Planar copolymers for high-efficiency polymer solar cells

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Triggered by the energy crisis and the demand on the clean energy sources in the future, organic solar cells especially conjugated polymer based polymer solar cells (PSCs) arise interests from both industrial and academic sides, due to their unique advantages, including mechanical flexibility, light weight, semi-transparence, solution processability and low fabrication cost. In the early stage, poly(3-hexylthiophene) (P3HT) has been widely studied and proven to be one of the most successful electron donors in PSCs, but the power conversion efficiencies (PCEs) are limited to around ~4% due to the narrow absorption and incompatible energy level to the fullerene derivatives ($PC_{61}BM$ and $PC_{71}BM$). In a long period, the exploration of donor materials is one of the popular research topics in the field of PSCs, since fullerene derivatives present universal compatibility to different type polymer donors. For better tailoring the absorption spectra, highest occupied molecular orbital & lowest unoccupied molecular orbital (HOMO & LUMO) energy levels and transport properties, donor-acceptor (D-A) type alternating copolymers have been designed so as to improve the light harvesting ability in virtue of the new hybridized molecular orbitals and narrowed band gaps. Subsequently, researchers were mainly focusing on band gap engineering via developing new donor or acceptor moieties and the absorption coverage could be successfully extended to the NIR region of about 1100 nm by some narrow band gap polymers, but the photovoltaic performances still lag behind.

With extensive research and accumulated practical experience, researchers noticed that the integrated PCEs may be not only determined by the band gaps, but also be significantly influenced by the packing of polymer backbones, which is directly correlated with the hopping of charge carriers. It is well known that conjugated polymers normally carry lateral flexible chains to guarantee their processability, but the side chains could also prevent the polymer backbones from forming closely packing. Additionally, due to the freely rotated single bonds in the main chain, torsion of the main chain and amorphous aggregation could be formed as shown in Figure 1. In 2009, we brought the concept of planar polymer design to the organic photovoltaics (OPV) field for the first time and **HXS-1** was designed, which comprises two octyloxy chains on the benzothiadiazole (BT) ring and one octyl chain on the carbazole ring [1]. The well-arranged flexible alkyl chains (three octyl chains in each repeating unit) and the S⋯O supramolecular interactions ensure a coplanar configuration for the polymer backbone, leading to closely packing of polymer chains, which are consistent with the sharp and intensified X-ray diffraction (XRD) signals as reported. Although the intensive main chain packing and high M_w of 15.9 kg/mol are obtained, good solution processability can still be achieved at elevated temperature. Through elaborated molecular design, a tradeoff between good solubility and closely packing can be achieved. Finally, a PCE of ~5.4% was achieved by the PSCs based on **HSX-1**: $PC_{71}BM$ blend, which is also one of the best results at that time.

However, the carbazole units in **HSX-1** could be freely rotated around the C–C single bond, so the coplanar conformation for the backbones is not always guaranteed. To further fix the backbone at the coplanar conformation, the

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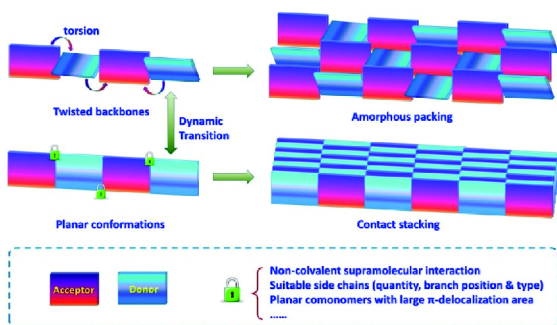
Figure 1 Schematic for the conformations of the D-A polymers and the corresponding packing styles (color online).

fluoro-modified carbazole was utilized for the preparation of the polymer **PDFC-DTBT**. Assisted by the F···O & F···H supramolecular interactions, the main chain planarity was greatly increased as confirmed by the intense XRD signals and the close π-π stacking distance. With further sidechain optimization, the PCE for **HD-PDFC-DTBT** was improved to 7.39% [2]. This is the first example that fluorinated donor unit could exhibit positive effect in enhancing the performance of PSCs. By simple replacement of the carbazole with the octyloxy modified dibenzothiophene, another type coplanar polymer **P3** could be produced by virtue of the more incorporated S···O supramolecular interactions [3]. In addition, Woo *et al.* [4] further made best use of the weak interplay of dipole-dipole, H-bond, and chalcogen-chalcogen interactions for polymer main chain design. They also reported that the two alkoxy side chains on the phenylene moiety would greatly improve the chain planarity via the intrachain dipole-dipole interactions (O···S) and/or hydrogen bonding interactions (O···H) and the corresponding polymer **PPDT2FBT**, which displayed nanofibrillar structures, strong interlamellar scattering peaks and tight face-on π-π stacking, demonstrated a PCE of 8.28%. Whereas, the alkylthio-substituted **PPsDT2FBT** only obtained a PCE of 0.55, which is ascribed to the S···S repulsion induced twisted polymer chain. With the exchanged positions for fluorine and the alkoxy chains, a high PCE of 9.80% was achieved by the **PDTBTBz-2F$_{anti}$** [5]. Similarly, by replacing the single bond connected thiophene-benzene-thiophene with the fused dithienothiophene unit, coplanar main chain could be obtained as well by the aid of the alkoxy substituents and a PCE of 9.21% could be reached by **PDTT-BOBT** as reported by Lee *et al.* [6].

In the meanwhile, using π-extended ladder skeletons could improve the planar composition for the conjugated backbones and result in coplanar conformations. Chen *et al.* [7] utilized the pentacyclic indacenodithiophene (IDT) to design the alternating copolymer *a*-**PTPTBT** and a PCE of 6.4% was achieved. Hsu *et al.* [8] further developed a heptacyclic ladder unit (BDCPDT) via replacing the benzene with benz

[1,2-*b*:4,5-*b′*]odithiophenes (BDT) in IDT. The forced planarization greatly suppresses the interannular twisting to extend the effective conjugation length and an enhanced PCE of 6.6% was achieved by **PBDCPDT-TPD**. Later, various chemical modification methods have been applied for design of new ladder type building blocks including bridging atom alternation, conjugation length extension and lateral chain modification. Very recently, we reported a new oxygen-functionalized pentacyclic block (DTDP) and the corresponding polymer **PDTDP-4** displayed a super-planar backbone. With such enhanced electron-donating ability induced by oxygen, a PCE of 7.26% is obtained for its photovoltaic devices [9]. In addition, electron deficient ladder block as pentacyclic lactam could be applied for efficient planar polymer donors as well. With such building block, Ding *et al.* [10] designed a polymer **PThTPTI** and a PCE of 7.80% is obtained for the corresponding devices.

Notably, the alkoxy chains on the BT segment neighboring to the thiophene units (vide supra) can increase the planarity of the polymer main chains. But the side chains on the electron donating segments would also influence the planarity, since these side chains are generally connected to the sp^3 hybridized carbon atoms, which would stick out from the main chain plane and may impede close packing and carrier transport. Alkyl side chains could guarantee the desired solubility, but crystallinity and close packing are also essential factors for high performance donors. With this idea in mind, we replaced the sp^3-carbon with the sp^2-hybridized one and introduced an ethylene side chain at the 9-position of fluorene. The π-π overlapping area for the donor segments have been expanded and such conformation would definitely alleviate the undesired steric hindrance of the side chains, leading to a more planar conformation for the final polymer **PAFDTBT**, which displayed greatly improved PCEs of 6.2% in relative to the ordinary fluorene based control polymer (PCE of 3.1%) [11]. Similar finding was also reported by Liu *et al.* [12], where not only the coplanar configuration of the **EI-PFDTBT** was schematically illustrated, the temperature-dependent aggregation phenomenon and the XRD results were also confirmed the contact stacking for the main chains. Very recently, Song *et al.* [13] further developed this molecular designing strategy and designed a novel two-methylene-modified IDT building block (DMIDT) with four lateral phenyl substituted groups and the super planar configuration has been confirmed by the single crystal structure. Such 2D type ladder skeleton will offer even larger π-delocalization and stacking area, facilitate carrier transport and prevent rotational disorder. Combined with the supramolecular interactions between the donor and acceptor moieties, **PDMIDT-TPD** (in Figure 2) presents nearly flat configurations and a PCE of about 8.26% was achieved, which is also the champion result among the IDT-based polymer donors.
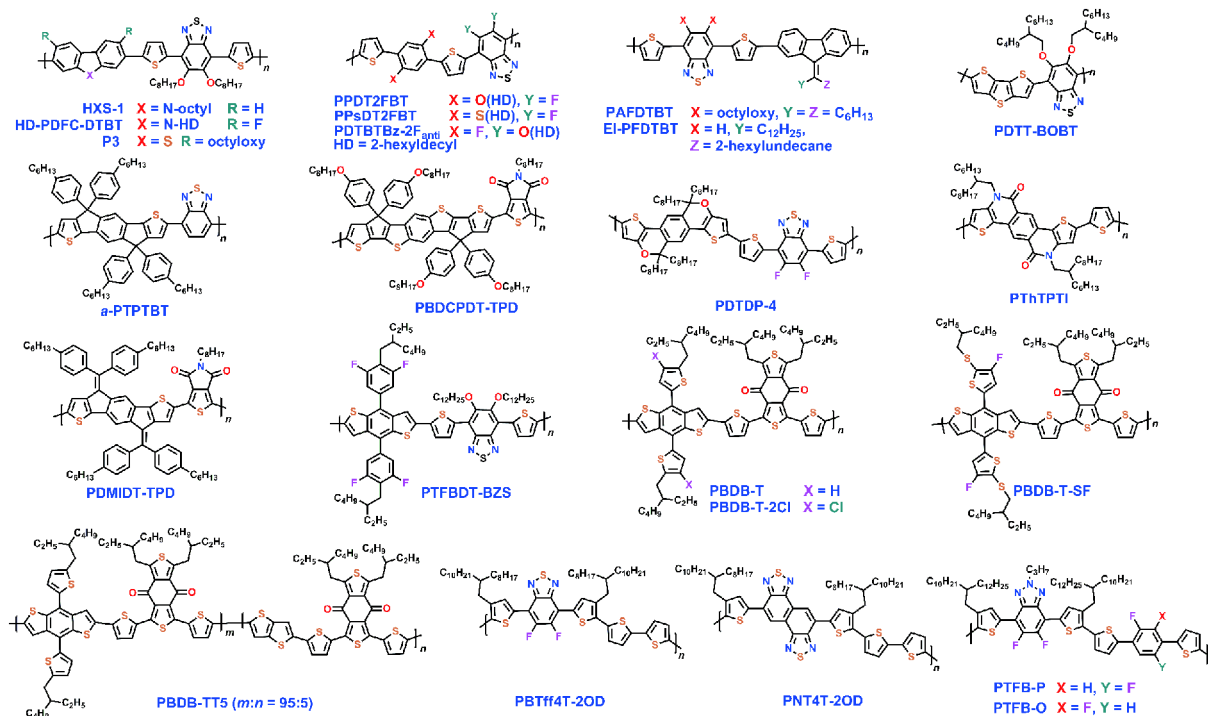
Figure 2   Representative planar copolymers for high efficiency PSCs (color online).

As an alternative, replacing the phenyl based donor moiety (e.g. carbazole, fluorene) with the thienyl capping blocks may reduce the twisting angles between the donor and acceptor segments and provide coplanar configuration for the final polymers. For example, we replaced the carbazole in **HSX-1** with the 4-alkyl-3,5-difluorophenyl modified BDT and a wide band gap polymer donor **PTFBDT-BZS** was designed. With the coplanar conjugated polymeric backbones, the final PCE of 8.24% was achieved [14]. In the meantime, by utilization of the benzo [1,2-c:4,5-c′]-dithiophene-4,8-dione (BDD) to substitute the BT electron-deficient moieties, Hou *et al.* [15] reported a new BDT based polymer donor **PBDB-T**, which has been predicted to have excellent planar conjugated backbones by the quantum chemistry as the dihedral angels of BDT-thiophene and BDD-thiophene are only 2.8° and 5.2°, respectively. In addition, the good planarity gives reasonable interpretations for the strong interchain π-π interaction induced aggregation in solutions and endows the absorption spectra with temperature dependent characteristics. Furthermore, it suggests an interesting approach via control the solution temperature to modulate domain size without changing crystallinity of the blend films in PSCs. Very recently, Yan *et al.* [16,17] also noticed the importance for the processing temperature and they developed a series of quaterthiophene (4T) based polymer donors (**PNT4T-2OD**, **PBTff4T-2OD**, **PTFB-P** and **PTFB-O**), which could form coplanar conformations also by virtue of the reduced dihedral angles among thiophene moieties and the supramolecular interactions. They claimed that the branching position, size of the branched alkyl side chains and the symmetry of the monomer could influence the main chain stacking for the target polymers and fluorination could strengthen the well-controllable temperature-dependent aggregation behaviors. In addition, they made best use of this property during the film drying process with spin-coating so as to achieve the favored morphology with a suitable crystallinity. Finally, thick film devices based on PBTff4T-2OD displayed >10% efficiencies in fullerene based devices owing to the high mobility of the highly ordered and sufficiently pure polymer domains formed by these coplanar polymers.

Since the A-D-A type fused-ring electron acceptors (FREAs) invented by Zhan *et al.* [18], the dominance of fullerene at the acceptor category has been disintegrated and the rapid advance on non-fullerene acceptor (NFAs) based PSCs arises intensive interests because of their tunable energy levels, adjustable light absorption and regulated solid aggregation properties induced by the the synthetic flexibility etc. So most efforts have been spent on the exploration of novel NFAs in the last three years and it seems to be halted for the development of the polymer donors. Interestingly, some high performance polymers designed to pair with fullerene derivatives also displayed excellent photovoltaic performances when blended with NFAs. For example, **PTFBDT-BZS** displayed an excellent PCE of 11.03% when utilized by Zhan *et al.* [18] for mapping the polymer donors toward high-efficiency NFAs PSCs and such excellent performances may be ascribed to the extremely efficient charge

generation from both donor and acceptor channels. The temperature dependent aggregation characteristics induced by the coplanar main chain could be also utilized in NFAs PSCs fabrication, and the quaterthiophene based polymer **PTFB-O** reached a PCE of 10.88% by Yan [17]. **PBDB-T**, which became one of the famous polymer donors in the NFAs field, exhibits excellent compatibility to a variety new developed NFAs and a PCE of 14.1% has been achieved very recently by Chen *et al.* [19] via utilization of the analogue **PBDB-T-SF** as the polymer donor. Via the chlorine modification on **PBDB-T**, another analogue **PBDB-T-2Cl** could achieve a PCE of 14.4% when combined with the ITIC-4F [20]. Interestingly, not only alternating D-A copolymers could produce the planar conjugated backbones, random copolymers may also form the coplanar skeletons as reported by Yang *et al.* [21–23]. One of the typical example (**PDBD-TT5**) is shown in Figure 2 and a PCE of 11.14% could be reached for the corresponding device with *m*-ITIC as the acceptor [22]. The energy levels and photovoltaic parameters of the related planar conjugated polymer donors are also summarized in Table 1 for convenience.

In summary, the developments of acceptors and polymer donors move forward alternately in the past few years. Though the state-of-the-art donor polymers used in fullerene cells perform well when they are combined with NFAs, yet the high performance PSCs still greatly rely on the progress in the customized polymer donors to specific fullerene or nonfullerene acceptors. Planar conjugated polymers could be prepared via tuning the density, branching position and size of the alkyl side chains, adoption of supramolecular conformation locks in between the segments, extending the flatten conjugated area etc., which would inevitably bring in close main chain stacking, highly crystalline, efficient carrier transport and temperature-dependent aggregation phenomenon. In addition, the coplanar conformations are dynamic and they could be transfer to the non-planar state when processed at high temperature. Such characteristics would guarantee the polymers precipitate prior to the fullerene or nonfullerene acceptors to form relative pure polymer phases as the temperature cools down and the morphology could be tuned via the processing temperature. In short, limited planar polymer donors are summarized in this perspective, but the

Table 1 Summarized energy levels and the photovoltaic parameters of the representative planar conjugated polymer donors

Polymer	HOMO (eV)	LUMO (eV)	E_g (eV)	Acceptor	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)	Ref.
HXS-1	−5.21	−3.35	1.95	**PC$_{71}$BM**	0.81	9.80	0.69	5.40	[1]
HD-PDFC-DTBT	−5.32	−3.30	1.96	**PC$_{71}$BM**	0.93	14.11	0.56	7.39	[2]
P3	−5.34	−3.37	1.98	**PC$_{71}$BM**	0.83	9.30	0.58	4.48	[3]
PPDT2FBT	−5.41	−3.65	1.76	**PC$_{71}$BM**	0.80	15.40	0.67	8.28	[4]
PDTBTBz-2F$_{anti}$	−5.50	−3.49	1.90	**PC$_{71}$BM**	0.97	14.00	0.72	9.80	[5]
PDTT-BOBT	−5.47	−3.72	1.75	**PC$_{71}$BM**	0.82	15.07	0.74	9.21	[6]
a-**PTPTBT**	−5.36	−3.52	1.75	**PC$_{71}$BM**	0.85	11.20	0.67	6.41	[7]
PBDCPDT-TPD	−5.36	−3.20	1.88	**PC$_{71}$BM**	0.87	12.21	0.62	6.60	[8]
PDTDP-4	−5.31	−3.65	1.66	**PC$_{71}$BM**	0.72	15.30	0.66	7.26	[9]
PThTPTI	−5.42	−2.77	1.86	**PC$_{71}$BM**	0.92	12.47	0.63	7.21	[10]
PAFDTBT	−5.32	−3.48	1.84	**PC$_{71}$BM**	0.89	9.90	0.70	6.20	[11]
EI-PFDTBT	−5.31	−3.61	1.84	**PC$_{71}$BM**	0.85	11.04	0.54	5.07	[12]
PDMIDT-TPD	−5.46	−3.69	1.77	**PC$_{71}$BM**	0.89	13.40	0.70	8.26	[13]
				ITIC	0.91	13.91	0.57	6.88	[13]
PTFBDT-BZS	−5.50	−3.69	1.81	**PC$_{71}$BM**	0.89	12.67	0.73	8.24	[14]
				IDIC	0.91	17.30	0.71	11.03	[18]
PBDB-T	−5.23	−3.18	1.83	**PC$_{71}$BM**	0.86	10.70	0.72	6.67	[15]
PBDB-T-2Cl	−5.51	−3.65	1.86	**IT-4F**	0.86	21.80	0.77	14.40	[20]
PBDB-T-SF	−5.40	−3.60	1.80	**NCBDT-4Cl**	0.85	22.35	0.74	14.10	[19]
PNT4T-2OD	−5.24	−3.71	1.53	**PC$_{71}$BM**	0.76	19.80	0.68	10.10	[16]
PBTff4T-2OD	−5.20	−3.57	1.63	**TC$_{71}$BM**	0.77	18.80	0.75	10.80	[16]
				PC$_{71}$BM	0.77	18.40	0.74	10.50	[16]
PTFB-P	−5.30	−3.33	1.97	**ITIC**	0.92	12.8	0.65	7.85	[17]
PTFB-O	−5.36	−3.36	2.00	**ITIC-Th**	0.92	17.1	0.67	10.88	[17]
PBDB-TT5	−5.45	−3.54	1.77	**PC$_{71}$BM**	0.85	14.04	0.70	8.42	[22]
				m-**ITIC**	0.91	17.53	0.70	11.14	[22]

planarization strategy is one promising option for the design of high performance polymer donor and more efforts spent on it would definitely advance this field to even higher PCEs.

Conflict of interest   The authors declare that they have no conflict of interest.

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