

Benzothiadiazole-based Conjugated Polymers for Organic Solar Cells

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Abstract Benzothiadiazole (BT) is an electron-deficient unit with fused aromatic core, which can be used to construct conjugated polymers for application in organic solar cells (OSCs). In the past twenty years, huge numbers of conjugated polymers based on BT unit have been developed, focusing on the backbone engineering (such as by using different copolymerized building blocks), side chain engineering (such as by using linear or branch side units), using heteroatoms (such as F, O and S atoms, and CN group), etc. These modifications enable BT-polymers to exhibit distinct absorption spectra (with onset varied from 600 nm to 1000 nm), different frontier energy levels and crystallinities. As a consequence, BT-polymers have gained much attention in recent years, and can be simultaneously used as electron donor and electron acceptor in OSCs, providing the power conversion efficiencies (PCEs) over 18% and 14% in non-fullerene and all-polymer OSCs. In this article, we provide an overview of BT-polymers for OSCs, from donor to acceptor, *via* selecting some typical BT-polymers in different periods. We hope that the summary in this article can invoke the interest to study the BT-polymers toward high performance OSCs, especially with thick active layers that can be potentially used in large-area devices.

Keywords Benzothiadiazole; Conjugated polymer; Organic solar cells; Electron donor; Electron acceptor

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INTRODUCTION

Solar cells, which are capable of converting solar energy into electrical energy, are considered as one of the most promising and efficient technologies to alleviate the global energy crisis.^[1] In recent years, organic solar cells (OSCs) have attracted extensive attention in the photovoltaic field due to their advantages, such as flexibility, light weight, facile fabrication technique and low cost compared to the conventional inorganic solar cells.^[2–5]

The photoactive layers, which consist of donor and acceptor materials, play important roles in OSCs.^[6–13] Fullerene derivatives were usually used as electron acceptor due to their high electron mobility and three-dimensional electron transport properties. Although the power conversion efficiencies (PCEs) of fullerene-based OSCs have been enhanced to over 11%, the inherent disadvantages of fullerene derivatives, such as the limited chemical structures and the difficulty to tune the energy levels, hamper the further improvement of photovoltaic properties. For comparison, non-fullerene acceptors have been demonstrated to out-perform fullerenes in OSCs,^[14–19] in which the PCEs have reached up to 18%.^[20]

Additionally, the donor materials also play important roles in OSCs, since they are responsible for matching with the electron acceptor to convert photons into free charges.^[21–26] Nowadays, the donor polymers are usually constructed *via* donor-acceptor (D-A) motif, in which the electron-donating and electron-deficient units are incorporated into one polymer. Therefore, the intramolecular charge transfer between donor and acceptor segments can be generated, resulting in the lower optical band gap. Simultaneously, the other properties of the polymers, such as energy levels, crystallinity and charge transport properties, can also be effectively adjusted. Therefore, D-A conjugated polymers have dominated the development of OSCs. Among them, benzothiadiazole (BT) as electron-deficient unit has been widely used to design conjugated polymers for high performance OSCs.^[27–29]

BT-based monomers can be simply prepared and modified with F atom or different side chains to tune the optoelectronic properties and solubility (Scheme 1),^[30–34] By choosing copolymerized units with different properties, BT-based copolymers can be simply synthesized *via* Suzuki or Stille coupling polymerization. BT-based polymers usually own high crystallinity, good charge transport characteristics, low band gaps and excellent optoelectronic properties. Based on those excellent properties, researchers can construct BT-polymers with tunable physical and optoelectrical properties toward efficient OSCs.

Since Dhanabalan *et al.* reported the first BT-based conjugated polymer for application in OSCs in 2001,^[35] BT-based

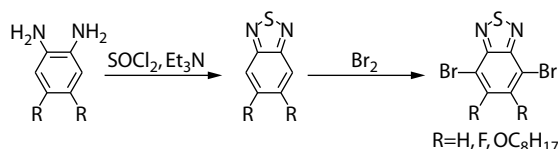
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Scheme 1 The synthetic routes to BT cores.

conjugated materials have been widely developed both as electron donor and acceptor in OSCs. As summarized in Fig. 1, when BT-based polymers were used as donor materials, the highest PCE of fullerene-based OSCs reached up to 11.7% and that of non-fullerene OSCs reached up to 18.22%.^[20,36] When BT-based polymers act as electron acceptor, the PCEs of OSCs can achieve 14.4%.^[37] In this review, we highlight the recent developments of BT-based conjugated polymers and their application in OSCs, including: (i) BT-based polymer donors in fullerene solar cells, (ii) BT-based polymer donors in non-fullerene solar cells and (iii) BT-based polymer acceptors in all-PSCs. It is worth mentioning that there are so many publica-

tions about BT-polymers, and herein, we intentionally select some typical BT-polymers in order to show their physical properties, so that hopefully the importance of BT-polymers in OSCs can be revealed.

BT-BASED DONOR POLYMERS IN OSCS

BT-based Donor Polymers in Fullerene-based OSCs

BT-based donor polymers play important roles in fullerene-based OSCs.^[38–44] In the year of 2001, the first D-A polymer **P1** (Fig. 2) was constructed from BT unit with the thiophene-pyrrole-thiophene as the copolymerized unit, but the PCE was only 0.34%, possibly due to the poor solubility and low charge carrier mobility.^[45] The solubility was then improved by introducing a fluorene unit with two pendent soluble alkyl side units into the BT-polymer **P2**, providing a PCE of 2.4% in OSCs.^[46] The PCE of BT-polymer (**P3**) solar cells was further enhanced to 3.6% when using 2,7-carbazole as comonomer, which was due to the enhanced planarity of conjugated backbones *via* 2,7-substitution.^[47] The planarity of this polymer could be further improved by using two alkoxy side units attached to BT backbone (**P4**), providing a high PCE of 5.4% in OSCs.^[30] All these pioneer works constructed the cornerstone of BT-polymers, prompting their developments for application in OSCs. In this section, we will briefly discuss BT-polymers for fullerene-based OSCs (Fig. 2).

Poly(3-hexylthiophene) with thiophene backbones exhibited strong crystallinity and high charge transport, which also represent the star conjugated polymers for OSCs. Therefore, researchers tried to introduce oligothiophene segments into BT-polymers. In 2005, Krebs *et al.* developed the BT-polymer **P5** with bithiophene units, in which hexyl side units were used to improve the solubility of the polymer (Fig. 2).^[48] Unfortunately, the PCEs of OSCs by using **P5** as donor were very low (~0.024%). The low PCEs might originate from the steric hindrance between hexyl side units and BT core, which could result in large twist backbones and hence poor charge transport. The contradiction between solubility and crystallinity *via* alkyl side units could be perfectly solved by using cyclopentadithiophene as comonomer, in which two alkyl units located at the center of bithiophene units. This structure also enabled the polymer **P6** to show the optical band gap of 1.4 eV, and the OSC based on **P6** as donor exhibited a PCE of 3.5%.^[49]

Then, the well-known BT-polymer PCDTBT (as **P3** in this work) with 2,7-carbazole as comonomer was reported by Leclerc *et al.* (Fig. 2).^[47] This polymer showed the absorption spectrum in the range of 300–700 nm and provided a PCE of 3.6% in OSCs. The solar cells were fabricated and characterized in air, indicating the high stability of OSCs based on **P3**. After that, lots of works focused on **P3**, from the aspect of synthetic methods, crystallinity, fabrication process, cost, *etc.*^[50] A typical example is to use [6,6]-Phenyl C₇₁ butyric acid methyl ester (PC₇₁BM) to replace of [6,6]-Phenyl C₆₁ butyric acid methyl ester (PC₆₀BM) as electron acceptor in **P3**-based OSCs, in which the PCE was enhanced to 6.1% due to the enhanced photocurrent. In particular, the internal quantum efficiency of the solar cells approached 100%, indicating the efficient charge separation and transport.^[51] Another outstanding work was done by Bo *et al.*, in which they developed a BT

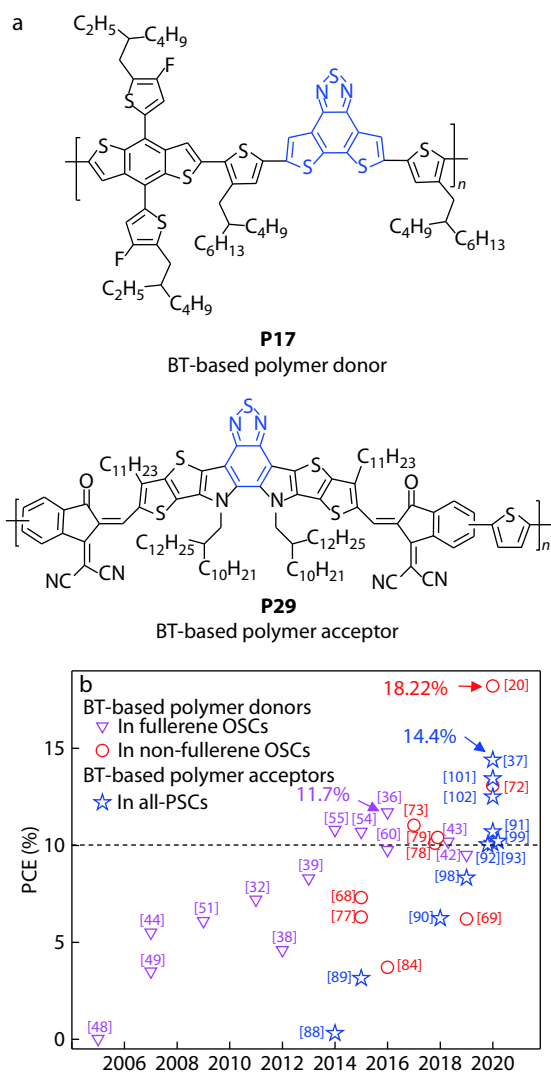


Fig. 1 (a) The chemical structures of BT-based polymers as donor or acceptor that exhibited the highest PCEs in this review. (b) Summary of the PCEs for BT-based OSCs in recent years.

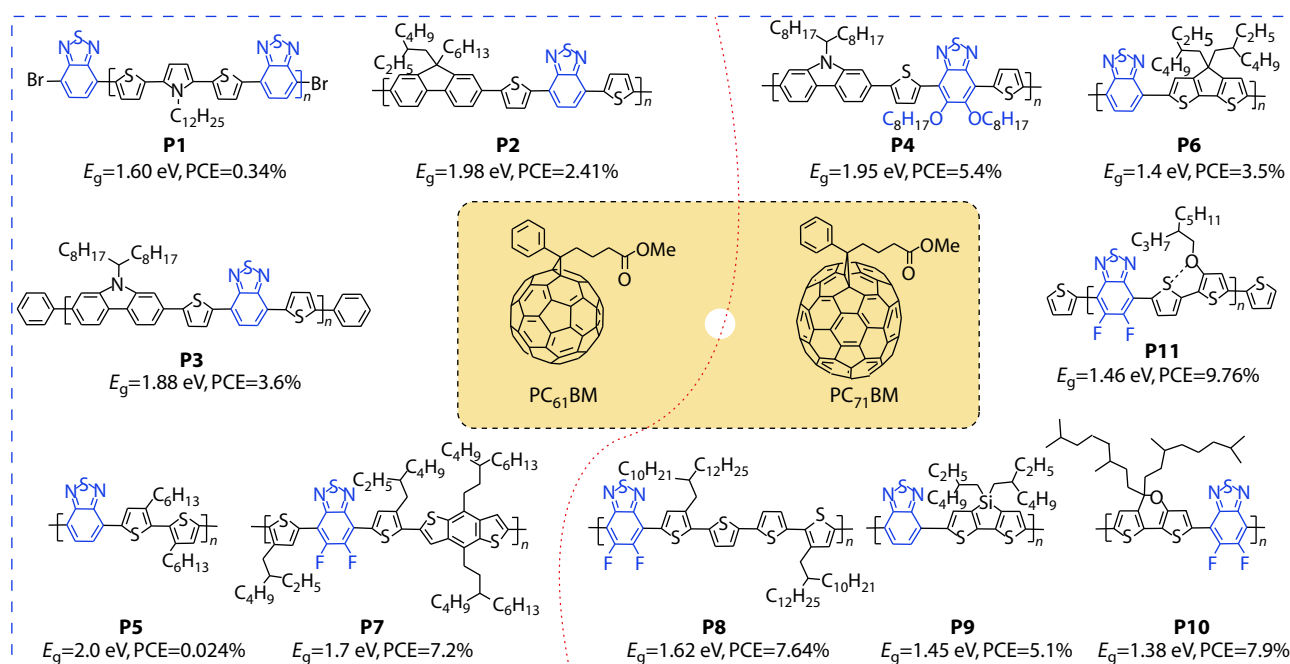


Fig. 2 Chemical structures of BT-based donor polymers in fullerene-based OSCs.

unit with two alkoxy side chains to improve the solubility of the polymer. The corresponding polymer HXS-1 (named as **P4**) provided a PCE of 5.4% in solar cells.^[30] This design motif was then widely used in developing BT-polymers with prominent photovoltaic performance.^[52]

Benzodithiophene (BDT) is another copolymerized unit that is widely used in BT-polymers. For example, in 2011, You *et al.* firstly introduced fluorine atoms into the BT core to construct the BT-polymer **P7** with BDT as comonomer (Fig. 2).^[32] The introduction of fluorine atoms can effectively lower the frontier energy levels and improve the crystallinity of the polymer, resulting in high open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}) and fill factor (FF) in solar cells. Therefore, **P7**-based OSCs exhibited a PCE of 7.2%, while the corresponding polymer without fluorine atoms only showed a PCE of 5.0%. The PCEs of BT-BDT based polymers could be further enhanced to over 9% when enhancing the molecular weight and using a fullerene derivative as interfacial layer.^[53]

BT-polymers with oligothiophene are the representative conjugated polymers.^[54–56] Researchers introduced long branched alkyl side units into the 3-position of thiophene, so that two alkyl side units in the monomer containing BT and four thiophenes can ensure the enough solubility for the polymers. This design can also significantly reduce the steric hinderance between alkyl side units and conjugated backbones, and therefore the advantages of polythiophene can be maintained in BT-polymers. For example, the BT-polymer **P8** (Fig. 2) was found to show near-infrared absorption property (onset close to 800 nm), high hole mobility (1.92 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ in organic field-effect transistors) and high PCEs (7.64% at 230 nm) at thick films due to high crystallinity.^[57] The PCE of this polymer was further enhanced to over 10% after controlling the aggregation behavior at high temperature.^[55] These polymers also exhibited promising photovoltaic performance in

non-fullerene OSCs (NFOSCs), which will be discussed in the following section.

In addition to the wide (<700 nm) and medium (<800 nm) band gaps, BT units can also be used to design narrow band gap conjugated polymers with absorption onset over 800 nm. Yang *et al.* used the silicon-contained fused bithiophene as comonomer into the BT-polymer **P9** (Fig. 2), providing an absorption onset at 800 nm. OSCs based on **P9**:PCBM blends exhibited a PCE of up to 5.1%.^[58] Later, they inserted a strong electron-donating oxygen atom into the cyclopentadithiophene unit to form the dithienopyran unit. The resulting polymer **P10** based on dithienopyran and fluoro-substituted BT units exhibited absorption up to 900 nm. Single-junction OSCs based on **P10** as donor and PC₇₁BM as acceptor provided a PCE of 7.9% with the spectral response from 300 nm to 900 nm.^[59] The narrow band gap property enabled **P10** to be applied into tandem solar cells, providing a high PCE of 10.6%. Guo *et al.* developed a novel electron-donating unit 3-alkoxy-3'-alkyl-2,2'-bithiophene with the head-to-head linked alkyl and alkoxy units for the BT-polymer **P11** (Fig. 2). The new polymer exhibited an absorption spectrum over 900 nm and showed a high PCE of 9.76% when using PC₇₁BM as the acceptor in solar cells.^[60] These results reveal that, by using the rational selection of copolymerized units, BT-polymers can provide distinct absorption properties, which can facilitate their application in non-fullerene solar cells.

BT-based Donor Polymers in Non-fullerene OSCs

Before discussing BT-polymers for application in non-fullerene OSCs, we intend to briefly summarize the characteristics of BT-polymers. Firstly, as mentioned above, the chemical structures of BT-polymers can be tailored to show distinct absorption spectra from visible light to near-infrared region, indicating that they can perfectly match with non-fullerene acceptors with complementary absorption. Secondly, BT-polymers always have

high crystallinity, especially for the polymers with oligothiophenes as comonomer (such as **P8**). Therefore, we could observe highly-ordered diffraction peaks in grazing incidence wide angle X-ray scattering (GIWAXS) images (Fig. 3a)^[55] and fibrous structures in blended films from transmission electron microscope (TEM) images (Fig. 3b).^[61] This characteristic is quite similar to diketopyrrolopyrrole-based conjugated polymers.^[62] Thirdly, BT-polymers exhibited high hole mobilities, in which the mobilities over $1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ could be obtained in organic field-effect transistor devices.^[63] High crystallinity and hole mobilities enable BT-polymers to show good charge transport properties, exhibiting high performance in thick photoactive layers due to the reduced charge recombination.^[55,64] In addition, from the aspect of synthesis and chemical structure, BT units can be easily prepared and there are also several modification sites. All these merits demonstrate the great potential application of BT-polymers in OSCs.

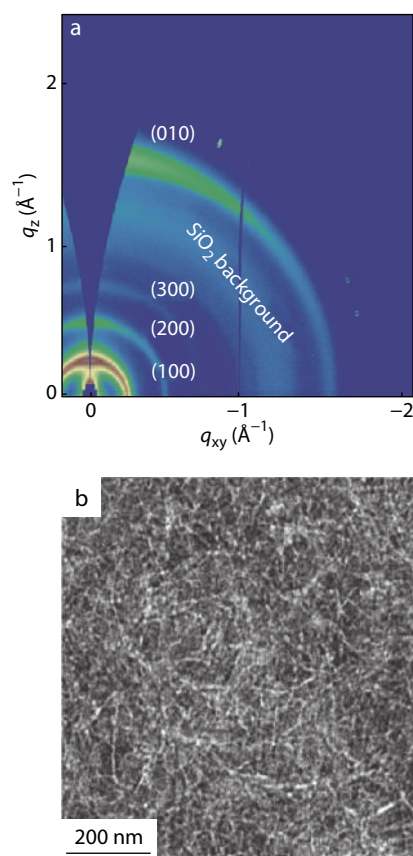


Fig. 3 (a) GIWAXS pattern of a neat **P8** film. (Reproduced with permission from Ref. [55]; Copyright (2014) Spring Nature). (b) TEM image of **P8**:PC₇₁BM film. (Reproduced with permission from Ref. [61]; Copyright (2018) Elsevier).

Although the PCEs of BT-polymer based fullerene OSCs have been enhanced to 11.7%,^[36] the drawbacks of fullerene acceptors, such as weak absorption in the visible region and difficulty to tuning chemical structures and purification, limited the further improvement of PCEs. Fortunately, these drawbacks have been successfully overcome by developing new non-fullerene acceptors (NFAs) with excellent properties. With the development of those new NFAs, the PCE of BT-

based OSCs was further improved up to 18.22%.^[20]

BT-based donor polymers in fused-ring electron acceptor based NFOSCs

Since Zhan *et al.* reported the first fused-ring electron acceptor (FREA) ITIC with 2-(3-oxo-2,3-dihydroinden-1-ylidene)malononitrile as end groups,^[15] ITIC and its derivatives have attracted much attention in recent years.^[19,65–69] In general, wide band gap conjugated polymers with absorption onset below 700 nm are used as electron donor to match with these near-infrared FREAs in order to realize complementary absorption spectra,^[70] in which the electron-deficient unit benzo[1,2-c:4,5-c']dithiophene-4,8-dione (BDD) is the most widely reported building block to construct donor polymers toward high performance NFOSCs with PCEs over 17%.^[24] BT-polymers have also been applied into FREA based OSCs, and it provides a record PCE of 18.22%.^[20]

When ITIC was published in the year of 2015, Yan *et al.* used an ITIC derivative ITIC-Th to work with the BT-polymer **P8** for application in NFOSCs, in which the donor and acceptor exhibited complementary absorption spectra (Fig. 4).^[71] A PCE of 6.6% with spectra response from 300 nm to 800 nm could be obtained. Zhu *et al.* developed a series of non-fullerene acceptors (ZITI-N-EH) to improve the miscibility with **P12** that has the similar structure to **P8**.^[72] As a consequence, the blend thin films could be fabricated at room temperature, and also provided the high PCE of 13.07%. It is also worthy to mention that the PCE could be maintained at 12.35% at a 200 nm thick film. Huang *et al.* also used a random copolymer design strategy to develop a BT-polymer **P13** (Fig. 4). The blend thin films based on **P13** could be fabricated from non-halogenated solvents, and the solar cells exhibited PCEs over 10% with the thickness of photoactive layers from 100 nm to 300 nm.^[73] These merits indicate the potential application of BT-polymers for large-area OSCs.

In addition to oligothiophene-based BT-polymers, BDT-based BT-polymers have also been applied into IC-based NFOSCs. Zhan *et al.* reported a BT-polymer **P14** with alkyloxy side chains at BT backbones and fluoro-benzene side units attached to BDT (Fig. 4).^[74] They used the acceptor IDIC to work with **P14**, providing a PCE of 11.03% in OSCs. Bo *et al.* developed the asymmetric BT monomers with alkyloxy/alkylthio unit and fluorine atom, in which oxygen and sulfur atoms significantly influenced the photovoltaic performance (Fig. 4).^[75] Oxygen-based BT polymer **P15** showed the PCEs of 7.28%, while the PCE was reduced to 1.55% in sulfur-based polymer **P16**. This example revealed the importance of finely tunable chemical structures in designing BT-polymers for OSCs.

Sun *et al.* used the narrow band gap polymer **P10** as donor to work with a near-infrared acceptor FOIC (Fig. 4).^[76] The blend exhibited strong photo-response in the NIR region, and meanwhile the blend could be transparent in the visible light region. Therefore, the corresponding solar cells could be used as semitransparent solar cells by using the thin metal contact. They found that a PCE of 4.2% could be obtained with a high transparency in the visible light region.

Recently, Ding *et al.* reported a wide band gap BT-based donor polymer for NFOSC with an amazing result.^[20] They constructed BT-based donor polymer **P17** with a fused-ring

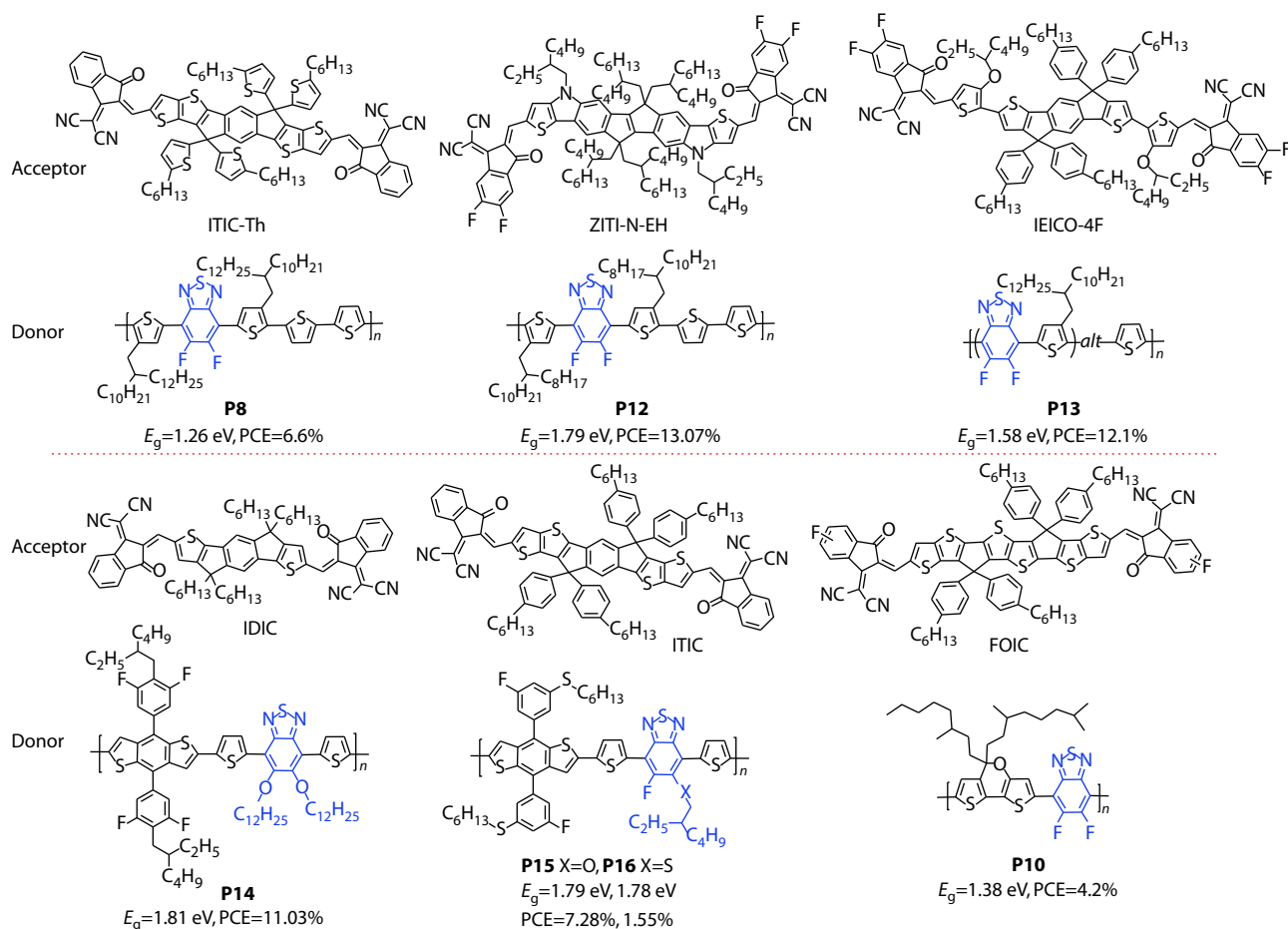


Fig. 4 Chemical structures of BT-based donor polymers and fused-ring electron acceptors for NFOSCs.

electron-deficient unit, dithieno[3',2':3,4;2'',3'':5,6]benzo[1,2-c][1,2,5]thiadiazole (DTBT) (Fig. 5). The high planarity of DTBT backbone gifted **P17** a higher hole mobility ($1.59 \times 10^{-3} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$). When **P17** was used as donor material to construct Y6 (Fig. 5)-based NFOSC, it provided an exciting PCE of 18.22%, which was the highest PCE in the stated-of-the-art NFOSCs.

BT-based donor polymers with other types of electron acceptors in NFOSCs

Besides fused-ring electron acceptors, there are also several kinds of small molecules as electron acceptor in BT-polymer based NFOSCs.^[77,78] For example, Yan *et al.* used the rhodamine end-capped acceptor O-IDTBR combined with the BT-polymer **P18** as electron donor to fabricate NFOSCs (Fig. 6).^[79] **P18** and O-IDTBR exhibited similar absorption spectra with onset at ~800 nm. NFOSCs based on their blends provided a high PCE of 10.4% with a high V_{oc} of 1.08 V and a very low energy loss (E_{loss}) of 0.55 eV. Yan *et al.* also reported a series of work focusing on NFOSCs based on the BT-polymers as donor and perylene bisimide (PBI) derivatives as acceptor. A typical work was that they developed a BT-polymer **P19** containing fluoro-substituted BT units and alkylthiophene units to simultaneously obtain small band gap and deep frontier energy levels (Fig. 6).^[80] Additionally, a bis-PBI molecule SF-PDI₂ with spirofluorene as core was developed as a wide band gap acceptor to match with

P19 to show complementary absorption spectra. A high PCE of 9.5% was obtained with the high V_{oc} of 1.11 V and hence a low E_{loss} of 0.61 eV. They also provided systematical studies about the origination of low E_{loss} , mainly due to the low non-radiative recombination. The E_{loss} could be further reduced to 0.53 eV together with a high PCE of 10.58% when using a new fused and star-shaped PBI-based acceptor FTTB-PDI4.^[81]

Bo *et al.* also used a series of 1,8-naphthalimide (NI) based electron acceptor for BT-based NFOSCs.^[82–84] NI-based acceptors exhibit wide band gap absorption spectra and high-lying energy levels, which can enable the high V_{oc} in solar cells. For example, they used the coplanar BT-polymer **P20** (Fig. 6) as donor and NI-based molecule NI-AA-NI with ethynyl units as acceptor to fabricate OSCs, in which a high V_{oc} of 1.07 V and a PCE of 3.71% could be obtained.^[84]

BT-based donor polymers in all-polymer solar cells

All-polymer solar cells (all-PSCs) as one type of OSCs have also attracted tremendous attention, not only for their tunable structural, optical and electrochemical properties, but also for their general merits over small molecules, such as good thermal stability and robust mechanical property. However, the performance of all-PSCs still lags behind fullerene-based or fused-ring electron acceptor-based OSCs (Fig. 7).

In 2015, in order to study the relationship between chemical structures and photovoltaic properties, Kim *et al.* de-

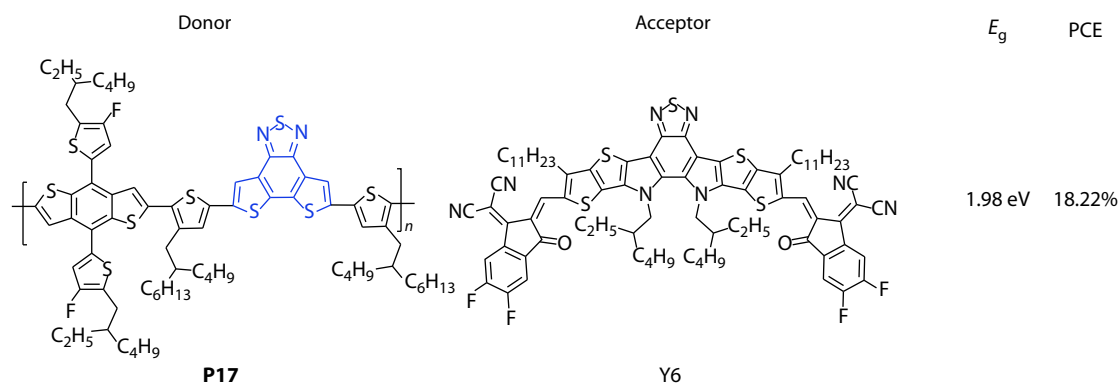


Fig. 5 Chemical structures of BT-based donor polymer **P17** and fused-ring electron acceptor **Y6** for NFOSC with the highest PCE.

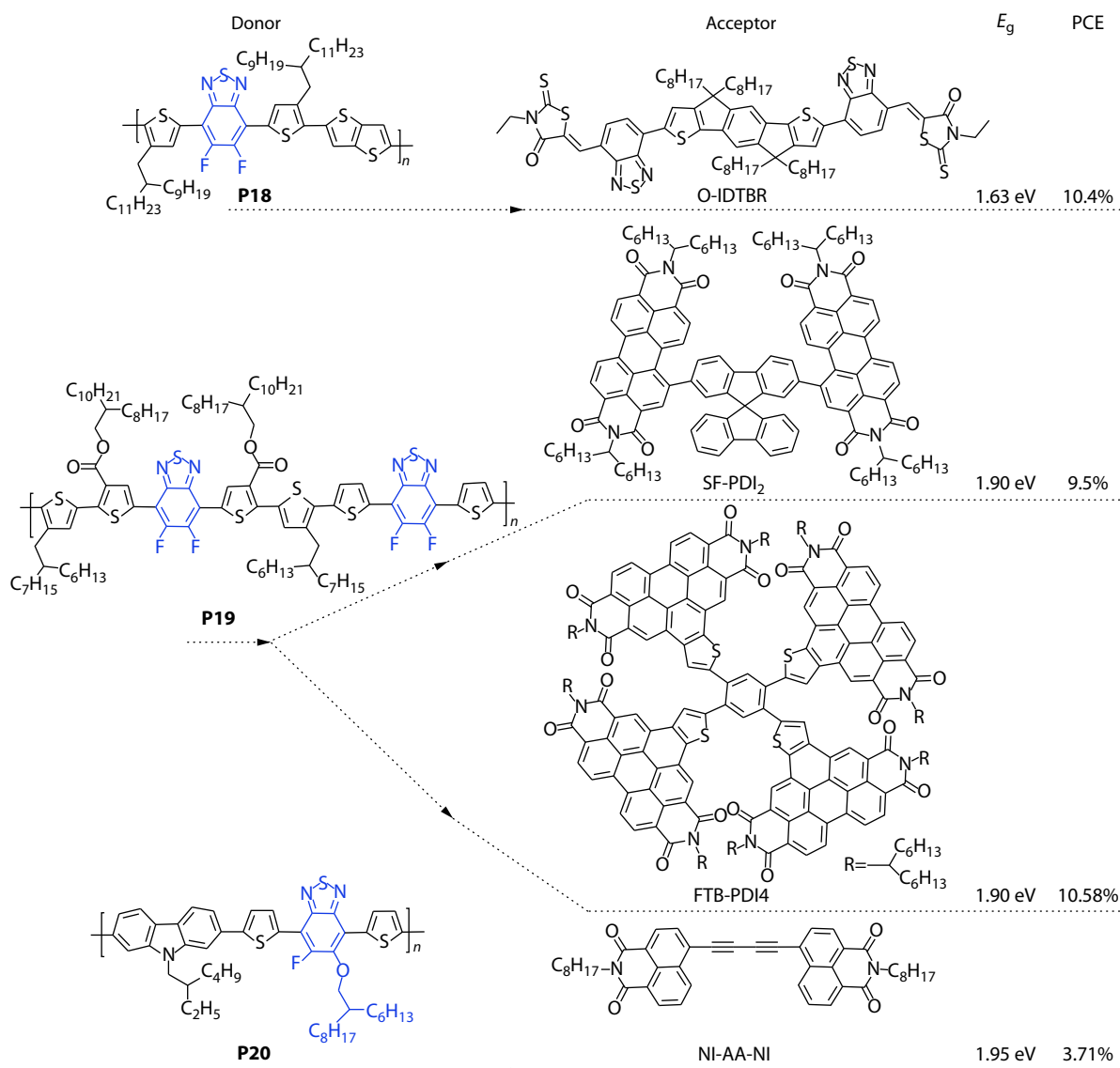


Fig. 6 Chemical structures of BT-based donor polymers and other types of electron acceptors for NFOSCs.

veloped a series of BT-polymers with different number-average molecular weights (**P21_L**, $M_n=12$ kg/mol; **P21_M**, $M_n=24$ kg/mol; **P21_H**, $M_n=40$ kg/mol) to investigate their photovoltaic performances (Fig. 7).^[85] The **P21_H** with high M_n im-

proved the miscibility with the polymer acceptor (NDI2OD-T2) and hence inhibited the formation of crystalline region. Therefore, the hole and electron mobilities of the optimized all-PSCs based on **P21_H**:P(NDI2OD-T2) are significantly higher

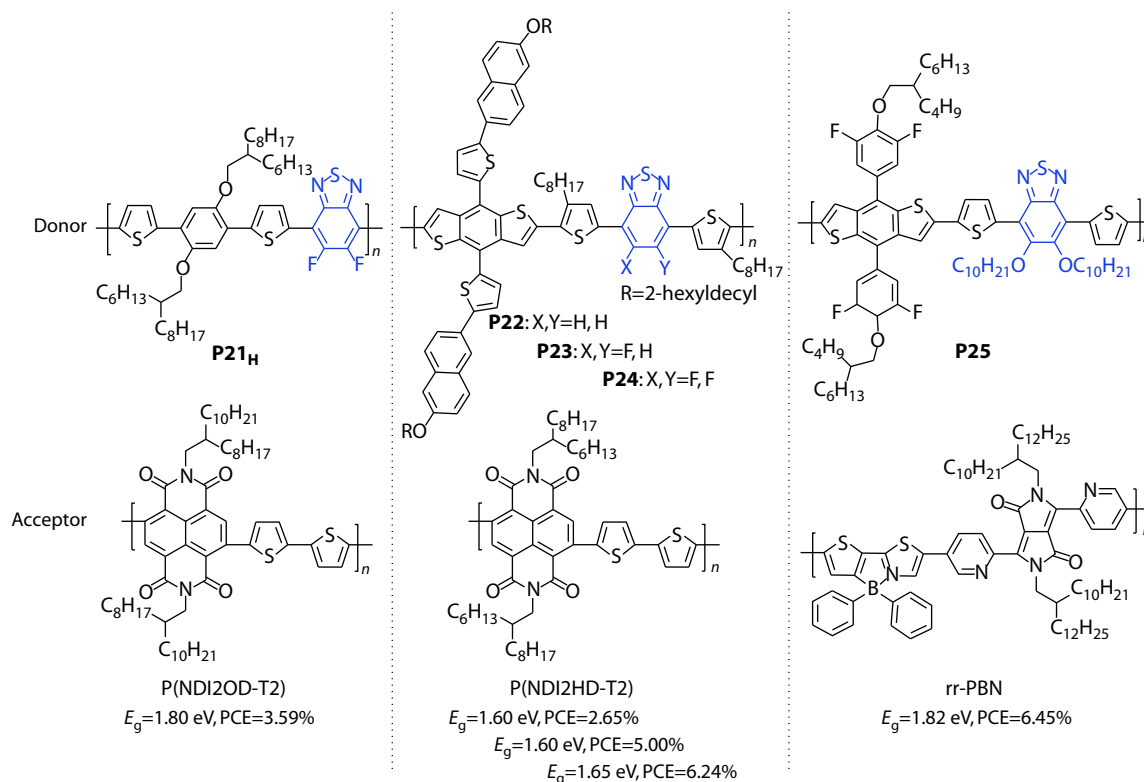


Fig. 7 Chemical structures of polymers involved in BT-based all-PSCs.

than those of **P21_L**:P(NDI2OD-T2), and the PCE is more than 5%, which is one of the highest values reported at that time. For comparison, **P21_L**:P(NDI2OD-T2) cells exhibited a low PCE of 3.78%. In 2017, Kim *et al.* further developed a series of BT-polymers (**P22**, **P23** and **P24**) with different numbers of fluorine atoms on the backbones (Fig. 7).^[86] They found that when enhancing the content of fluorine atoms, the polymers exhibited enhanced dipole moment difference between the ground and excited states ($\Delta\mu_{ge}$). The large $\Delta\mu_{ge}$ of **P24** was helpful for exciton dissociation and meanwhile suppressed charge recombination in solar cells when using P(NDI2HD-T2) as electron acceptor. As a consequence, **P24** based all-PSCs provided a high PCE of 6.42% with simultaneously enhanced V_{oc} , J_{sc} and FF, while **P22** only showed a low PCE of 2.65%. Liu *et al.* also introduced different numbers of fluorine atoms into BT-polymers to tune the crystallinity so as to match with the B→N polymer rr-PBN that has been developed in their group.^[87] **P25** with four fluorine atoms on each monomer exhibited a high PCE of 6.45% in all-PSCs (Fig. 7). Apparently, all-PSCs based on BT-polymers as donor are far to be explored.

BT-BASED POLYMER ACCEPTORS IN ALL-POLYMER SOLAR CELLS

The electron-deficient nature of BT indicates that BT-polymers can be used as electron acceptor for all-PSCs when providing rational design of chemical structures. Indeed, in recent years, there are many BT-polymers that have been developed for this purpose.^[88–93] As early as 2007, the BT-polymer named as F8TBT (**P26** here) that had been previously used as electron donor to

work with PCBM in OSCs was also found to exhibit electron transport property,^[94] so that **P26** could also be used as electron acceptor in solar cells (Fig. 8). All-PSCs based on P3HT:**P26** exhibited PCEs up to 1.2% when using a thermal annealed process.^[95] This P3HT:**P26** blend was then used as model system to study the crystallinity, morphology control and device physics in all-PSCs.^[95–97]

The deficient nature of **P26** can also be clearly observed, that is, it has the high-lying frontier energy levels so that only P3HT can be used as electron donor in OSCs. In order to lower the frontier energy levels of BT-polymers, Guo *et al.* creatively introduced two cyano units into BT core.^[98] Cyano unit as strong electron-deficient group can effectively lower the frontier energy levels, while the absorption spectra can still be maintained at the near-infrared region. The corresponding polymer **P27** (Fig. 8) with indacenodithiophene as comonomer showed a narrow band gap of 1.43 eV and suitable energy levels of -3.75 and -5.59 eV as the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels. The optical and electrochemical properties of **P27** are similar to those of the polymer acceptor based on NDI unit. More importantly, **P27** exhibited high extinction coefficient in the near-infrared region, which perfectly solved the problem of low extinction coefficient of NDI-polymers. Therefore, **P27** was used as electron acceptor in all-PSCs, providing a PCE of 8.32% with a broad photo-response from 300 nm to 850 nm. The solar cells also exhibited very high V_{oc} , resulting in a low E_{loss} of 0.53 eV. In a recent work, they introduced a strong electron-donating comonomer into the polymer **P28** (Fig. 8) to further broaden the absorption spectra, and a very low band gap of 1.28 eV could be obtained in this

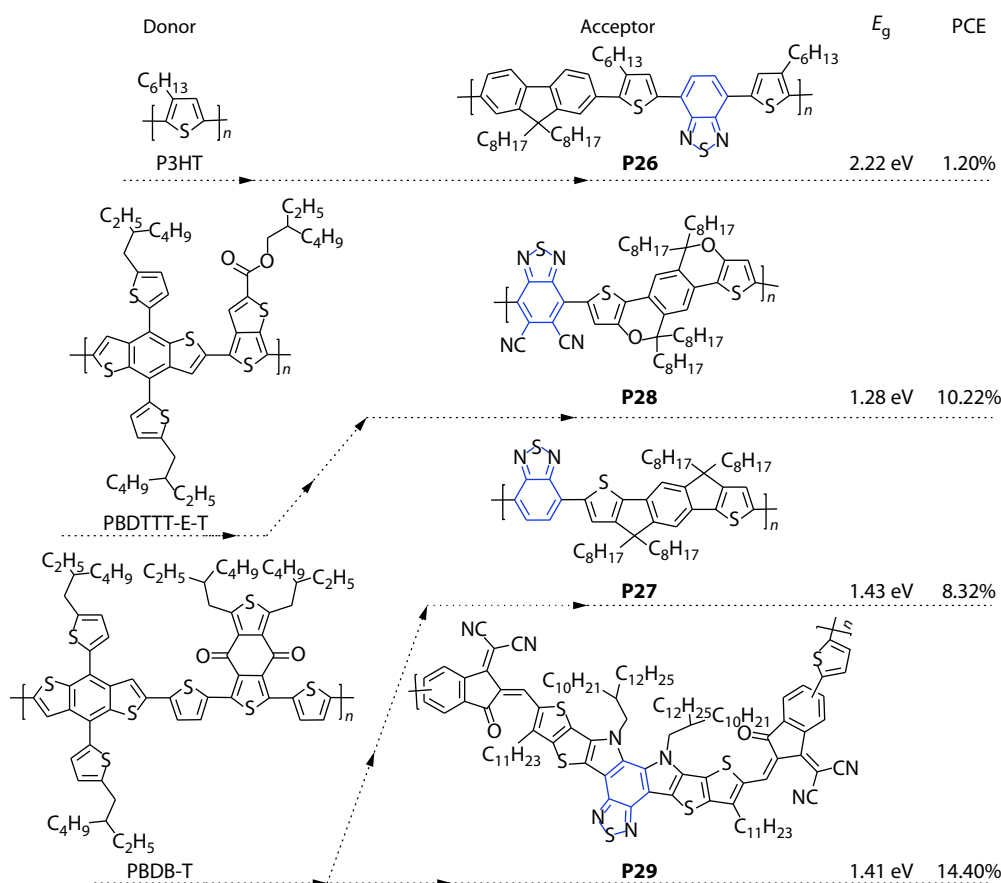


Fig. 8 Chemical structures of BT-polymers as electron acceptor for application in all-PSCs.

polymer.^[99] All-PSCs based on **P28** as electron acceptor exhibited a PCE of 10.2% with a high J_{sc} of 22.52 mA·cm⁻². These excellent polymer designs and their consequence undoubtedly prove that BT-polymers as electron acceptor have the great potential application in all-PSCs.

Another interesting type of BT-polymer acceptors is based on the well-known near-infrared acceptor Y6 developed by Zou *et al.*^[100] Y6 and its derivatives have been widely used as electron acceptor for high performance OSCs, in which BT is usually used as core. Inspired by the pioneer work that used ITIC as core to construct polymer acceptors by Li *et al.*, several works focused on using Y6 to construct new polymers (for example, **P29** with one thiophene as copolymerized unit).^[37,91,101,102] These polymers exhibited near-infrared absorption up to 900 nm, well-aligned frontier energy levels and good electron transport properties. Therefore, the PCEs based on these polymers as electron acceptors could realize PCE over 14% (Fig. 8) when providing rational control of molecular weight, copolymerized units and so on. It can be envisioned that further development of Y6-based polymer acceptor can enable the PCEs of all-PSCs to be over 17%.

CONCLUSIONS

In this review, we provided an overview of BT-polymers for OSCs, from the aspect of electron donor and electron acceptor. With the judicious molecular design and device engineering, the PCEs based on BT-polymers have achieved over 18% and

14% when using as donor and acceptor. These outstanding achievements reveal the great potential of BT-polymers in OSCs, and the high PCE (18.22%) was one of the highest PCEs at the state-of-the-art NFOSCs. However, if looking into the studies of NFOSCs, we will find that BT-polymers are far to be explored, so that it also leaves many tasks to be explored.

Firstly, it is necessary to explore BT-polymers as donor for NFOSCs, such as by using the known BT-polymers that have been used in fullerene-based OSCs and also developing new BT-polymers. The structural engineering includes BT core and comonomers, from the aspect of tuning the frontier energy levels and crystallinity, such as by introducing heteroatoms, different side units and the molecular weight. It is worth mentioning that direct arylation polymerization method as a green synthetic method is an important topic in the future, which should be considered in the synthesis of BT-polymers.^[103]

Secondly, BT-polymers usually show strong crystallinity as diketopyrrolopyrrole-polymers, which is different from BDD-polymers with strong aggregation.^[104] Apparently, fused-ring electron acceptors tend to work with BDD-polymers possibly due to the well-organized phase separation, but would be incompatible with BT-polymers. To solve this problem, it would be the possible way to design BT-polymers with low crystallinity or develop suitable fused-ring acceptors. Additionally, it is very important to reveal the impact of crystallinity of BT-polymers on the morphology and hence the photovoltaic performance in solar cells.

Thirdly, it is important to focus on the photovoltaic devices based on BT-polymers, such as thick films, large-area and flexible devices, semitransparent cells and stability. The high crystallinity of BT-polymers enables to show high carrier mobilities, so that they still can exhibit high performance in thick films. This is in particular important for large-area devices. It seems that BT unit is very stable under thermal stress and heat, but there are still very few studies focusing on the stability of BT-polymers.

In conclusion, BT-polymers exhibit many characteristics in organic electronics, which can act as the important conjugated materials for OSCs. Further studies, from material design, morphology control to device engineering, are urgently needed to endow BT-polymers based OSCs with high stability as well as high performance even under thick films, which will be the promising system for industry application.

BIOGRAPHIES

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