

Review

Furan-containing Conjugated Polymers for Organic Solar Cells^{*}

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Abstract Development of organic semiconductors is one of the most intriguing and productive topics in material science and engineering. Many efforts have been made on the synthesis of aromatic building blocks such as benzene, thiophene and pyrrole due to the facile preparation accompanied by the intrinsic environmental stability and relatively efficient properties of the resulting polymers. In the past, furan has been less explored in this field because of its high oxidation potential. Recently, furan has attracted obsession due to its weaker aromaticity, the greater solubilities of furan-containing π -conjugated polymers relative to other benzenoid systems and the accessibility of furan-based starting materials from renewable resources. This review elaborates the advancements of organic photovoltaic polymers containing furan building blocks. The uniqueness and advantages of furan-containing building blocks in semiconducting materials are also discussed.

Keywords Conjugated polymers; π -Electron; Furan; Semiconductors; Organic solar cells

INTRODUCTION

In the past two decades, development of conjugated polymers has become an important topic in material science because of the wider applications of these materials in electronics and photonics^[1, 2]. Electronic properties, low cost, versatility of functionalization, thin film flexibility and ease of processing are among the top features of these materials. The most exciting aspect of these materials is their chemistry that allows the synthesis of conjugated polymers with narrow bandgaps, tunable energy levels, and desired electronic properties^[1, 2]. These low-bandgap polymers (having a bandgap less than 1.6 eV) are especially attractive in organic photovoltaics (OPV), and ambipolar field-effect transistors (FETs)^[3, 4]. Many efforts have been made to create new polymers for such applications and excellent results have been obtained. For instance, organic solar cells with > 10% power conversion efficiency (PCE)^[5], and organic transistors with ambipolar mobilities of $10\text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ have been achieved^[6]. This class of materials also possesses some interesting physical properties other than its smaller bandgap. For instance, in photovoltaic devices, many polymers have open circuit voltages (V_{oc}) closer to the bandgap (or smaller bandgap- V_{oc} offset) than wider bandgap materials, probably because the electronic orbitals

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of these low bandgap polymers very closely overlap and the π -electrons are easily delocalized^[7]. Apart from this, charge separation in these materials is very efficient, possibly due to larger dielectric constant, stronger dipole moment and lower exciton binding energy^[8]. Consequently, in organic semiconductors, the photophysics and charge transport are unique.

In organic semiconducting materials, σ bonds are formed by the hybridization of sp^2 atomic orbitals with the neighbor atoms in the same plane. The perpendicular p_z orbitals of adjacent atoms overlap to form the π -bonds. This process results in the delocalization of π -electrons along the polymer backbone and achieves specific optoelectronic properties. Poly(aniline) was the first compound to show different colors in different redox states^[9], which implied the presence of resonance structures^[10]. Later on, the studies on some other compounds such as poly(acetylene) and its iodine-doped complexes^[11–13] poly(pyrrole)^[14, 15], poly(thiophene)^[16–18], poly(*p*-phenylenevinylene)^[19, 20], and alkyl/alkoxy substituted aromatic rings^[21, 22] promoted the area of organic conductive polymers. The solubility of the π -conjugated polymers in organic solvents was increased by the attachment of alkyl/alkoxy side chains on the sp^2 hybrid. A few examples of semiconducting polymers are shown in Fig. 1.

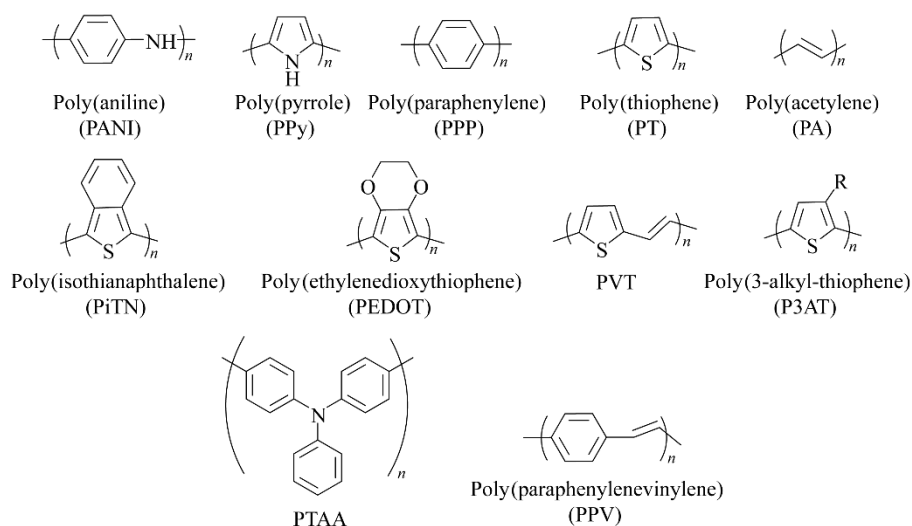


Fig. 1 Structures of some semiconducting polymers used in PSCs

Organic semiconducting materials are classified into *p*-type and *n*-type depending on the relative energy levels of the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs). HOMO levels of most of the donor-acceptor (D-A) alternating copolymers are high, which is responsible for their *p*-type behavior in applications^[23, 24]. Fullerenes and their functionalized derivatives such as [6,6]-phenyl- C_{61} -butyric acid methyl ester (PC₆₁BM) are typical *n*-type semiconductors. Very limited number of polymeric *n*-type materials have been developed^[25, 26]. Polymers based on heteroaromatic monomers have also shown good performance due to their interesting electrical, electrochemical, structural, mechanical, and optical properties. Among the heteroatomic monomers: furan, thiophene, pyrrole, aniline, *etc.* are the common examples. Furan has received less attention than other monomers because of its high oxidation potential.

This review highlights the development of furan-containing polymers for solar cell application. More emphasis is given on the furan-containing polymers, their advantages and future prospects.

PROGRESS IN FURAN-CONTAINING POLYMERS IN PSC

Harvesting clean solar energy has become very important due to increasing energy requirements and environmental impact concern^[27–29]. Furan and its derivatives fall into the category of renewable and sustainable synthetic resources because of their synthesis from natural products. Furan is prepared from the metal catalyzed

decarbonylation of furfural (furan-2-carboxaldehyde)^[30], which is obtained from the vegetable residues in food industry and agriculture^[29].

While the efficiency of PSCs is approaching 10%^[31], renewable furan and its derivatives have received an attention for the application in organic semiconductors. Furan is a five membered aromatic heterocycle containing one sp² hybridized oxygen atom instead of the sulfur atom in thiophene. Oxygen of furan affects the electronic and optoelectronic properties, as well for its enlarged π -conjugated derivatives. Due to being in a lower row of the periodic table, oxygen has a relatively smaller covalent radius than sulfur, which could decrease the distance of π - π stacking for the charge carrier transfer. According to Pauling's electronegativity scale^[32], electronegativity of oxygen is around 3.5, whereas electronegativity of sulfur is 2.5. Similar to thiophene, the dipoles in furan are also directed towards the heteroatom. At the same time, the furan has a dipole moment of 0.71 D which is larger than the thiophene ring of 0.54 D^[29]. The aromatic building blocks containing different heteroatoms generate various dipole moments in the structures and ultimately can make fine tuning of the HOMO/LUMO levels and band gaps possible^[33].

Poly(thieno[3,4,b]furan) (**P1**) is one of the earliest semiconducting polymers having furan fused rings (Fig. 2), prepared by Sotzing and coworkers *via* electrochemical polymerization on an inert electrode^[34]. The bandgap of this polymer was low (1.04 eV) and showed stable redox behavior. The application of furan containing π -conjugated materials bulk heterojunction (BHJ) solar cells is very interesting.

Polymer Backbones Containing Furan Ring

The backbone links to the conjugated system along the polymer chain, and many fundamental optoelectronic properties of conjugated polymers, such as bandgap, position of energy levels, charge carrier mobilities and conductivity depend on the backbone of the polymer. To get the desired properties, it is necessary to modify the donor and acceptor units separately while designing backbones for D-A-type polymers, particularly with respect to the bandgap and energy levels of the conjugated polymers.

In 2010, Decurtins and coworkers synthesized π -conjugated copolymers (**P2–P4**, Fig. 2) based on a soluble electroactive benzo[1,2-b:4,5-b']difuran (BDF) chromophore by introducing thiophene/benzo[c][1,2,5]thiadiazole/9-phenylcarbazole comonomer units^[35]. These copolymers showed absorption from 250 nm to 700 nm with wide optical band gaps of 1.71–2.01 eV. Their electronic and photovoltaic properties were easily tuned by incorporating different comonomers into the polymer backbone at different ratios. Bulk heterojunction solar cell devices were fabricated using these copolymers as the electron donor and PC₆₁BM as the electron acceptor. PCEs of 0.17%–0.59% were achieved. In the same year, first examples of furan-containing low bandgap polymers (**P5–P7**, Fig. 2), with significant power conversion efficiencies in organic solar cells were reported by Woo *et al.*^[36]. By inserting furan moieties in the backbone of the conjugated polymers, the overall solubility of the polymer was significantly improved in common organic solvents. BHJ solar cells fabricated by employing these furan-containing polymers and PC₇₁BM as the acceptor achieved PCEs approaching 5.0%.

Because of furan-containing fused aromatic unit, BDF possesses unique properties. Five-member furan ring shows weak steric hindrance as compared to thiophene due to small diameter of the oxygen than that of the sulfur atom in thiophene^[37]. BDF is copolymerized with other conjugated moieties, to form a planar and well conjugated backbone. BDF-based conjugated polymers are expected to achieve smaller band gap and better charge carrier mobility. In addition to this, furan-based compounds have a strong potential in making biodegradable and biorenewable materials^[38]. A new building block of BDF was made using 4,7-dithienyl-2,1,3-benzothiadiazole (DTBT) as an electron withdrawing unit to build a D-A backbone^[39]. The calculated HOMO and LUMO energy levels were –5.10 and –3.24 eV, respectively. A low bandgap polymer **P8** (Fig. 2) was developed by using this building block for photovoltaic devices, which exhibited a promising PCE of 5.0%. Apart from this, Biewer and coworkers synthesized two new semiconducting polymers (**P9**) and (**P10**) (Fig. 2) displaying a granular morphology^[40]. BHJ solar cells using these polymers showed PCEs of 1.19% and 0.79%, respectively. In the work of Decurtins and coworkers, two well-defined alternating π -conjugated polymers containing a soluble electroactive BDF chromophore, poly(BDF-(9-phenylcarbazole)) (**P12**, Fig. 3), and poly(BDF-benzothiadiazole) (**P13**, Fig. 3) were synthesized^[41]. BHJ solar cells were fabricated using these

polymers as the electron donor and PC₆₁BM as the electron acceptor, resulting in PCEs of 0.24%–0.57%.

D-A alternating copolymerization is a very promising approach. To find a complete understanding of the structure-property relationships and improve the performance of D-A copolymers is a big challenge^[42]. A low bandgap and high charge carrier mobility are the essential and important requirements for the development of efficient, stacked and coplanar BDF-based conjugated polymers^[37, 43, 44]. Also, high V_{oc} , and stability can be achieved due to higher electronegativity of oxygen atom (O, 3.5; S, 2.5). Liu *et al.* reported three new BDF-based D-A conjugated polymers (**P14–P16**) (Fig. 3)^[45]. All the three polymers showed red-shifted and broader absorption in the film states as compared to solution. This is attributed to better planarity of the polymer and stronger electronic interaction between the individual polymer chains in the film states. The corresponding HOMO levels of **P14**, **P15** and **P16** were –5.12, –5.02, and –5.19 eV, respectively. The bulk heterojunction PSCs were fabricated with a device structure of ITO/PEDOT:PSS/polymers:PC₇₁BM/Ca/Al. A blend of **P14** and PC₇₁BM showed a high mobility of $6.7 \times 10^{-2} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$. A PCE of 4.5% was obtained from **P14** based polymer solar cells with $V_{oc} = 0.69 \text{ V}$, short circuit current density (J_{sc}) = $9.87 \text{ mA} \cdot \text{cm}^{-2}$ and fill factor (FF) = 65.3%.

Because of multiple advantages such as fine tuning of the bandgap and absorption spectra, alternating copolymerization has been received extensive attention to synthesize promising polymer donors. One of the widely used examples of building blocks in low bandgap conjugated polymers is thieno-[3,4-b]thiophene (TT) unit with a strong electron-withdrawing substituent. In 2013, the same group published a new low bandgap conjugated polymer **P17** (Fig. 3) from TT and BDF units^[46]. The HOMO and LUMO energy levels are –5.27 and –3.69 eV, respectively. The absorption in the film was broader and red-shifted than in solution due to aggregation or stronger molecular interactions in the solid state. A PCE of 4.4% with a J_{sc} of $10.45 \text{ mA} \cdot \text{cm}^{-2}$, V_{oc} of 0.66 V and a FF of 0.64 was demonstrated by the photovoltaic cells fabricated with the structure of ITO/PEDOT:PSS/**P16**:PC₇₁BM (1:1.5, *W:W*)/Ca/Al using 1,8-diiodooctane (DIO) as the solvent additive.

Aromatic-quinoid (A-Q) approach is also an effective strategy to design efficient low bandgap polymers. One of the most successful examples of this approach is the polymer family based on benzo[1,2-b:4,5-b']dithiophene (BDT) and TT units^[47]. All the important parameters of OPV devices, such as J_{sc} , V_{oc} and FF can be tuned through modulation of HOMO and LUMO energy levels of the materials. An impressive progress has been made by modulating the molecular energy levels of low band gap polymers^[48]. A series of low bandgap photovoltaic copolymers (**P18–P22**) (Fig. 3) containing benzodifuran-*alt*-thieno[3,4-b]thiophene (BDF-*alt*-TT) were reported by Hou *et al.*^[49]. Different electron-withdrawing functional groups such as carbonyl, ester, fluorine, sulfuryl and cyano were introduced to the TT unit to tune the molecular energy levels of these copolymers. **P18**, **P19**, **P20** and **P21** exhibited very similar absorption spectra and their peak values are located at *ca.* 700 nm. But the absorption spectra of the solution and the film of **P21** were blue-shifted as compared to the other four polymers with absorption peak located at 620 nm. This was attributed to the strong effect of cyano group on the conjugation of BDF-TT backbone, resulting in the fact that cyano groups may create stronger steric hindrance to the conjugated backbones. The highest efficiency of 5.23% with a V_{oc} of 0.63 V was achieved from **P19**/PC₇₁BM based devices. These findings confirmed that effective tuning of molecular energy levels is possible by changing the electron withdrawing ability of the substituted functional groups on the quinoid units in A-Q polymers.

Furthermore, another way to improve the photovoltaic properties of the materials is the introduction of the two-dimensional (2D) conjugated structure^[50, 51]. By using this strategy, a low bandgap D-A copolymer **P23** (Fig. 3) units were synthesized by Zou's group^[52]. The calculated LUMO and HOMO energy levels as well as the electrochemical band gap were –3.11, –5.21 and –2.10 eV, respectively. The BHJ PSCs were fabricated with a device structure of ITO/PEDOT:PSS/polymer:PC₇₁BM/Ca/Al. The PSCs based on **P23**:PC₇₁BM (1:1.5, *W:W*) achieved a promising PCE of 6.0% with a high J_{sc} of $12.04 \text{ mA} \cdot \text{cm}^{-2}$ and a V_{oc} of 0.76 V.

Different donor moieties (*e.g.* furan versus thiophene) polymer solubility is also maintained while adjusting the HOMO level of the polymer^[36]. Apart from this, polymers synthesized from different donor moieties exhibit several self-assembling properties in thin-films^[53]. Warnan *et al.* prepared polymers (**P24–P27**, Fig. 3) by microwave-assisted synthesis and investigated the effects of replacing BDT for its furan-based comparable motif

BDF in these polymers, focusing on material solubility, bandgap and polymer self-assembly^[54]. Earlier, the same group has demonstrated that for polymers with branched alkyl-substituted BDT motifs, a fine modulation of the number of aliphatic carbons in linear *N*-alkyl-substituted thieno-[3,4-*c*]pyrrole-4,6-dione (TPD) moieties generate significant variations in polymer solubility^[55]. The lower PCEs (by *ca.* 1%) of some **P24**-based devices cast from blend solutions containing CN (5%) were attributed to a less ideal nanoscale morphology rather than from the weak propensity of the polymers to self-assemble and form π -aggregates in thin-films. BHJ solar cells fabricated with **P25** approached 7.4% PCE.

Lower HOMO level and stronger absorption of benzodichalcogenophene (BDC) derivatives compared to alkoxy-substituting units are beneficial for achieving high V_{oc} and J_{sc} , 2D structures, in particular 2D-conjugated BDF and BDT. Many groups have extensively used and studied these BDC derivatives in BHJ PSCs^[56, 57]. Recently, two new alkoxy phenyl substituted thieno[2,3-*f*]benzofuran (TBFP)-based polymers (**P28** and **P29**) (Fig. 3) were developed by Zou and colleagues^[58], showing broad absorption in solid state and deep HOMO energy levels (−5.47 and −5.61 eV) for **P28** and **P29**, respectively. Compared with solution, these polymers have stronger intermolecular interactions in the film state due to planar geometry and close packing in the solid state.

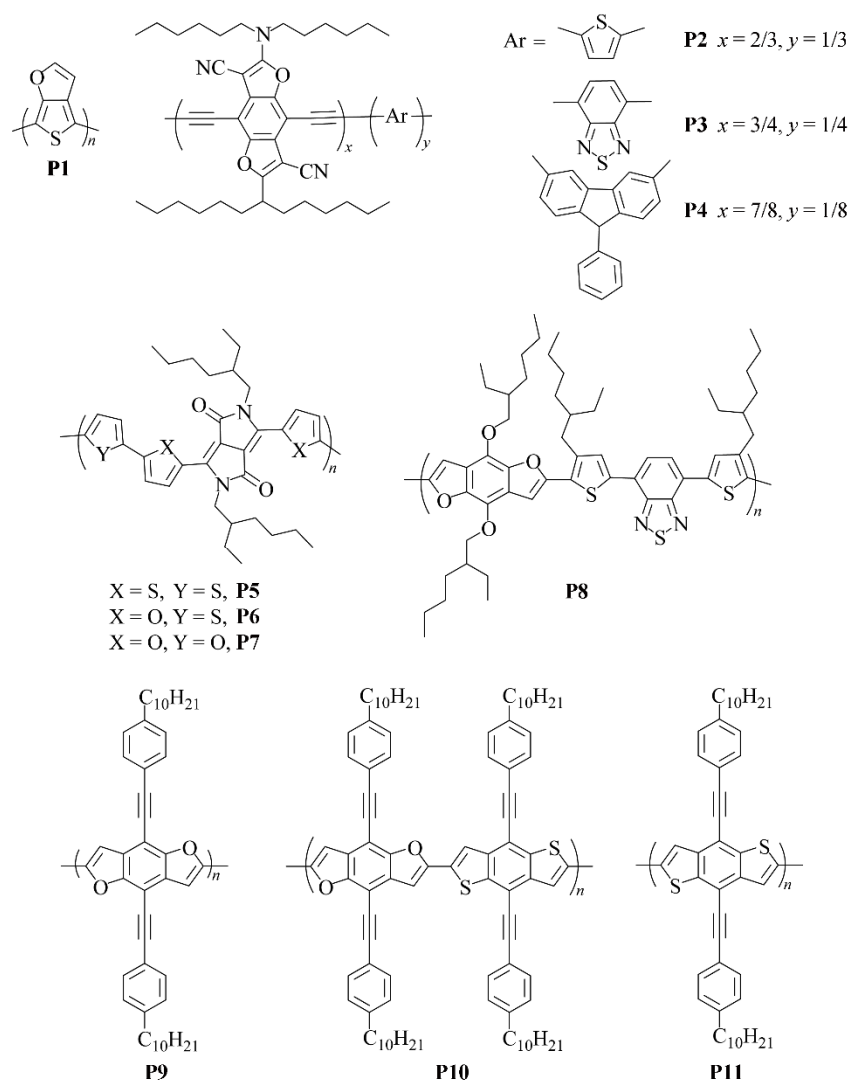
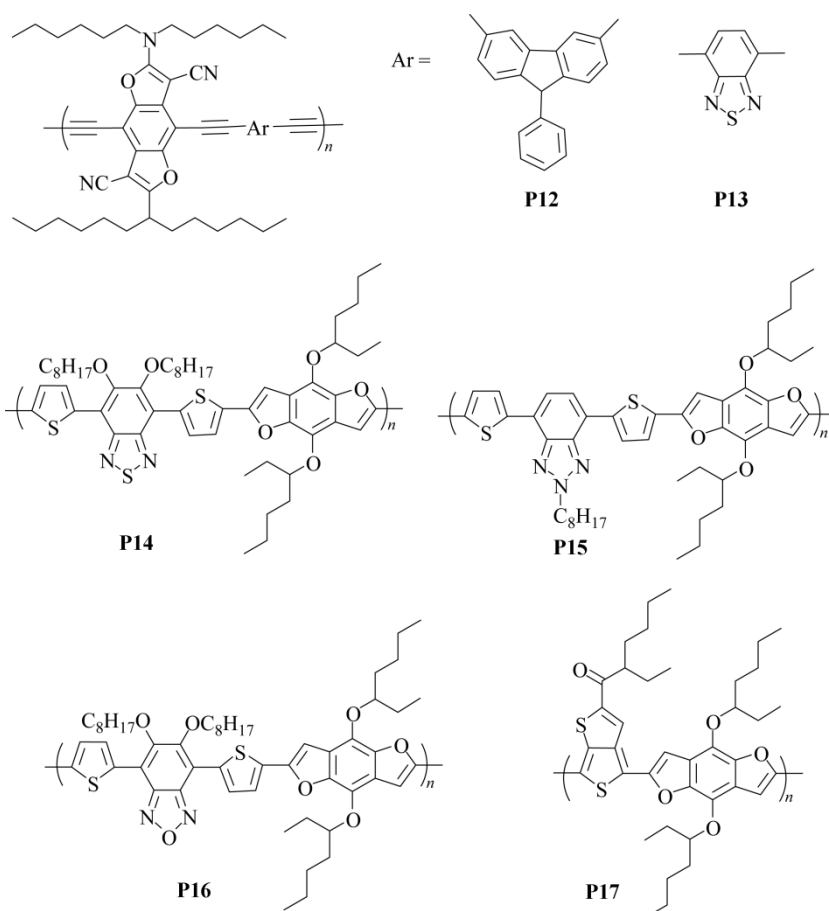


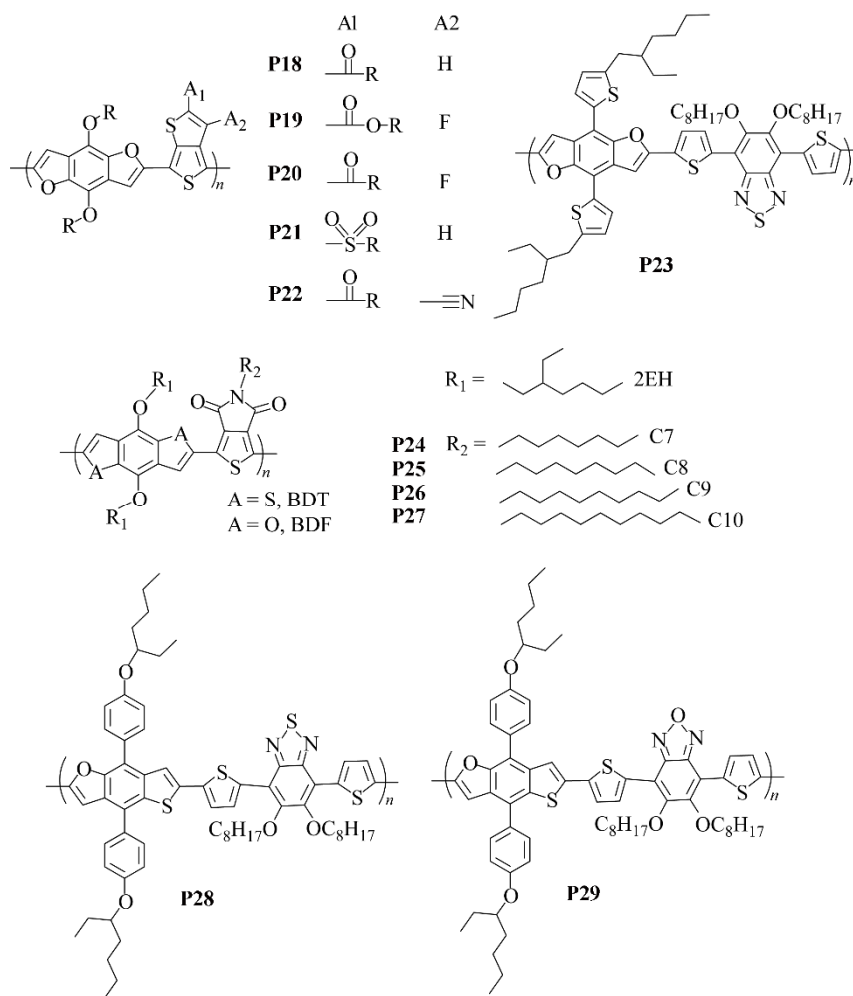
Fig. 2 Structures of polymers **P1**–**P11**

The solar cell fabricated with **P28**:PC₇₁BM (1:2) demonstrated a balanced hole and electron mobility of 2.49 and 9.12 cm²·V⁻¹·s⁻¹, respectively, than those of **P29** based devices. The PSCs based on the single layer device structure of ITO/PEDOT:PSS/**P28**:PC₇₁BM (1:2, *W:W*)/ZrAcac/Al with 3 vol% DIO as additive, demonstrated a relatively high PCE of 6% with a high FF of 0.69. Photovoltaic properties of polymers **P8–P29** were summarized in the Table 1.

Table 1 Photovoltaic properties of polymers with furan in backbones

Polymer	J_{sc} (mA·cm ⁻²)	V_{oc} (V)	FF	PCE (%)	Ref.
P8	11.77	0.78	0.55	5.01	[39]
P14	9.87	0.69	0.653	4.45	[45]
P17	10.45	0.66	0.638	4.4	[46]
P18	13.13	0.54	0.6	4.26	[49]
P19	15.75	0.61	0.538	5.17	[49]
P20	13.88	0.63	0.598	5.23	[49]
P21	14.21	0.59	0.607	5.08	[49]
P23	12.04	0.76	0.65	6	[52]
P24	10.8	0.94	0.65	6.6	[54]
P25	11.2	0.97	0.68	7.4	[54]
P26	10.6	0.93	0.69	7.3	[54]
P27	11.1	0.94	0.6	6.3	[54]
P28	12.63	0.69	0.69	6.02	[58]
P29	8.69	0.84	0.56	4.41	[58]



Fig. 3 Structures of polymers **P12–P29**

Polymers with furan in the backbones have demonstrated promising results. PCE of more than 6% have been achieved. By the optimization of donor and acceptor units as well as conjugation length of polymer backbone, high performance and cost effective furan polymers can be developed for efficient solar cells.

Polymers Containing Furan in Side Chains

The side chain plays a key role in finding the intermolecular interactions between different polymer chains and polymer-fullerene interaction at the interface between regions and affecting the processability of the polymers in PSCs. Generally, the solubility of polymers in common organic solvents is improved using bigger side chains. Thus, processability of conjugated polymers is enhanced by reducing π - π interchain interaction. However, a balance must be achieved in this reduced π - π interchain interaction to avoid its harmful effects on solar cell properties. Apart from this, side chains may affect the mixing of donor polymers with acceptor materials such as fullerene. The shape of the side-chain is also important; for example, the solubility can be increased by long and branched side chains. But too long size creates much steric hindrance that may affect the conjugation of the backbone and can increase the intermolecular π -distance, leading to diminished absorption, low charge-transport character, and poor overall performance. Lastly, the position of the side chains is also important. McCulloch reported the importance of structure and orientation of side chains on the remarkable electric properties of polythiophene^[59]. Mei and Bao also published a review on the side-chain engineering in OFETs and OPVs^[60].

In 2012, D-A conjugated polymers based on **syn-P30** or **anti-P30** (Fig. 4) as donors and isoindigo as acceptors were reported^[61]. The **anti-P30** demonstrated lower optical bandgap and higher HOMO energy level than **syn-P30**, whereas the **syn-P30** showed better solubility than **anti-P30**. The results suggest that the HOMO energy level of polymer can be lowered by the utilization of less conjugated repeating units such as **syn-P30** and the elimination of electron donating groups on the central phenyl ring of BDF.

The solubility of conjugated polymers in organic solvents has been improved through the variation in the size and branching of alkyl substituents appended to the backbone. Frechet and coworkers reported that linear alkyl side chains can be used to promote thin-film nano-structural order in solar cells^[62]. Particularly, linear side chains reduce π - π stacking distances between backbones and increase the correlation lengths of both π - π stacking and lamellar spacing, resulting in an increase in the efficiency of bulk heterojunction solar cells. BHJ solar cells fabricated from *n*-alkyl-substituted **P31–P36** (Fig. 4) polymer donors and the electron acceptor PC₇₁BM demonstrated PCEs reaching 6.5% (**P35**). This high performance showed a reasonable improvement over the PCE of *ca.* 5% achieved with the branched-alkyl substituted derivative **P33**.

Henssler and Matzger synthesized dimers (**P37–P42**) (Fig. 4) containing thieno[3,2-*b*]furan^[63]. Furan is part of the fused aromatic ring in this study. Three different dimers with different regioregularity can be obtained due to the asymmetrical structure of thieno[3,2-*b*]furan. Six different types of dimers were synthesized in combination with TT. The relationship between the position of the oxygen atoms and the optoelectronic properties was studied by UV/Vis, fluorescence spectroscopy and cyclic voltammetry (CV). Crystal *p-p* stacking motifs were observed for all the six dimers in the solid state.

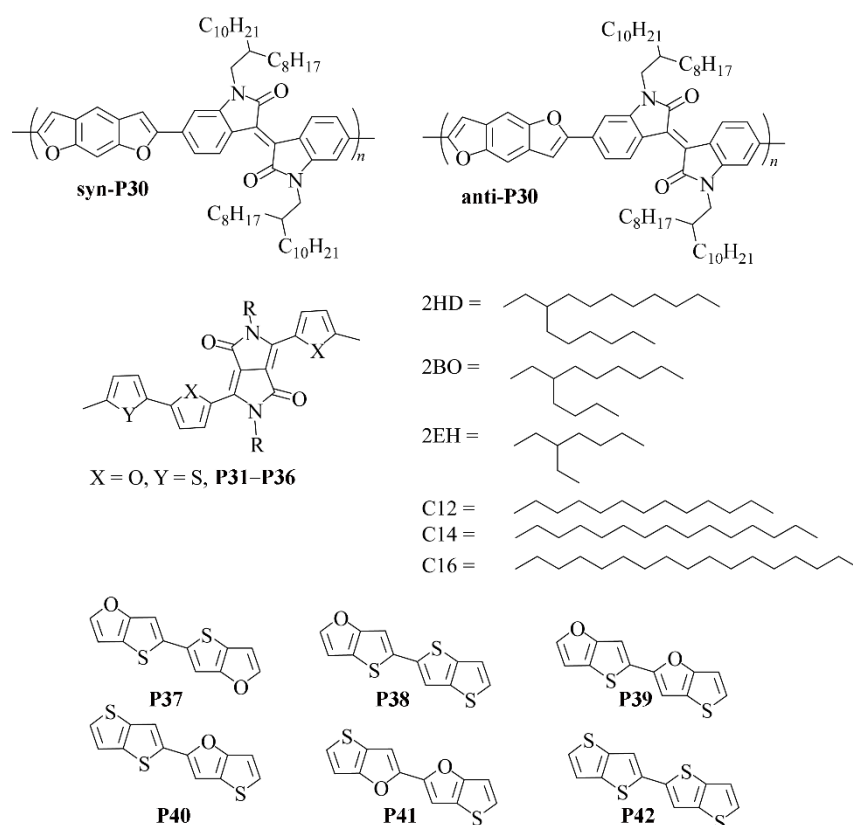


Fig. 4 Structures of polymers **P30–P42**

In 2013, our group had developed two new alkylfuran-yl-substituted conjugated donor-acceptor polymers **P43** and **P44** (Fig. 5)^[64]. Alkylfuran-yl-substituted polymers exhibited smaller optical bandgaps, broader

absorption range and lower HOMO energy levels, thus leading to a larger J_{sc} and higher V_{oc} in photovoltaic devices. Under the same fabricating conditions, the efficiency of the PSCs based on **P43** and **P44** achieved 3.5% and 5.1%, respectively. After thermal annealing, the efficiency of the PSCs based on **P44**:PC₇₁BM was further improved to 6.1%, indicating a great potential for largely improving the efficiency of the PSCs by replacing alkoxy with alkylfuranyl group in creating extraordinary efficient materials for PSCs. The V_{oc} of 0.69 V was obtained by the alkylfuranyl-substituted polymer PBDTF-DPP with 0.07 V higher than the alkoxy analogue PBDT-DPP, due to their lower-lying HOMO energy level. The higher J_{sc} obtained by the PSCs based on alkylfuranyl-substituted polymers was attributed to the lower bandgaps and broader absorption range. An improved efficiency of over 5% was achieved from the optimized device by prethermal annealing. From the above results, it is concluded that furan-containing conjugated polymers can show good performance in solar cells. In addition to this, the substitution of furan for thiophene in the backbone of the polymer will enhance polymer solubility, allowing for the use of shorter side chains maintaining high performance of the PSCs. Remarkably, the availability of furan derivatives from biorenewable sources is a step toward the “green” electronic materials.

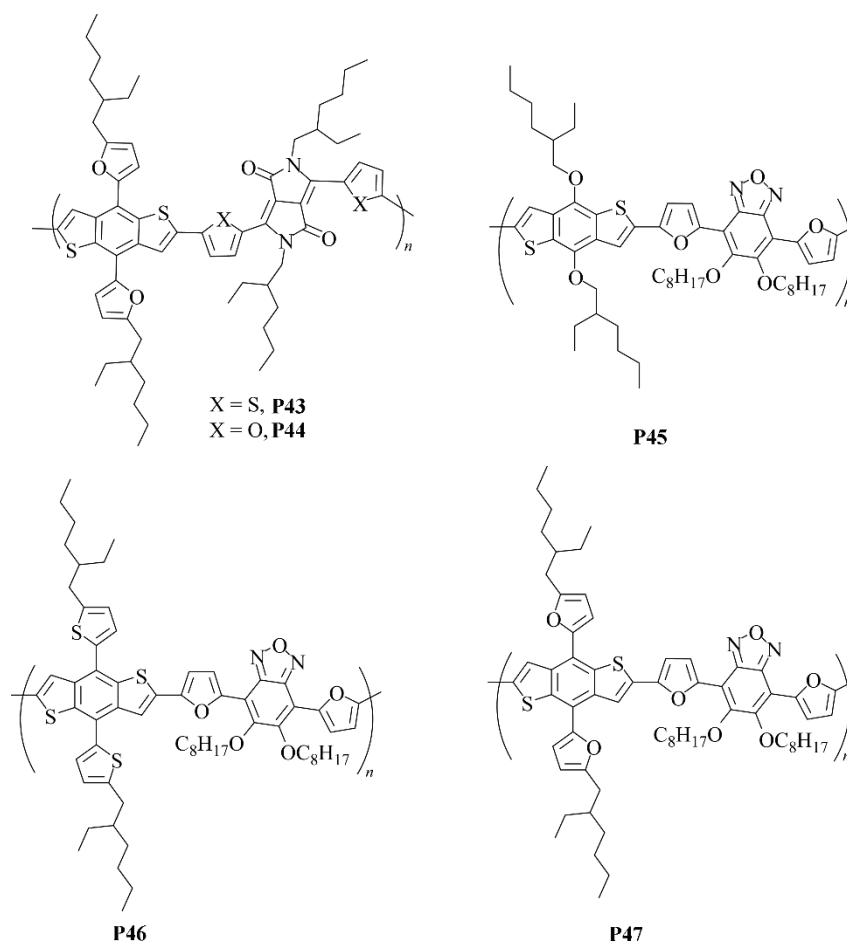


Fig. 5 Structures of polymers **P43**–**P47**

BHJ solar cells fabricated from a combination of electron-donating π -conjugated polymers and electron-accepting fullerene derivatives have received great academic and industrial attraction due to advantages such as low cost, light weight, flexibility, and large-area manufacturing compatibility. After that, we also reported a new series of benzodithiophene-difuranylbenzooxadiazole-based D-A co-polymers, **P45**, **P46**, and **P47** (Fig. 5), with

various side groups for BHJ PSCs^[65]. Our results showed that the reduction of the bandgap of polymers and the enhancement of charge mobility in the devices can be accomplished simultaneously by substituting the alkylthienyl side group with its furan counterpart. PSCs fabricated with these copolymers showed a PCE of 2.1% for **P45** with an alkoxyl side chain, 2.2% for **P46** with an alkylthienyl side group, and 3.0% for **P47** with an alkylfuran side group. After optimizing the device conditions *via* simple solvent treatment, the PSCs based on **P47**-DFBO:PC₇₁BM achieved 7.0% PCE, which exhibited an enhancement of 130%. The improved photocurrent of PBDTF-DFBO from PBDTT-DFBO is ascribed to its higher charge carrier mobility and broader absorption range. Because of higher HOMO energy level, V_{oc} value of PBDTF-DFBO was slightly decreased as compared to PBDTT-DFBO. Morphological study revealed that the effects of polar solvent treatment on the improved performance originate from higher and more balanced charge transport and the formation of fiber like interpenetrating morphologies, leading to the increase of J_{sc} and FF.

In 2014, Wei and coworkers prepared a series of 2D, conjugated, D- π -A polymers (**P48**, **P49**, and **P50**) (Fig. 6)^[66]. The side chains of the BDT units changed the solubility, conformations, and electronic properties of

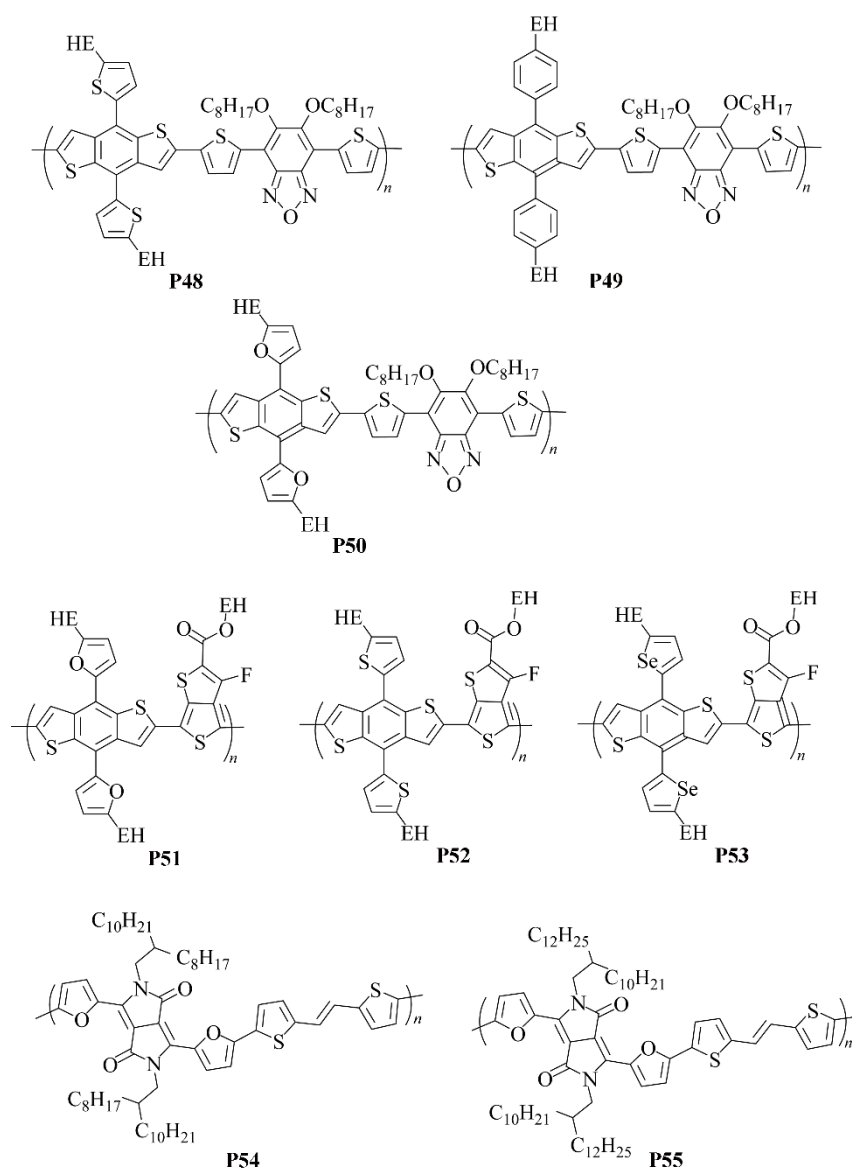


Fig. 6 Structures of polymers **P48**–**P55**

the synthesized conjugated polymers, allowing tuning of their photovoltaic performance when blended with fullerenes. DFT calculations indicated the effects of these side chain groups on the BDT donor units on the torsion angles between the side chain groups and the conjugated main. The efficiencies of photovoltaic devices incorporating **P48**, **P49**, or **P50** polymers and PC₇₁BM varied greatly from 3.6% to 5.9% due to the difference of the structure of side chains. The PCEs of photovoltaic devices incorporating blends of **P50**, **P48**, or **P49** and PC₇₁BM (1:2) improved to 5.4%, 6.4% and 7.4%, respectively, because of their optimized morphologies.

In another attempt to improve efficiency of PSCs through side chain selection, Hou's group synthesized three conjugated polymers (**P51–P53**) (Fig. 6) based on BDT and TT units with furan, thiophene and selenophene as side groups^[67]. The photovoltaic devices fabricated with **P52** and **P53** showed similar photovoltaic performance in device, and PCEs of 9.0% and 8.78% respectively were achieved. The device based on **P51** showed a V_{oc} of 0.69 V and a J_{sc} of 11.77 mA·cm⁻², which are lower than those in the devices based on the other two polymers.

High performance photovoltaic materials can be obtained by carefully tuning the side chain length of the conjugated polymers, because the side chains significantly influence the morphology. Very recently, two furan-flanked diketopyrrolopyrrole copolymers (**P54**, **P55**) (Fig. 6), poly(3,6-difuran-2-yl-2,5-di(alkyl)-pyrrolo[3,4-c]pyrrole-1,4-dione-altthienylenevinylene) with different alkyl side chains (PDVFs), have been reported^[68]. The PSC based on a blend of **P54** with 2-octyldodecyl and PC₇₁BM as an active layer has demonstrated a better device performance as compared to that based on a blend of **P55** with 2-decyltetradecyl and PC₇₁BM. Tuning the alkyl side chains attached on the PDVFs results in an enhancement of PCE from 3.57% (**P55**) to 4.56% (**P54**) due to increase of J_{sc} and FF.

Alternate thiophene/furan oligomers were also developed by Miyata *et al.* in 2005^[69]. Overall, polymers containing furan in the side chains have achieved an efficiency of > 7%, which is very much encouraging. Polymers with furan in side chains can be proved efficient materials for the fabrication of low cost and high performance solar cells. Photovoltaic properties of polymers **P34–P54** were listed in the Table 2.

Table 2 Photovoltaic properties of polymers with furan in side chains

Polymer	J_{sc} (mA·cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)	Ref.
P34	12.2	0.65	60	5.2	[62]
P35	14.8	0.65	64	6.5	[62]
P36	12.3	0.65	69	6.2	[62]
P43	12.64	0.72	56.5	5.1	[64]
P44	10.6	0.83	64.7	5.6	[64]
P45	9.1	0.86	58.6	5	[65]
P46	12.7	0.83	62	7	[65]
P47	12.8	0.86	67	7.4	[65]
P48	11.8	0.85	64	6.4	[66]
P49	11.2	0.81	60	5.4	[66]
P50	11.77	0.69	64.81	5.28	[66]
P53	10.56	0.65	66.6	4.56	[67]
P54	8.58	0.65	64.1	3.57	[68]

CONCLUSIONS AND OUTLOOK

Conjugated polymers have gained great attention in cost-effective, rapidly processed, large-area organic solar cells. Understanding of the structure-property relationships is crucial to enhance the solar cell properties. However, through proper selection of donor and acceptor units, incorporation of appropriate side chains, and modification of the backbone, a significant progress has been made in the preparation of new polymers for highly efficient organic solar cells. The choice of furan moiety is a bright prospect in OPVs due to its advantages of low bandgap, good solubility and especially biorenewable source. Polymers with furan in the side chains have

shown better results compared to those containing furan in the backbones. Furan-based solar cells have achieved high PCE of above 9% and shown promising potential for the application in cost-effective organic solar cells.

In terms of structural modifications and relatively low molecular weight, 2D conjugated BDF polymer has less been explored as compared to BDT polymer. BDF units are not focused much in the area of small molecule materials for OPVs. But the methods reported for the preparation of furan oligomers are useful to develop more novel furan based π -conjugated materials.

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