structure to the IC donor, which enhance the spectral sensitivity range, photosensitivity, and photoconductivity^[64]. Hence, this section mainly focused on the copolymers with IC as the donor and 2,1,3-benzothiadiazole (BT) as the electron acceptor unit.


Figure 9. Indolocarbazole derivatives.

Lu et al. intend to synthesize a narrow band gaped PSC with excellent charge mobility by incorporated the high mobility indolocarbazole. They have successfully fabricated a favourable copolymer, i.e., In1, by incorporated indolocarbazole with benzothiadiazole through oligothiophenes. Based on the absorption peaks present in the spectra of In1, it can be concluded that intramolecular charge-transfer (ICT) and π - π transitions were present along the In1, which indicates that the energy has been efficiently transferred from the indolocarbazole units to the electron accepting moieties. Besides that, the low HOMO energy level of In1 is c.a. -5.17 eV, which resulted in favourable V_{oc} value and high air stability. The PCE value achieved by In1:PC₆₁BM (1:2 w/w) s PSC is 3.6% [57].

In 2009, Tsai et al. reported several indolocarbazole based polymer, one of them is In2, which the indolocarbazole units are directly linked to the benzothiadiazole units via 2,8 linkage without any thiophene π -bridges. Unfortunately, the PCE value obtained from In2:PC₆₁BM (1:4 w/w) blend film is relatively low, i.e., only 0.49%. This is because the HOMO energy level of In2 is relatively higher as compared with the other copolymers, which account for the low V_{oc} value, and finally result in low PCE value [59]. According to Blouin et al., the preferable range for the HOMO and LUMO energy level of an ideal copolymer for PSC are -5.2 to -5.8 eV and -3.7 to -4.0 eV [17], respectively, which the HOMO and LUMO values of In2 are completely out-landed these ranges.

The donor-acceptor moieties of In3 were arranged in D- π -A- π -A- π form, which will be further elaborated in the later section. The photovoltaic properties of the In3:PC₇₁BM with 1:1 and 1:2 (w/w) blend films were studied, and the result shows that, 1:2 blend film (2.21%) possesses better PCE value than 1:1 blend film (1.45%). Besides that, the SEM images show that the surface morphology improved when the ratio of In3:PC₇₁BM blend film increased from 1:1 to 1:2, which also result in much higher J_{sc} value for 1:2 blend PSC. The details tabulated in **Table 3** is based on 1:2 w/w In3:PC71BM PSC [65].

Table 3. A summary of experimental and characterization data for indolocarbazole-based PSC.

Characteristics	Copolymers						BHJ PSC								Ref
	Polymer	M_n^a (kDa)	M_w^a (kDa)	T_d^b ($^{\circ}$ C)	HOMO ^{cv} (eV)	LUMO ^c (eV)	PDI	$E_g^{elec\ d}$ (eV)	$E_g^{opt\ film^e}$ (eV)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	μ_h^f (cm ² /Vs)	μ_e^f (cm ² /Vs)	
ICBT1	19.5	n.a.	410	-5.17	-3.15	2.1	2.02	1.89	0.69	9.17	0.6	n.a.	n.a.	3.6	[57]
ICBT2	n.a.	3.1	464	-4.9	-2.81	1.3	2.09	2.09	0.55	2.11	0.4	1.93×10^{-4}	n.a.	0.49	[59]
ICBT3	18.2	44.4	380	-5.42	-3.62	2.4	1.8	1.8	0.8	6.4	0.4	n.a.	n.a.	2.21	[65]
ICBT4	7.4	12.2	326	-4.95	-3.38	1.7	1.57	1.7	0.46	4.55	0.4	n.a.	n.a.	0.82	[66]
ICBT5	8.5	14.6	328	-5	-3.54	1.7	1.46	1.65	0.54	4.79	0.4	n.a.	n.a.	1.63	
T-ICBT	13	n.a.	n.a.	-5.4	-3.3	1.3	2.1	1.77	0.84	8.54	0.4	9.11×10^{-5}	n.a.	2.62	[71]

^a Measurement conducted by differential refractive index(DRI) detection. ^b Onset of degradation temperature obtained from TGA with 5% of weight loss. ^c HOMO and LUMO energy level determined from the onset of oxidation and reduction, respectively. ^d Electrochemical energy gap= $|LUMO-HOMO|$ (eV). ^e Optical energy gap of the copolymeric thin film, E_g^{opt} . ^f μ_h represent hole mobility while μ_e represent electron mobility (cm²/Vs).

Two random copolymers, ICBT4 and ICBT5 (**Figure 10**) were prepared by varying the ratios of donor and acceptor moieties through Stille cross-coupling reaction. For the 1:1 w/w copolymer:PC₆₁BM, the ICBT5 (0.90%) achieved much higher PCE value than ICBT4 (0.82%), as ICBT5 possesses lower HOMO energy level and higher content of donor units along the copolymeric backbone than ICBT4. The PCE value of ICBT5:PC₆₁BM experienced a slight deduction (0.88%) when the weight ratio increased from 1:1 to 1:3. However, 1.63% PCE value was achieved when the PC₆₁BM was replaced with PC₇₁BM and the 1/1 ratio remain as 1:1 [66].

Interestingly, a thiadiazole-fused indolocarbazole (TIC) monomer was successfully synthesized by Balaji et al. and followed by a 3,9-linked TIC polymer (**Figure 11**) was obtained from the monomer through electropolymerization. The result of the optical band gap of TIC polymer (2.4 eV) is lower than its monomer (2.8 eV) due to the LUMO energy level of TIC monomer decreased from -2.59 eV to -3.14 eV after electropolymerization and yet only slight alteration for the HOMO energy level (i.e., 5.34 ± 5 eV) [67].

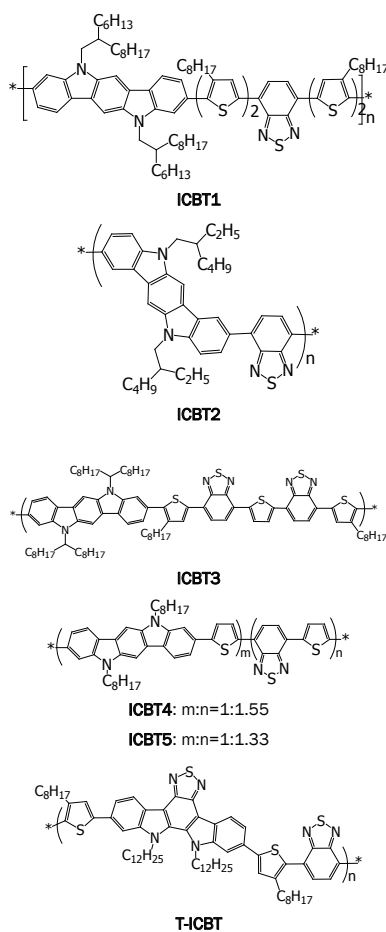


Figure 10. Indolocarbazole-based copolymers.

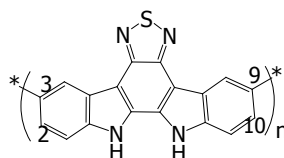


Figure 11. TIC polymer.

Moreover, when the meta-positions (i.e., 2- and 10- positions) of *N*-2-ethylhexyl TIC monomer was substituted with either halide (e.g. -Cl) or hydroxyl groups, the UV-vis spectra of both TIC derivatives are typical of planar conjugated systems, except the peaks which represent the meta-substitutes [68,69]. Besides that, based on the values of oxidation and reduction onsets, the estimated HOMO and LUMO energy levels are -5.49 eV and -3.05 eV, respectively for both TIC derivatives. Peculiarly, the obtained HOMO value is agreed upon the calculated value done by Balaji et al. for alkylated TIC monomers [67,69]. A few years later, a research paper about TIC copolymerized with alkylated-dithienosilole was published. Based on the research, the HOMO energy level increased to c.a. -5.03 eV and LUMO energy level experienced only slight increment, c.a. -2.98 eV. This has successfully reduced the electrochemical band gap of the TIC-based polymer [70].

Furthermore, Park et al. have successfully synthesized TIC-based copolymer, which incorporated with BT through oligothiophenes π -bridges. The experimental result shows that, the PCE value achieved by T-ICBT: PC71BM (1:2 w/w) blend PSC is 1.47%. However, the PCE of 1:2 T-ICBT-based PSC can be further soared to 2.62% by introducing 1 nm LiF thin-film as electron transporting layer [71]. This thin LiF interlayer helps to stabilize the V_{oc} , enhance the J_{sc} and FF of the BHJ solar cells, and finally improved the PCE value [72-74].

SUBSTITUTION OF SELENIUM

In the past few years, some researchers try to replace benzothiadiazole and thiophene present in the PCDTBT and PCDDTBT (**Figure 8**) with benzoselenadiazole and selenophene, respectively. This is because the researchers intend to harvest the lower energy photons in the solar spectra. To achieve this goal, conjugated polymer with lower bandgap is desired.

Recently, certain heavy atoms are applied to tune the band gap of the conjugated polymers. Selenium or tellurium are the candidates to replace sulphur atoms present in the heterocyclic polymer (**Figure 12**). However, selenium possesses much similar

chemical properties and electronegativity as the sulphur than the tellurium [75,76]. Besides that, selenophene has lower aromaticity than thiophene, which led to the elevation of the quinoid resonance property of the synthesized copolymers. This effect results in the enhancement of planarity, augmentation of the effective conjugation length, followed by lowering the bandgap [77]. Moreover, benzoselenadiazole was ascertained to have the ability to extend the absorption spectrum towards the infrared region and consequently lower the band gaps of the conjugated polymers [75,78].

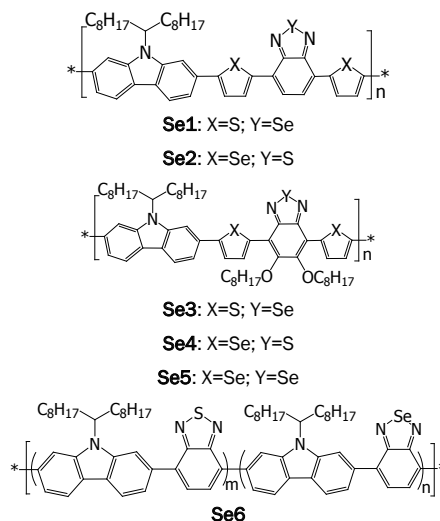


Figure 12. Selenium substituted PCDTBT derivatives.

First, Zhao et al. blended the Se1 copolymer with PC₆₁BM and discovered that the PCE value increased with the w/w ratio of Se1:PC₆₁BM from 1:1 to 1:4, i.e., 0.39% to 1.46%. Moreover, the PCE further increased to 2.58% when the PC₆₁BM replaced with PC₇₁BM acceptors [75]. The OPV devices based on Se2 and Se4, synthesized by Alghamdi et al., were fabricated by blending the copolymer (Se2 or Se5) together with PC₇₀BM in 1:2, 1:3, 1:4 w/w ratios. The best PV performance of Se2 and Se4-based OPVs were obtained from 1:3 and 1:4 blends, respectively. Meanwhile, the thickness of both Se2 and Se4-based active layer were 60 nm and the solvent used for the film casting were CHCl₃ and CB, respectively [79]. Before that, Kim et al. have annealed Se2 thin films, and the best hole mobility obtained was up to 1.0×10^{-3} cm²/Vs, which the film synthesized after thermal annealing at 150 °C. Moreover, the PV device with 1:4 w/w thermally annealed Se2:PC₇₁BM blend exhibits higher PCE value than the non-annealed Se2 based OPV, i.e., 4.12% and 2.76%, respectively [80].

Next, the highest PCE value achieved by PSC devices when Se3 and Se5 were blended with PC₇₁BM in 1:2 and 1:3 w/w ratio as compared with the other blend ratio. It was found that thermal annealing of Se3 and Se5 copolymers at 150 °C for c.a. 10 minutes causes a slight decrease in PCE value of Se3 OPVs, while improved the PCE for Se5 OPVs [81]. The other details were tabulated in **Table 4**. The fluorescence quantum yield of the conjugated polymers is inversely proportional to the number of selenium atoms present [76]. This also can be denoted by the following comparison, i.e., the Se5 exhibited higher PCE value than the Se3 [81].

Table 4. The characterization data for selenium substituted copolymers (**Se1-Se6, SeF1, SeF2**).

Characteristics	Copolymers						BHJ PSC								Ref.
	Polymer	M _n ^a (kDa)	M _w ^a (kDa)	T _d ^b (°C)	HOMO ^c (eV)	LUMO ^c (eV)	PDI	E _g ^{elec d} (eV)	E _g ^{opt film^e} (eV)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF	μ _h (cm ² /Vs)	μ _e (cm ² /Vs)	
Se1	14	17	390	-5.28	-3.55	1.2	1.73	1.73	0.75	7.23	0.5	3.9×10^{-4}	n.a.	2.58	[75]
Se2	3.9	9.4	n.a.	-5.46	-3.25	2.4	2.21	n.a.	0.85	6.62	0.6	5.08×10^{-5}	5.58×10^{-3}	3.34	[79]
	n.a.	n.a.	n.a.	-5.4	-3.7	n.a.	1.7	1.7	0.79	11.7	0.5	1×10^{-3}	n.a.	4.12	[80]
Se3	32	61	308	-5.29	-3.4	1.9	1.89	1.89	0.74	5.07	0.5	2.9×10^{-3}	n.a.	1.87	[81]
Se4	26	62.9	n.a.	-5.47	-3.09	2.4	2.38	n.a.	0.92	10.28	0.5	3.36×10^{-4}	n.a.	4.35	[79]
Se5	43	63	315	-5.35	-3.53	1.5	1.82	1.82	0.77	7.87	0.5	9.5×10^{-3}	n.a.	2.88	[81]
Se6	n.a.	n.a.	n.a.	-5.85	-3.67	n.a.	2.18	2.18	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	[85]
SeF1	21.1	44.3	382	-5.32	-3.59	2.1	1.73	1.74	0.78	4.29	0.3	4.63×10^{-7}	7.81×10^{-6}	1.09	[44]
SeF2	15.6	29.6	385	-5.35	-3.6	1.9	1.75	1.78	0.82	3.44	0.3	5.74×10^{-7}	8.08×10^{-6}	0.91	

^aMeasurement conducted by differential refractive index(DRI) detection. ^bOnset of degradation temperature obtained from TGA with 5% of weight loss.

^cHOMO and LUMO energy level determined from the onset of oxidation and reduction, respectively. ^dElectrochemical energy gap= $\text{LUMO}-\text{HOMO}$ I (eV).

^eOptical energy gap of the copolymeric thin film, E_g^{opt}. ^fμ_h represent hole mobility while μ_e represent electron mobility (cm²/Vs).

These copolymers exhibit two major absorption bands in the UV-vis spectra. The absorption band located at the longer wavelength region accredited to the intramolecular charge transfer (ICT) interaction between the donor-acceptor units. On the other hands, the absorption band in the shorter wavelength region attributed to the π - π^* transition of the conjugated polymeric chains [75,80-84].

Furthermore, Kutkan et al. synthesized and studied the characteristic of a random copolymer, Se6. Even though the details of this finding is not as completed as the others, yet the result still shows that the HOMO and LUMO energy level of Se6 is relatively deeper than the other Se-substituted copolymers. Besides that, from the **Table 3**, it can be clearly noticed that the optical band gap of the Se6-based copolymeric thin-film is >2 eV, which is the highest among the copolymers [85]. Based on **Table 4**, it can be concluded that PCDOTBT with its benzothiadiazole replaced with benzoselenadiazole exhibits highest PCE value than the other copolymers.

When fluorine atoms were introduced into the acceptor unit of Se1, the HOMO and LUMO energy levels were decreased, which result in higher V_{oc} for both SeF1 (0.78 eV) and SeF2 (0.82 eV) (**Figure 13**) as compared to the non-fluorinated Se1. Both SeF1 and SeF2 were blend with PC₆₁BM in 1:3 (w/w). The SeF2 blend PSC possesses higher PCE value than the SeF1 blend PSC, and yet both copolymer blend PSC possesses higher PCE than the non-fluorinated Se1 which synthesized by this research group, i.e., 0.73%. Moreover, fluorination of acceptor moieties able to finely tuned the PV properties, energy levels, and the charge mobility if the copolymers [44].

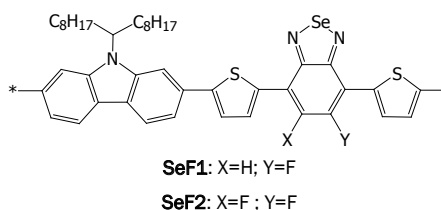


Figure 13. Fluorinated selenium substituted PCDTBT.

DESIGNATION D-A ARRANGEMENT

Lot efforts and ideas were input in the structural designation of the PCDTBT backbone. According to Zhou et al., the further extension of another set of acceptor unit, A- π in the repeating unit of the conjugated PCDTBT copolymer has improved the efficiency of the PSC. This is because of the D- π -A- π -A- π structure, P12 possesses narrower bandgap, a higher coefficient for molar absorption, and red-shifted UV-vis absorption spectra as compared with its analogous PCDTBT counterpart with the D- π -A- π arrangement. Besides that, P12-based PSC shows higher V_{oc} , J_{sc} , and PCE than PC-TBT-based PSC, which are 0.99 V, 9.70 mA cm^{-2} , and 4.74% respectively. Besides that, through the computational method, it was found that the addition of A- π unit along the repeating unit of PCDTBT narrowed down the bandgap by decreasing the LUMO energy level without causing a huge increment in HOMO energy level. Moreover, the film morphology of P20 was studied and compared with its analogous PCDTBT via transmission electron microscopy (TEM) and atomic force microscopy (AFM) by Zhou et al. The outcomes show that the P20:PC₇₁BM blended film exhibits smoother morphology than the PCDTBT. This favourable feature of the P20 blend film increases the D/A interface which leads to high hole mobility [86].

Before the synthesis of P12, Kim et al. had synthesized P13, where the π -bridges were eliminated out of the entire copolymeric backbone. However, the PCE obtained is extremely unfavourable, i.e., 0.42%, which indicates that the thiophene π -bridges play a vital role in the PV performance. Besides that, P14 with two thiophene units located adjacent to the carbazole donor moieties and no thiophene rings between the two benzothiadiazole units were synthesized and studied. The result shows that the P14 exhibit broad absorption band and the resulting PCE of the P14-based PSC are much higher than the P13 but yet lower than the P12 [87].

P16 copolymer that consists of carbazole trimer possesses lower efficiency in PSC device than the copolymer with carbazole dimer, P15. On the other hand, P17 with BT trimer and one carbazole as the repeating unit exhibit better PV performance with highest PCE value (1.25%) than P15 and P16. However, the PCE value for HXS-1 with only one donor and acceptor in the repeating unit, as tabulated in **Table 1**, is about five times higher than the P17 [88]. In addition, P18 copolymer was synthesized according to D- π -A- π -A- π arrangement, which possesses excellent thermal stability than the other copolymers in **Table 5**. Besides that, it has good solubility in the organic solvent. In this study, the P18:PC₇₁BM (1:2 w/w) blend PSC has higher PCE value than the 1:1 w/w blend [65].

Shi et al. have successfully synthesized three newly designed copolymers, i.e., P19, P20, and P21 (**Figure 14**), which have the different ratio of carbazole and BT present along the copolymeric backbone. When the copolymers were blended with PC₆₁BM in 1:2 w/w, the copolymer P21 PSC achieved highest PCE value (1.18%) than the other two copolymeric PSC. The PCE value for 1:2 w/w P19:PC₆₁BM blend PSC (0.62%) improved when the ratio is 1:1 w/w (1.09), and yet P12 still remained the highest PCE [89]. When this P19-P21 study is compared with the study of P15-P17, it can be concluded that increase of donor units does not improve the PV performance, but the increment of acceptor moieties along the copolymeric backbone can enhance the PCE value [88,89].

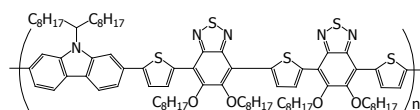
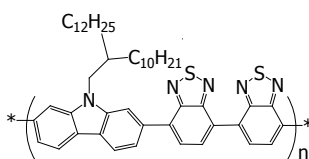
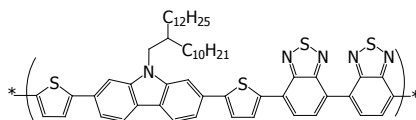
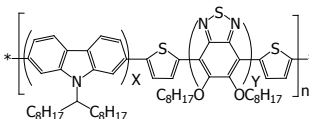
Table 5. A summary of experimental and characterization data for **P12-P21**.

Characteristics	Copolymers						BHJ PSC								Ref.
	Polymer	M_n^a (kDa)	M_w^a (kDa)	T_d^b ($^{\circ}$ C)	HOMO ^c (eV)	LUMO ^c (eV)	PDI	$E_g^{elec,d}$ (eV)	$E_g^{opt, film^e}$ (eV)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	μ_h (cm ² /Vs)	μ_e (cm ² /Vs)	
P12	n.a.	31.1	310	-5.43	-3.51	2.5	1.92	1.92	0.99	9.7	0.5	2.67×10^{-4}	n.a.	4.74	[86]
P13	8	n.a.	n.a.	-5.42	-3.66	2.8	1.76	2.11	0.62	2.24	0.3	n.a.	n.a.	0.42	[87]
P14	3.2	n.a.	n.a.	-5.42	-3.76	1.2	1.65	1.82	0.66	7.16	0.4	n.a.	n.a.	2.07	
P15	6.27	11.6	318	-5.35	-3.39	1.8	1.96	n.a.	0.75	2.79	0.2	n.a.	n.a.	0.43	[88]
P16	1.17	2	312	-5.25	-3.31	1.8	1.94	n.a.	0.54	1.93	0.2	n.a.	n.a.	0.23	
P17	2.13	2.39	344	-5.42	-3.11	1.1	2.31	n.a.	0.71	4.87	0.4	n.a.	n.a.	1.25	
P18	23.3	42.2	424	-5.5	-3.74	1.8	1.76	1.76	0.75	6.47	0.4	n.a.	n.a.	2.07	[65]
P19	8.6	15.4	420	-5.1	-3.32	1.8	1.78	1.64	0.69	3.02	0.3	n.a.	n.a.	0.62	[89]
P20	9.7	12.6	442	-5.12	-3.33	1.1	1.79	1.62	0.64	3.23	0.5	n.a.	n.a.	1.12	
P21	10.4	13.2	439	-5.12	-3.34	1.3	1.78	1.59	0.67	4.04	0.4	n.a.	n.a.	1.18	

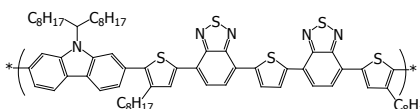
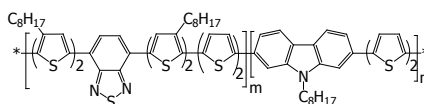
^aMeasurement conducted by differential refractive index(DRI) detection. ^bOnset of degradation temperature obtained from TGA with 5% of weight loss.

^cHOMO and LUMO energy level determined from the onset of oxidation and reduction, respectively. ^dElectrochemical energy gap= $|LUMO-HOMO|$ (eV).

^eOptical energy gap of the copolymeric thin film, E_g^{opt} . ^f μ_h represent hole mobility while μ_e represent electron mobility (cm²/Vs).


P12

P13

P14

P15: X=2; Y=1

P16: X=3; Y=1

P17: X=1; Y=3

P18

P19: m:n=51:49

P20: m:n=72:28

P21: m:n=81:19

Figure 14. Various arrangement of donor and acceptor units along the copolymeric backbone.

CONCLUSION

All in all, the PV performance of well-known PCDTBT can be further improved through various modifications. Fluorination of carbazole donor units has successfully narrowed the optical bandgap by lifting the HOMO energy level. Moreover, π -bridges are crucial for the D-A bulk heterojunction solar cells as they enhance the conjugation of the copolymeric backbone. Thienothiophene is a better choice as π -bridges than thiophene and dithiophene. Overall, there is not much improvement in the PV efficiency of the PSCs which replace the carbazole with much larger indolocarbazole units. Substitution of selenium into the π -bridges or benzothiadiazole acceptors able to lower the band gap and extended the absorption spectra of the copolymers. Amongst the various newly designed D-A arrangement, copolymers with D- π -A₁- π -A₂ structural arrangement possesses the best PCE result.

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