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Benzo triazole Based 2D-conjugated Polymer Donors for High Performance Polymer Solar Cells

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Abstract To design high efficiency polymer solar cells (PSCs), it is of great importance to develop suitable polymer donors that work well with the low bandgap acceptors, providing complementary absorption, forming interpenetrating networks in the active layers and minimizing energy loss. Recently, we developed a series of two-dimension-conjugated polymers based on bithienylbenzodithiophene-alt-benzo triazole backbone bearing different conjugated side chains, generally called J-series polymers. They are medium bandgap polymers (\(E_g\) of ca. 1.80 eV) with strong absorptions in the range of 400–650 nm, and exhibit ordered crystalline structures, high hole mobilities, and more interestingly, tunable energy levels depending on the structure variations. In this feature article, we highlight our recent efforts on the design and synthesis of those J-series polymer donors, including an introduction on the polymer design strategy and emphasis on the crucial function of differential conjugated side chain. Finally, the future opportunities and challenges of the J-series polymers in PSCs are discussed.

Keywords Polymer solar cells; Benzotriazole based 2D-conjugated polymer; J-series polymers

INTRODUCTION

Polymer solar cells (PSCs) are attracting extensive studies for the generation of affordable, clean, low-cost, and renewable energy due to their advantages of lightweight, flexibility and solution processing.\[^1\]\ Generally, PSCs are fabricated with a bulk heterojunction structure using a p-type conjugated polymer as donor and an n-type organic semiconductor (n-OS) as acceptor (traditional fullerene derivatives, such as PC\(_{71}\)BM in Fig. 1).\[^2\]\ Recently, PSCs have witnessed a dramatical progress with power conversion efficiencies (PCEs) up to 17%,\[^3\]−\[^6\]\ which greatly benefits from the advances of n-OSs and n-type conjugated polymer (n-CP) as acceptors with favorable advantages of accessibility, strong absorption in the visible-near infrared region and adjustable energy levels.\[^7\]−\[^11\]\ Inspired by the attractive features, a variety of n-OSs and n-CPs (such as N2200 in Fig. 1) are designed. Notably, special interests are with those A-D-A (acceptor-donor-acceptor) based small molecular acceptors (SMAs), such as ITIC and their derivatives in Fig. 1) and the polymerized SMAs (PSMAs), due to their low bandgap (LBG), strong absorption in the near-infrared region (NIR) and suitable lowest unoccupied molecular orbital (LUMO) energy level.\[^12\]−\[^14\]\ Among the polymer donors, D-A type medium band gap (MBG) ones are of particular interest due to their complementary absorption with the LBG acceptor for a broad wavelength range of light harvest and thus a high short circuit current (\(J_{sc}\)) in the PSCs. Based on the D-A approach, recently, Li and coworkers have developed a series of such MBG copolymers composed of bithienylbenzodithiophene (BDTT)-alt-benzo triazole (BTA) backbone, generally named as J-series polymers for convenience.\[^15\]\ They exhibit a strong absorption in the range of 400–650 nm with an optical bandgap of ca. 1.80 eV. These polymers are designed in consideration with the special features of the LBG SMAs (also called as “non-fullerene acceptor”) with planar molecular structure. That is why those J-series polymers are designed with conjugated side chain, due to the better matching of the 2D conjugated polymer donor with the non-fullerene acceptors, especially in the aspects of morphology and charge transportation.\[^16\]\ One attractive feature of the J-series polymer donors is that their crystalline behavior and the energy levels can be flexibly tuned via molecular structure variation, such as the side chains, thus making them match well with a variety of LBG.
In some cases, the J-series polymers possess a deep-lying highest occupied molecular orbital energy level (\(E_{\text{HOMO}}\)) that even approaches to the \(E_{\text{HOMO}}\) of LBG acceptors used. Notably, even at a negligible HOMO energy offset between the polymer donor and the SMAs, efficient hole transfer from acceptors to donor does happen, which provides a solution to address the trade-off between \(V_{\text{oc}}\) (open-circuit voltage) and \(J_{\text{sc}}\), both of which are closely related to PCE.\(^{23}\)

In this feature article, we highlight our efforts on the design and synthesis of high-performance MBG polymer donors. Starting with a short illustration on the molecular design strategy, the detailed chemical engineering and special side-chain engineering on these J-series polymers are discussed, followed by a highlight on the basic functions of the J-series polymer, that is, providing a complementary absorption with the LBG acceptors, minimizing voltage loss, and tuning the blend morphology. Finally, future opportunities and challenges to further increase the device performance and towards realization of the commercialization are also provided.

**DESIGN STRATEGY FOR J-SERIES POLYMERS**

Generally, conjugated polymers are constructed by an alternating copolymerization of electron-donating and -accepting units in the backbones, in which the orbital mixing of the D-unit and the A-unit provides a means for narrowing the bandgap and tuning the energy levels of the conjugated D-A copolymers (Fig. 2a).\(^{24}\) For the BTA unit, its structure can be regarded as replacing the sulfur atom in the benzo thiadiazole (BT) unit (the widely used strong A-unit) with nitrogen atom (Fig. 2b). The incorporation of the nitrogen atom in BTA unit weakens its electron-accepting ability relative to that of BT unit. For the donor part, the fusion of benzene units with electron-rich thiophene unit generates a donor unit of benzodithiophene (BDT, structure provided in Fig. 2c), showing a moderate electron-donating ability.\(^{24}\) Fig. 2(d) gives the BTA-based D-A copolymers of PDTS-DTBTA,\(^{25}\) PBDT-HBTA (J50),\(^{35}\) and PCz-DTBA\(^{26}\) with DTS, BDT and Cz as the D-unit, respectively, where the electron-donating ability is weak for DTS, medium for BDT and strong for Cz. As a result, the polymers display different optical bandgaps, showing that the combination of moderate electron-donating and -accepting units is the best choice for designing MBG copolymers, such as J-series polymers discussed here.

In the molecular architectures, using BTA as A unit provides an advantage of the capability of attaching alkyl chains onto the top nitrogen atom of BTA unit to insure the solubility of the resultant polymers and a more planar conformation.\(^{27}\) Furthermore, the introduction of fluorine atom on BTA units can further improve the planar conformation of the backbone through intramolecular F…H and F…S interactions. And the planar conformation can promote close packing of the polymer chains for an ordered crystalline structure and thus a higher hole mobility in film.\(^{27,28}\) Meanwhile, another function of the fluorine atom is to down-shift the \(E_{\text{HOMO}}\) of the polymer donor for a higher \(V_{\text{oc}}\) of the PSCs. For the BDTT units, the unique arrangement of the conjugated side chains is to construct 2D-conjugated polymers, as they have advantages of better matching with the n-OS (or n-CP) acceptor in the aspects of morphology and exciton separations.\(^{11}\) Besides, the HOMO energy levels and the aggregation behavior of the resultant polymers can be further tuned by attaching suitable side chains,\(^{16}\) such as alkysilyl substitution or the alk yli thio substituent. And the engineering of the side-chains and the main chain has been proved to be effective strategies for producing various highly efficient J-series polymer donors suitable for LBG non-fullerene PSCs.

**Fig. 1** Chemical structures of typical acceptors discussed in this feature article.

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THE SIDE CHAIN AND MAIN CHAIN ENGINEERING OF J-SERIES POLYMERS

Under the 2D molecular architecture, the photophysical properties of the J-series polymers can be well regulated via a variety of chemical approaches on their building blocks (such as on the BDT unit, BTA unit, and π bridges between them) as well as the conjugated side chain attaching on the BDT unit and flexible side chain on the BTA unit. Related side chain engineering and main chain engineering have created a family of efficient photovoltaic polymer donors (Figs. 3 and 4).

Tables 1 and 2 list the photoelectronic and photovoltaic properties of the J-series polymers. It can be seen that among versatile chemical approaches mentioned above, the conjugated side-chain engineering on the donor parts is of particular interest and thus being systematically studied. Related investigation results indicate that this approach is more effective in fine-tuning the photophysical properties, such as energy levels and aggregation properties. The substitutional effect of alkyl chain of BTA unit was not fully investigated; at present, the most efficient J-series polymers are mostly based on a hexyldecyl group on the BTA units. Thus, in the following section, the J-series polymers are primarily classified into three categories based on the solubilizing side chains attached on the conjugated side chains of the BDT unit, namely, alkyl, alkylthio, and trialkysilyl substituents. In addition, for simplicity, in each category, their chlorinated or fluorinated derivatives are also included in Fig. 4. Related discussions on the effect of halogen substitutions and other approaches are given followed by the discussion on the flexible side chains.

Our exploration on the J-series polymers starts from 2012 with the report of two 2D-conjugated D-A copolymers, PBDT-HBTA (J50) and PBDT-FBTA (J51), bearing alternative main-chain units of BDT as D-unit, BTA as A-unit with or without fluorine substitution, and thiophene π bridges between the BDT and BTA units. The design on the main-chain was based on the works of You and Zou, in which they investigated flexible side chain substituted copolymers of PBnDT-FTAZ and PBnDTBFTz, respectively (Fig. 3). Interestingly, You et al. found that attaching fluorine substitution on the BTA units increased its crystallinity and suppressed carrier recombination in device, which are desirable for designing thickness-insensitive PSCs. For our design on J50 and J51, attaching thiophene-conjugated side chain on the BDT unit is to gener-
ate 2D-conjugated polymers as they have advantages of broadened absorption, down-shifted HOMO energy level and enhanced hole mobility compared with their counterpart with flexible side chains. Compared to J50, J51 with fluorine substitution on the main chain shows a lower $E_{\text{HOMO}}$ of $-5.26$ eV, higher hole mobility, and significantly better photovoltaic performance. The PSCs based on J51:PC$_{71}$BM demonstrated a PCE of 6.0% with a $J_{\text{sc}}$ of 11.9 mA·cm$^{-2}$, and a $V_{\text{oc}}$ of 0.75 V. J51 and J50 aroused people’s particular interest in 2016 when we explored them as donors pairing with a LBG polymer acceptor based on naphthalene diimide-alt-bithiophene (N2200, structure provided in Fig. 1), realizing a high PCE of 8.27% together with a high FF of 70.24% for all the polymer solar cells (all-PSCs). The PCE value of 8.27% was the highest one reported for all-PSCs at that time. The high efficiency mainly benefits from the higher hole mobility of J51 with a crystalline structure, and more importantly complementary absorption of J51 with N2200. This is the first example using J-series polymers in non-fullerene PSCs.

To further increase the device efficiency, we replaced N2200 with an n-OS of ITIC (Fig. 1), with a high absorption coefficient relative to N2200 in the NIR region, while N2200 has obviously weak absorption in the NIR region and thus low photo-response in the long wavelength range in device. In comparison with the J51:N2200 devices, the J51:ITIC device demonstrated a high external quantum efficiency (EQE) in the long wavelength range and thus an increased $J_{\text{sc}}$ value of 16.5 mA·cm$^{-2}$ and a higher PCE of 9.26% along with a $V_{\text{oc}}$ of 0.82 V. The large energy loss ($E_{\text{loss}}$) of 0.76 eV in the J51:ITIC-based PSCs indicated that the PCE can be further increased by using a lower-lying $E_{\text{HOMO}}$ polymer donor to increase $V_{\text{oc}}$ and decrease $E_{\text{loss}}$ of the PSCs. Thus, we performed a systematic side-chain engineering to down-shift $E_{\text{HOMO}}$ of the J-series polymer donors by using alkylthio side chains. Thus, three polymers with branched alkyl (J52), branched alkylthio (J60) and linear alkylthio (J61) substituent on the BDTT units were designed and synthesized. Among the three polymers, J61 with linear alkylthio side-chain exhibited a maximum PCE of 9.53% with an enhanced $J_{\text{sc}}$ of 17.43 mA·cm$^{-2}$ and a high $V_{\text{oc}}$ of 0.89 V in the ITIC-based PSCs. Compared with the J51:ITIC based devices, the higher efficiency mainly benefits from the increased $V_{\text{oc}}$ of 0.89 V (and reduced $E_{\text{loss}}$ value of 0.68 eV) in the PSCs based on J61:ITIC due to the down-shifted $E_{\text{HOMO}}$ of J61 than that of J51. Further device optimization with a side chain isomer of ITIC (m-ITIC, structure provide in Fig. 1) as acceptor promoted the J61-based PCE to 11.77%.

To check the possibility of reducing $E_{\text{loss}}$ by further decreasing HOMO energy level of the J-series copolymers, we synthesized J71 (Fig. 4) by introducing trialkylsilyl substituents on BDTT unit, yielding a further down-shifted $E_{\text{HOMO}}$ of $-5.46$ eV. Very interestingly, the PSCs based on J71 as donor and ITIC as acceptor demonstrated a high PCE of 11.41% along with a high $V_{\text{oc}}$ of 0.94 V, a high $J_{\text{sc}}$ of 17.32 mA·cm$^{-2}$ and a low $E_{\text{loss}}$ of 0.63 eV. Notably, the high device performance was attained even with a very small HOMO energy offset of 0.11 eV between J71 and ITIC. With m-ITIC as the acceptor, the PCE of the J71-based PSC was further increased to 12.01%. On the basis of highly efficient J71, its derivatives were synthesized by changing the alkyl chain length and shape of its alkylsilyl side chains. It was found that the shorter (J70) and linear (J74) alkylsilyl side chain produced ordered molecular packing, stronger absorption coefficient, higher charge carrier mobility, and thus afforded higher $J_{\text{sc}}$ and FF in their corresponding PSCs, while the J71 derivatives with a longer (J73) or branched (J72) trialkylsilyl group generated lower-lying HOMO energy levels which resulted in higher $V_{\text{oc}}$ of the PSCs. In addition to the solubilizing side chains (alkylthio or trialkylsilyl substituent), another approach to lower the HOMO...
energy levels is with the halogen substitution. We can call this approach “halogen atom substitution”. Like the effect of fluorine substitution on the BTA units, for the J-series polymers, the fluorination or chlorination on their thiophene conjugated side chains usually down-shifts its HOMO energy level. As shown in Tables 1 and 2, with the chlorine substituent, PBZ-CISi and PBZ-Cl[37] reported by Zhang et al. have down-shifted HOMO energy levels relative to those of their respective counterparts (J71 and J52). It is notable that PBZ-Cl was also reported by Zhou et al. with the name of J52-Cl[38]. Interestingly, with a BTA unit-containing acceptor of BTA3 (structure provided in Fig. 1), a concept of “Same-A-Strategy” was well demonstrated to well control the energy offsets between J52-Cl and BTA3 (ΔE_HOMO=0.10 eV, ΔE_LUMO=0.28 eV), yielding a decreased nonradiative recombination loss of 0.24 eV and a very high V_OC of 1.24 V under a high PCE of 10.5% and a low ΔE_DSS of 0.52 eV. For J52-FS[39] and PFBZ[40] with the fluorine substituent on thiophene conjugated side chains, their HOMO
energy levels are also down-shifted, relative to those of J60 and J52, respectively. As a typical example, a highly fluorinated J-series polymer donor (J91)\(^{[41]}\) was synthesized by attaching the difluoroalkylthienyl side groups on the BDT donor units, resulting in a lower \(E_{\text{HOMO}}\) of –5.50 eV. With m-ITIC as acceptor, J91 produced a high efficiency of 11.67% with a simultaneously high \(V_{\text{oc}}\) of 0.984 V and \(J_{\text{sc}}\) of 18.03 mA·cm\(^{-2}\) and a further reduced \(E_{\text{b eff}}\) of 0.61 eV\(^{[41]}\) while for its analogue of J52 without the difluorothiophenyl side chain, the \(E_{\text{HOMO}}\) was only –5.17 eV and \(V_{\text{oc}}\) was 0.70 V in the m-ITIC-based devices.\(^{[41]}\) Notably, the high efficiency of J91-based PSCs also greatly benefits from the suppressed triplet exciton formation with the difluoroalkylthienyl side chain groups as discussed below. Interestingly, the change of fluorene with chlorine is more effective in tuning the energy levels due to the free 3d empty orbital of chlorine available for \(n\)-electron delocalization.\(^{[93,\text{51}]}\)

On the basis of J71, Min et al. replaced fluorine with chlorine on the BTA unit, yielding J101 with a further down-shifted \(E_{\text{HOMO}}\) (0.03 eV lower than that of J71), a higher oscillator strength, and a slightly higher absorption coefficient compared to its counterpart of J71.\(^{[47]}\) With ITIC as acceptor, \(V_{\text{oc}}\) and PCE for the J101-based PSCs were increased to 0.951 V and 12.47%, respectively, while with another LBG acceptor of ZITI, its efficiency was further increased to 14.12%. So is the case for PB4TCl-Bz, synthesized by He et al. by replacing the difluoroalkylthienyl side chain in J91 with the dichloroalkylthienyl side chain.\(^{[42]}\) PB4TCl-Bz has a lower \(E_{\text{HOMO}}\) of –5.64 eV relative to its analog of J91 (−5.50 eV). Besides chlorine substitution at the \(\beta\) position, Qiu et al. moved chlorine atom to a position, and to insure the solubility of the resultant polymers, flexible side chains were attached at the \(\beta\) position, and accordingly, J11 with alkoxyl chains and J12 with the alkyl groups were synthesized.\(^{[38,\text{39}]}\)
chains were synthesized through a relatively simple synthetic method. Compared with J12, J11 displayed slightly better aggregation and miscibility with m-ITIC, resulting in a higher PCE of 12.32% with a high FF of 73.0%.

Another approach to tune the photophysical properties of the J-series polymers is based on the "aromatic ring engineering", that is, the variation of polymer building blocks or conjugated side chains of the thiophene unit with furan, thieno[3,2-b]thiophene (TT), or selenophene unit. Although these approaches are not always effective in increasing the efficiency, the structure-property relationship disclosed can also give some useful guidance for molecular design. For example, replacing the thiophene unit with furan units in the BDT unit or in the n bridges usually weakens the electron-donating ability of the polymer backbone and hence lowers their HOMO energy levels for higher $V_{oc}$ values. With the replacement of the thiophene with furan unit in the BDT unit, J81 was synthesized with an $E_{HOMO}$ of $-5.43$ eV, which is slightly lower than that ($-5.40$ eV) of its analogous polymer J71. So is the case for J61-F, constructed by replacing the thiophene with furan units in the $n$ bridges of J61. J61-F has a lower $E_{HOMO}$ of $-5.45$ eV relative to its analog of J61 ($-5.32$ eV).

To study the effect of TT substitution, J46 and J47 were designed and synthesized by using TT units to replace thiophene conjugated side chains on the BDT units of the corresponding copolymers of J52 and J71. The resultant polymers demonstrate a slightly lower HOMO energy levels due to the big size chains and thus a higher $V_{oc}$ in the ITIC-based devices, showing $V_{oc}$ values of 0.74 V for J46 (0.73 V for J52) and 0.96 V for J47 (0.94 V for J71). However, The PCEs of J46 (2.34%) and J47 (9.01%) with TT side chains are lower compared with their polymer analogue, mainly due to the weakened $n\pi$ interaction between the polymer chains. Different from the side chain engineering with the TT unit, the main chain engineering with the TT unit as the $n$-bridge can change the backbone from a zigzagged conformation to a linear one, which is beneficial to a stronger $n\pi$ stacking.[45,46] Thus, on the basis of J52-CI, PE4 with TT as the $n$ bridge was synthesized by Zhou et al., showing an obviously enhanced crystallinity and charge mobility. With Y6 as acceptor, PE4 gives a high PCE of 14.0% with a high FF of 75.0% and $J_{sc}$ of 22.21 mA cm$^{-2}$, superior to those of J52-CI (PCE=12.31% and FF=61.0%).

On the basis of J71, the effect of selenophene substitution was also investigated, which usually leads to red-shifted absorption band and lower bandgap due to the enhanced $n\pi$ interaction between the polymer chains. In addition to the side-chain engineering, other approaches, such as aromatic ring engineering and halogen atom substitution, are also discussed. These effects have enriched the family of J-series polymers and promoted the progress of non-fullerene PSCs for a better device performance and/or an insightful understanding on how to rationally pair a donor with a certain acceptor. To better understand the critical role of the J-series polymer as donors in PSCs, more specially, the effect of structure variation on their photovoltaic properties, the basic functions of the J-series polymers are discussed in terms of absorption, energy losses, charge dynamics, and morphology. In addition, the discussions can give useful guidance for further molecular design and the study on the effect of structure variations on device performance.

**Absorption**

The absorption properties of the active layer in PSCs are the primary factor directly associated with the $J_{sc}$ in devices. To harvest more light in the solar spectrum range and thus maximize the $J_{sc}$, the active layer should have a broad absorption coverage with strong absorption intensity, so LBG photovoltaic material is particularly interesting, such as the LBG non-fullerene acceptors (ITIC and N2200, Fig. 1). Compared with traditional fullerene-based PSCs, non-fullerene acceptor-based PSCs have distinct advantages of harvesting light both from the donor and acceptor part. Nevertheless, this does not mean that the material selection based on the LBG donor and LBG acceptor is effective in designing high performance PSCs. For example, PSCs using LBG polymer donor of PTB7-Th (with absorption band from 550 nm to 780 nm) as donor component achieved primary PCEs of only 6.8% with low bandgap ITIC as acceptor and 5.7% with N2200 as acceptor. Obviously, if the polymer donors have a complementary absorption with those LBG acceptors, $J_{sc}$ and thus PCEs of related devices could be further improved. Under this consideration, we used a MBG polymer of J51 to replace PTB7-Th as donor for providing well-matched complementary absorption with ITIC or N2200. Fig. 5(a) shows the absorption of J51 and ITIC. As a result, corresponding devices demonstrated an increased $J_{sc}$ and PCE with J51 as donor relative to those with PTB7-Th. For the ITIC-based PSCs, $J_{sc}$ of 14.21 mA cm$^{-2}$ and PCE of 6.80% for the device with LBG PTB7-Th as donor are respectively increased to 16.47 mA cm$^{-2}$ and 9.26% for the devices with MBG polymer J51 as donor, while for the N2200-based all-polymer PSCs, $J_{sc}$ of 13.00 mA cm$^{-2}$ and PCE of 6.80% for the device with LBG PTB7-Th...
Th as donor were respectively increased to 16.47 mA cm$^{-2}$ and 8.27% for the devices with MBG polymer J51 as donor.[68,69] The results show that the complementary absorption is very important to harvest light in a broad range, and J-series donor polymers can provide absorptions at a wavelength range of 400–650 nm that match well with those LBG acceptors.

**Voltage Loss**

Generally, in PSCs, the driving force for exciton dissociation and non-radiative recombination loss are the two main sources for the voltage loss, creating a great challenge to simultaneously obtain a large $V_{OC}$ and a high $J_{SC}$.[67,68] As a primary requirement in PSCs, donor and acceptor are paired with cascading energy levels to provide a driving force for exciton dissociation at the heterojunction interface. Thus, between the donor and acceptor, larger LUMO/HOMO energy offset ($\Delta E_{LUMO}$ and $\Delta E_{HOMO}$) can result in efficient exciton dissociation, unfortunately, which is usually accompanied with the sacrifice of energy loss. In most of high efficiency fullerene-PSCs, the driving force is usually larger than 0.3 eV to split the tightly bound excitons, while in non-fullerene-based PSCs, the driving force could be quite small. As a typical example, we explored the trialkylsilyl substituted J71 as an $E_{HOMO}$ lower-lying donor ($E_{HOMO}$=−5.46 eV) to pair with ITIC, and found a highly efficient and long-lived exciton dissociation at the J71/ITIC interface as observed by transient absorption spectroscopy (TAS) even though the $\Delta E_{HOMO}$ between J71 and ITIC is extremely small (only 0.11 eV).[23] The PCE reached 11.41% with a simultaneously high $V_{OC}$ of 0.94 V and a high $J_{SC}$ of 17.32 mA cm$^{-2}$. These results provide a plausible approach of minimizing the energy offset (or the driving force, Fig. 5b) to well address the trade-off between the $V_{OC}$ and $J_{SC}$ in PSCs.

As for the non-radiative recombination loss, previous works mostly focused on the discussion of the carrier recombination with the electroluminescence efficiencies of the photovoltaic materials. We found that the suppression of the triplet excitons (CT) formation is a plausible approach to suppress the bimolecular recombination as the lowest-energy molecular triplet exciton (T1) for the polymer is lower in energy than the intermolecular charge transfer state (Fig. 5c). As mentioned above, the J52:m-ITIC based PSCs demonstrated low efficiency of 5.98% with $V_{OC}$ of 0.701 V and FF of 49.73% due to a strong triplet formation in the blend along with a much longer lifetime of ground state bleaching signal,[43] while its polymer analogue J91 with difluorine substituted thiophene conjugated side chains demonstrated suppressed triplet formation in its blend film with m-ITIC acceptor as disclosed by the TAS, thus resulting in a significantly high efficiency of 11.63% with simultaneously high $V_{OC}$ of 0.984 V and high $J_{SC}$ of 18.03 mA cm$^{-2}$. Moreover, this finding endows the side chain with a new function to tune the photovoltaic properties.

**Morphology**

In addition to the issues of absorption and energy losses as discussed above, it is also of critical importance for the polymer donors to form favorable aggregation and achieve suitable domain sizes in the blend active layer to use all of the excitons created, as the exciton diffusion length in PSCs is only ca. 10 nm. If we want to relate the chemical structure with their local morphology, more attention should be paid to the intermolecular and intramolecular interactions of the photovoltaic material.[69]

We developed a feasible approach to tune the aggregation and their crystallization behavior of the polymer donors by simple side chain engineering,[29] as demonstrated by a comparative study on the aggregation behavior of J52 with branched alkyl, J60 with branched alkylthio, and J61 with linear alkylthio substituent (Fig. 4). The lamellar distances and the facial $n$-$n$ stacking distances are affected by the length and topology of the substituents as shown in Figs. 5(e) and
TZBI-based 2D copolymers

Fig. 6  BTA-derived acceptor units and corresponding 2D-conjugated polymer donors.

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Table 3  Photoelectronic and photovoltaic properties of the D-A copolymers based on the BTA-derived acceptor units and corresponding 2D-conjugated polymers.

| Donor     | Photoelectric properties | Photovoltaic characteristics of corresponding PSCs | Ref. |
|-----------|--------------------------|---------------------------------------------------|------|
|           | $E_{g}^{tot}$ (eV) | $E_{LUMO}$ (eV) | $E_{HOMO}$ (eV) | $E_{g}^{exc}$ (eV) | Acceptor | $V_{oc}$ (V) | $J_{sc}$ (mA·cm$^{-2}$) | FF (%) | PCE (%) |
| PTZBiBDT  | 1.81        | -5.34       | -3.46         | 0.88          | PC$_{71}$BM | 0.87       | 13.5       | 74.0   | 8.63    |
| P2F-EHp   | 1.82        | -5.46       | -3.13         | 2.33          | Y6        | 0.81       | 26.7       | 74.1   | 16.02   |
| P2F-EHp   | 1.85        | -5.38       | -3.06         | 2.32          | IT-2F     | 1.02       | 13.0       | 54.8   | 7.28    |
| PTZBi-Si  | 1.78        | -5.31       | -3.10         | 2.21          | IT-F      | 0.96       | 16.9       | 61.9   | 10.06   |
| PTZBi-Si  | 1.78        | -5.31       | -3.10         | 2.21          | IT-2F     | 1.02       | 13.0       | 54.8   | 7.28    |
| P32       | 1.68        | -5.32       | -3.64         | 1.68          | N2200     | 0.87       | 14.6       | 72.7   | 9.30    |
| P33       | 1.79        | -5.24       | -3.46         | 1.78          | N2200     | 0.88       | 17.6       | 75.8   | 11.76   |
| P33       | 1.79        | -5.24       | -3.46         | 1.78          | ITIC      | 0.77       | 17.4       | 64.4   | 8.59    |
| P2        | 1.93        | -5.23       | -3.30         | 1.93          | ITIC      | 0.77       | 17.4       | 64.4   | 8.59    |
| PBDSF-TZNT| 1.97        | -5.45       | -3.41         | 2.04          | PC$_{71}$BM| 0.92       | 11.7       | 65.0   | 7.11    |
|           |             |             |               |               | IT-4F     | 0.93       | 19.23      | 0.74   | 13.25   |
|           |             |             |               |               |           | 1.82       | 11.58      | 0.69   | 14.25   |

*a Calculated from the absorption edge of the polymer films.  b Electrochemical bandgap.  c Homo-tandem device.

By fusing two BTA units together in the angular shape, Huang et al. constructed naphthobistriazole (TZNT) with enlarged planar aromatic structure.[77] One advantage of using TZNT as a basic acceptor unit in D-A copolymers is enlarging the planar conformation of the polymer backbone for improving interchain packing of the resultant polymer, and another is providing extra positions for incorporating solubilizing alkyl side chains onto the resulting copolymers. Accordingly, P2 was synthesized with an MBG of ca. 1.9 eV, showing a promising efficiency of 7.11% in fullerene-based PSCs with P2 as donor. The result suggested that TZNT can be a promising acceptor building block in constructing the D-A polymer donors.[77] With the alkylthio and fluorine substitution on the conjugated side chains, Peng et al. synthesized PBDSF-TZNT (Fig. 6) and investigated its application as donors in IT-4F based PSCs, which showed a high PCE of 13.25% along with a $V_{oc}$ of 0.93 eV. Based on PBDSF-TZNT:IT-4F, homo-tandem PSC exhibited a high PCE of 14.52% along with a $V_{oc}$ of 1.82 V and a $J_{sc}$ of 11.58 mA·cm$^{-2}$, which is the best value for homo-tandem non-fullerene based PSCs at that time.[78]

CONCLUSIONS

In this feature article, recent advances on BTA based 2D-conjugated polymers, so called J-series polymers, as donors in PSCs are briefly summarized with the discussion on the structure-property relationships of typical photovoltaic J-series polymers. With the attachment of appropriate conjugated side chain, the crucial properties of the polymers, such as energy levels, aggregation behavior, and energy losses are effectively tuned, creating them as an important family of polymer donors in high performance PSCs. In addition, BTA derivatives-based 2D-conjugated polymers are also briefly described. Besides the above mentioned BTA-based MBG polymer donors, there are also other high efficiency MBG polymer donors, the detailed structure-property relationships of which can refer to previous review papers[79-83] or research papers.[84-86] Challenges of the BTA-based polymer donors still exist with respect to further increasing the PCEs of PSCs and their commercial application. Thus, the future opportunities and challenges of the J-series polymers are offered as followings.

1. Advances in device physics to better understand the si-de-chain (especially the conjugated side-chain) effect are still needed to control the behavior of exciton creation, exciton dissociation, charge transportation, and charge recombination. Although some BTA-based materials have been used as electroluminescent materials, further efforts on molecular design of the J-series polymers to suppress the triplet exciton (TCT) formation should be taken for reducing the $E_{g}$ in PSCs.

2. The polymers are generally obtained via the Pd-catalyzed Stille cross-couplings reaction. Although such polymerization is highly efficient, the polymers synthesized usually show a large polydispersity of molecular weights and impurity residual, usually resulting in a batch-to-batch variation in device performance. Thus, developing new polymerization approach, such as C–H activation, is still highly needed.

3. The crystalline behavior of the donor polymers can derive the phase separation in their blend with the non-fullerene acceptors. At present, the FF of the device is still low, and thus appropriate conjugated side chain to tune the photophysical properties of the J-series polymers while maintaining a high crystalline structure is highly needed.

4. Currently, the J-series polymers are mainly paired with those ITIC- and IDIC-based acceptors to fabricate efficient PSCs. Recently, there are new developments on the LBG non-fullerene acceptors, such as the A-D’A-D’A structured acceptors with BT unit on the central core (such as Y6, structure provided in Fig. 1).[13,87] and their corresponding polymerized acceptors.[88-90] The pairing of the J-series polymers with those newly developed acceptors is also highly appealing to further increase their photovoltaic properties.

BIographies

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REFERENCES

1. Li, Y. Molecular design of photovoltaic materials for polymer solar cells: toward suitable electronic energy levels and broad absorption. Acc. Chem. Res. 2012, 45, 725−735.
2. Yu, G.; Gao, J.; Hummel, J. C.; Wudl, F.; Heeger, A. J. Polymer photovoltaic cells: enhanced efficiencies via a network of internal donor-acceptor heterojunctions. Science 1995, 270, 1789−1791.
3. Yao, J.; Qiu, B.; Zhang, Z. G.; Xue, L.; Wang, R.; Zhang, C.; Chen, S.; Zhou, Q.; Sun, C.; Yang, C.; Xiao, M.; Meng, L.; Li, Y. Cathode engineering with perylene-dimide interlayer enabling over 17% efficiency single-junction organic solar cells. Nat. Commun. 2020, 11, 2726.
4. Cui, Y.; Yao, H.; Hong, L.; Zhang, T.; Tang, Y.; Lin, B.; Xian, K.; Gao, B.; An, C.; Bi, P.; Ma, W.; Hou, J. 17% Efficiency organic photovoltaic cell with superior processability. Nat. Sci. Rev. 2020, 7, 1239−1246.
5. Ma, R.; Liu, T.; Luo, Z.; Guo, Q.; Xiao, Y.; Chen, Y.; Li, X.; Luo, S.; Lu, X.; Zhang, M.; Li, Y.; Yan, H. Improving open-circuit voltage by a chlorinated polymer donor endows binary organic solar cells efficiencies over 17%. Sci. China Chem. 2020, 63, 325−330.
6. Cui, Y.; Yao, H.; Zhang, J.; Xian, K.; Zhang, T.; Hong, L.; Wang, Y.; Xu, Y.; Ma, K.; An, C.; He, C.; Wei, Z.; Gao, F.; Hou, J. Single-junction organic photovoltaic cells with approaching 18% efficiency. Adv. Mater. 2020, 32, 1908205.
7. Lee, C.; Lee, S.; Kim, G. U.; Lee, W.; Kim, B. J. Recent advances, design guidelines, and prospects of all-polymer solar cells. Chem. Rev. 2019, 119, 8028−8086.
8. Zhang, Z. G.; Yang, Y.; Yao, J.; Xue, L.; Chen, S.; Li, X.; Morrison, W.; Yang, C.; Li, Y. Constructing a strongly absorbing low-bandgap polymer acceptor for high-performance all-polymer solar cells. Angew. Chem. Int. Ed. 2017, 56, 13503−13507.
9. Lin, Y.; Wang, J.; Zhang, Z. G.; Bai, H.; Li, Y.; Zhu, D.; Zhan, X. An electron acceptor challenging fullerenes for efficient polymer solar cells. Adv. Mater. 2015, 27, 1170−1174.
10. Jia, B.; Zhan, X. Fused-ring electron receptors in China. Sci. China Chem. 2020, 63, 1179−1181.
11. Wei, Q.; Liu, W.; Leclerc, M.; Yuan, Ji.; Chen, H.; Zou, Y. A DAD-D non-fullerene acceptors for high performance organic solar cells. Sci. China Chem. 2020, 63, 1352−1366.
12. Wan, X.; Li, C.; Zhang, M.; Chen, Y. Acceptor-donor-acceptor type molecules for high performance organic photovoltaics—chemistry and mechanism. Chem. Soc. Rev. 2020, 49, 2828−2842.
13. Yuan, J.; Zhang, Y.; Zhou, L.; Zhang, G.; Yip, H. L.; Lau, T. K.; Lu, X.; Zhu, C.; Peng, H.; Johnson, P. A.; Leclerc, M.; Cao, Y.; Ulanski, J.; Li, Y.; Zou, Y. Single-junction organic solar cell with over 15% efficiency using fused-ring acceptor with electron-deficient core. Joule 2019, 3, 1140−1151.
14. Li, S.; Li, C. Z.; Shi, M.; Chen, H. New phase for organic solar cell research: emergence of Y-series electron acceptors and their perspectives. ACS Energy Lett. 2020, 5, 1554−1567.
15. Min, J.; Zhang, Z. G.; Zhang, S.; Li, Y. Conjugated side-chain-isolated D-A copolymers based on benzo[1,2-b:4,5-b′]dithiophene-alt-dithienylbenzothiazole: synthesis and photovoltaic properties. Chem. Mater. 2012, 24, 3247−3254.
16. Zhang, Z. G.; Li, Y. Side-chain engineering of high-efficiency conjugated polymer photovoltaic materials. Sci. China Chem. 2015, 58, 192−209.
17. Hu, Z.; Zhang, F.; An, Q.; Zhang, M.; Ma, X.; Wang, J.; Zhang, J. Ternary nonfullerene polymer solar cells with a power conversion efficiency of 11.6% by inheriting the advantages of binary cells. ACS Energy Lett. 2018, 3, 555−561.
18. Li, Y.; Zhong, L.; Gautam, B.; Bin, H. J.; Lin, J. D.; Wu, F. P.; Zhang, Z.; Jiang, Z. Q.; Zhang, Z. G.; Gundogdu, K.; Li, Y.; Liao, S. A near-infrared non-fullerene electron acceptor for high performance polymer solar cells. Energy Environ. Sci. 2017, 10, 1610−1620.
19. Liu, X.; Li, X.; Zheng, N.; Gu, C.; Wang, L.; Fang, J.; Yang, C. Insight into the efficiency and stability of all-polymer solar cells based on two 2D-conjugated polymer donors: achieving high fill factor of 78%. ACS Appl. Mater. Interfaces 2019, 11, 43432−43440.
20. Sun, R.; Guo, J.; Sun, C.; Wang, L.; Luo, Z.; Zhang, J.; Xiao, J.; Zang, W.; Yang, C.; Li, Y.; Min, J. A universal layer-by-layer-processing approach for efficient non-fullerene organic solar cells. Energy Environ. Sci. 2019, 12, 384−395.
21. Luo, Z.; Bin, H.; Liu, T.; Zhang, Z. G.; Yang, Y.; Zhong, C.; Qiu, B.; Li, G.; Gao, W.; Xie, D.; Wu, K.; Sun, Y.; Liu, F.; Li, Y.; Yang, C. Fine-tuning of molecular packing and energy level through methyl substitution enabling excellent small molecule acceptors for nonfullerene polymer solar cells with efficiency up to 12.54%. Adv. Mater. 2018, 30, 1706124.
22. Liu, W.; Zhang, J.; Zhou, Z.; Zhang, D.; Zhang, Y.; Xu, S.; Zhu, X. Design of a new fused-ring electron acceptor with excellent compatibility to wide-bandgap polymer donors for high-performance organic photovoltaics. Adv. Mater. 2018, 30, 1800403.
23. Bin, H.; Gao, L.; Zhang, Z. G.; Yang, Y.; Zhang, Y.; Zhang, C.; Chen, S.; Xue, L.; Yang, C.; Xiao, M.; Li, Y. 11.4% Efficiency non-fullerene polymer solar cells with trialkylsilyl substituted 2D-conjugated polymer as donor. Nat. Commun. 2016, 7, 13651.
24. Zhang, Z. G.; Wang, J. Structures and properties of conjugated donor-acceptor copolymers for solar cell applications. J. Mater. Chem. 2012, 22, 4178−4187.
25. Min, J.; Zhang, Z. G.; Zhang, S.; Zhang, M.; Zhang, J.; Li, Y. Synthesis and photovoltaic properties of D-A copolymers based on dithienosilole and benzothiazole. Macromolecules 2011, 44, 7632−7638.
26. Zhang, L.; He, C.; Chen, J.; Yuan, P.; Huang, L.; Zhang, C.; Cai, W.; Liu, Z.; Cao, Y. Bulk-heterojunction solar cells with benzothiazole-based copolymers as electron donors: largely improved photovoltaic parameters by using PFN/Al bilayer cathode. Macromolecules 2010, 43, 9771−9778.
27. Song, J.; Bo, Z. Planar copolymers for high-efficiency polymer solar cells. Sci. China Chem. 2019, 62, 9−13.
28. Li, K.; Li, Z.; Feng, K.; Xu, X.; Wang, L.; Peng, Q. Development of large band-gap conjugated copolymers for efficient regular single and tandem organic solar cells. J. Am. Chem. Soc. 2013, 135, 13549−13557.
29. Bin, H.; Zhang, Z. G.; Gao, L.; Chen, S.; Zhong, L.; Xue, L.; Yang, C.; Li, Y. Non-fullerene polymer solar cells based on alkylthio and fluorine substituted 2D-conjugated polymers reach 9.5%
efficiency. J. Am. Chem. Soc. 2016, 138, 4657−4664.

30 Price, S. C.; Sturance, A. C.; Yang, L.; Zhou, H.; You, W. Fluorine substituted conjugated polymer of medium band gap yields 7% efficiency in polymer-fullerene solar cells. J. Am. Chem. Soc. 2011, 133, 4625−4631.

31 Zhang, Z.; Peng, B.; Liu, B.; Pan, C.; Li, Y.; He, Y.; Zhou, K.; Zou, Y. Copolymers from benzodithiophene and benzotriazole: synthesis and photovoltaic applications. Polymer. Chem. 2010, 1, 1441−1447.

32 Zhang, Q.; Kelly, M. A.; Bauer, N.; You, W. The curious case of fluorination of conjugated polymers for solar cells. Acc. Chem. Res. 2017, 50, 2401−2409.

33 Gao, L.; Zhang, Z. G.; Xue, L.; Min, J.; Zhang, J.; Wei, Z.; Li, Y. All-polymer solar cells based on absorption-complementary polymer donor and acceptor with high power conversion efficiency of 8.27%. Adv. Mater. 2016, 28, 1884−1890.

34 Gao, L.; Zhang, Z. G.; Bin, H.; Xue, L.; Yang, Y.; Wang, C.; Liu, F.; Russell, T. P.; Li, Y. High-efficiency nonfullerene polymer solar cells with medium bandgap polymer donor and narrow bandgap organic semiconductor acceptor. Adv. Mater. 2016, 28, 8288−8295.

35 Yang, Y.; Zhang, Z. G.; Bin, H.; Chen, S.; Gao, L.; Xue, L.; Yang, C.; Li, Y. Side-chain isomerization on an n-type organic semiconductor itic acceptor makes 11.77% high efficiency polymer solar cells. J. Am. Chem. Soc. 2016, 138, 15011−15018.

36 Bin, H.; Yang, Y.; Peng, Z.; Ye, L.; Yao, J.; Zhong, L.; Sun, C.; Gao, L.; Huang, H.; Li, X.; Qiu, B.; Xue, L.; Zhang, Z. G.; Ade, H.; Li, Y. Effect of alkylsilyl side-chain structure on photovoltaic properties of conjugated polymer donors. Adv. Energy Mater. 2018, 8, 1703234.

37 Su, W.; Li, G.; Fan, Q.; Zhou, Q.; Guo, X.; Chen, J.; Wu, J.; Ma, W.; Zhang, M.; Li, Y. Nonhalogen solvent-processed polymer solar cells based on chlorine and trialkylsilyl substituted conjugated polymers achieve 12.8% efficiency. J. Mater. Chem. A 2019, 7, 2351−2359.

38 Tang, A.; Song, W.; Xiao, B.; Guo, J.; Min, J.; Ge, Z.; Zhang, J.; Wei, Z.; Zhou, E. Benzotriazole-based acceptor and donors, coupled with chlorination, achieve a high VOC of 1.24 V and an efficiency of 10.5% in fullerene-free organic solar cells. Chem. Mater. 2019, 31, 3941−3947.

39 Tang, A.; Xiao, B.; Chen, F.; Zhang, J.; Wei, Z.; Zhou, E. The introduction of fluorine and sulfur atoms into benzotriazole-based n-type polymers to match with a benzotriazole-containing n-type small molecule: “the same-acceptor-strategy” to realize high open-circuit voltage. Adv. Energy Mater. 2018, 8, 1801582.

40 Fan, Q.; Su, W.; Meng, X.; Guo, X.; Li, G.; Ma, W.; Zhang, M.; Li, Y. High-performance non-fullerene polymer solar cells based on fluorine substituted wide bandgap copolymers without extra treatments. Solar RRL 2017, 1700020.

41 Xue, L.; Yang, Y.; Xu, J.; Zhang, C.; Bin, H.; Zhang, Z. G.; Qiu, B.; Li, X.; Sun, C.; Gao, L.; Yao, J.; Chen, X.; Yang, Y.; Xiao, M.; Li, Y. Side chain engineering on medium bandgap polymer copolymers to suppress triplet formation for high-efficiency polymer solar cells. Adv. Mater. 2017, 40, 1703344.

42 Chao, P.; Liu, L.; Zhou, J.; Qu, J.; Mo, D.; Meng, H.; Xie, Z.; He, F.; Ma, Y. Multichloro-substitution strategy: facing low photon energy loss in nonfullerene solar cells. ACS Appl. Energy Mater. 2018, 1, 6549−6559.

43 Yan, T.; Bin, H.; Yang, Y.; Xue, L.; Zhang, Z. G.; Li, Y. Effect of furan n-bridge on the photovoltaic performance of D-A copolymers based on 3,3′-bithiophene-thiophene conjugated side chains. Org. Electron. 2018, 57, 255−262.

44 Ren, Y.; Geng, Y.; Yang, L.; Wang, X.; Sun, Y.; Zhou, E. Changing the n-bridge from thiophene to thieno[3,2-b]thiophene for the D-n-A type polymer enables high performance fullerene-free organic solar cells. Chem. Commun. 2019, 55, 6708−6710.

45 Tang, A.; Zhang, Q.; Du, M.; Li, G.; Geng, Y.; Zhang, J.; Wei, Z.; Sun, X.; Zhou, E. Molecular Engineering of D-n-A copolymers based on 4,8-bis(4-chlorothiophen-2-yl)benzo[1,2-b:4,5-b′]dithiophene (BT-DCT) for high-performance fullerene-free organic solar cells. Macromolecules 2019, 52, 6227−6233.

46 Wang, T.; Sun, R.; Xu, S.; Guo, J.; Wang, W.; Guo, J.; Xiao, J.; Wang, J.; Jia, S.; Zhu, X.; Li, Y.; Min, J. A wide-bandgap D-A copolymer donor based on a chlorine substituted acceptor unit for high performance polymer solar cells. J. Mater. Chem. A 2019, 7, 14070−14078.

47 Bin, H.; Zhong, L.; Yang, G.; Gao, L.; Huang, H.; Sun, C.; Li, X.; Xue, L.; Zhang, Z. G.; Zhang, Z.; Li, Y. Medium bandgap polymer donor based on bis(trialkylsilylthienyl-benzol[1,2-b:4,5-b′]-difuran) for high performance nonfullerene polymer solar cells. Adv. Energy Mater. 2017, 7, 1700746.

48 Zhang, L.; Bin, H.; Angunawela, I.; Jia, Z.; Qiu, B.; Sun, C.; Li, X.; Zhang; Z.; Ahe, H.; Li, Y. Effect of replacing thiophene by selenophene on the photovoltaic performance of wide bandgap copolymer donors. Macromolecules 2019, 52, 4776−4784.

49 Zhang, Y.; Yao, H.; Zhang, S.; Qin, Y.; Zhang, J.; Yang, L.; Li, W.; Wei, Z.; Gao, F.; Hou, J. Fluorination vs. chlorination: a case study on high performance organic photovoltaic materials. Sci. China Chem. 2018, 61, 1328−1337.

50 Chao, P.; Johner, N.; Zhang, X.; Meng, H.; He, F. Chlorination strategy on polymer donors toward efficient solar conversions. J. Energy Chem. 2019, 39, 208−216.

51 Qiu, B.; Chen, S.; Li, H.; Luo, Z.; Yao, J.; Sun, C.; Li, X.; Xue, L.; Zhang, Z. G.; Yang, C.; Li, Y. A simple approach to prepare chlorinated polymer donors with low-lying homo level for high performance polymer solar cells. Chem. Mater. 2019, 31, 6558−6567.

52 Wang, X.; Dou, K.; Shahid, B.; Liu, Z.; Li, Y.; Sun, M.; Zheng, N.; Bao, X.; Yang, R. Terpolymer strategy toward high-efficiency polymer solar cells: integrating symmetric benzodithiophene and asymmetrical thieno[2,3-b]benzofuran segments. Chem. Mater. 2019, 31, 6163−6173.

53 Wang, X.; Han, J.; Jiang, H.; Liu, Z.; Li, Y.; Yang, C.; Yu, D.; Bao, X.; Yang, R. Regulation of molecular packing and blend morphology by finely tuning molecular conformation for high-performance nonfullerene polymer solar cells. ACS Appl. Mater. Interfaces 2019, 11, 44501−44512.

54 Liu, D.; Zhang, K.; Zhong, Y.; Gu, C.; Li, Y.; Yang, R. An effective strategy for controlling the morphology of high-performance non-fullerene polymer solar cells without post-treatment: employing bare rigid aryl rings as lever arms in new asymmetric benzothiophene. J. Mater. Chem. A 2018, 6, 18125−18132.

55 Chao, P.; Liu, L.; Qu, J.; He, Q.; Gan, S.; Meng, H.; Chen, W.; He, F. Overcoming the trade-off between VOC and JSC: asymmetric chloro-substituted two-dimensional benzo[1,2-b:4,5-b′]-dithiophene-based polymer solar cells. Dyes Pigments 2019, 162, 746−754.

56 Wen, S.; Chen, W.; Huang, G.; Shen, W.; Liu, H.; Duan, L.; Zhang, J.; Yang, R. 2D expanded conjugated polymers with non-fullerene acceptors for efficient polymer solar cells. J. Mater. Chem. C 2018, 6, 1753−1758.

57 Zhang, Y.; Wang, Y.; Ma, R.; Luo, Z.; Liu, T.; Kang, S. H.; Yan, H.; Yuan, Z.; Yang, C.; Chen, Y. Wide-bandgap two-dimension conjugated polymer donors with different amounts of chlorine substitution on alkoxyl conjugated side chains for non-fullerene polymer solar cells. Chinese J. Polym. Sci. 2020, 38, 797−805.

58 Liao, Z.; Xie, Y.; Chen, L.; Tan, Y.; Huang, S.; An, Y.; Ruy, H. S.; Meng, X.; Liao, X.; Huang, B.; Xie, Q.; Woo, H. Y.; Sun, Y.; Chen, Y. Fluorobenzotriazole (FTAZ)-based polymer donor enables
organic solar cells exceeding 12% efficiency. *Adv. Funct. Mater.* 2019, 29, 1800828.

60 Gao, Y.; Shen, Z.; Tan, F.; Yue, G.; Liu, R.; Wang, Z.; Su, S.; Wang, Z.; Zhang, W. Novel benzo[1,2-b:4,5-b′]difuran-based copolymer enables efficient polymer solar cells with small energy loss and high Voc. *Nano Energy* 2020, 76, 104964.

61 Chen, W.; Huang, G.; Li, X.; Wang, H.; Li, Y.; Jiang, H.; Zheng, N.; Yang, R. Side-chain-promoted benzothiadiazine-based conjugated polymers toward striking enhancement of photovoltaic properties for polymer solar cells. *ACS Appl. Interfaces* 2018, 10, 42747–42755.

62 Chen, W.; Huang, G.; Li, X.; Li, Y.; Wang, H.; Jiang, H.; Zhao, Z.; Yu, D.; Wang, E.; Yang, R. Revealing the position effect of an alkylthio side chain in phenyl-substituted benzothiadiazine-based donor polymers on the photovoltaic performance of non-fullerene organic solar cells. *ACS Appl. Interfaces* 2019, 11, 33173–33178.

63 Tang, Z.; Xu, X.; Li, R.; Yu, L.; Meng, L.; Wang, Y.; Li, Y.; Peng, Q. Asymmetric siloxane functional side chains enable high-performance donor copolymers for photovoltaic applications. *ACS Appl. Interfaces* 2020, 12, 17760–17768.

64 Cui, W.; Li, F.; Zhu, T.; Li, Y.; Yu, L.; Yang, R.; Sun, M. 1 V high open-circuit voltage fluorinated alkoxyphenyl side-chained benzothiadiazine based photovoltaic polymers. *Synth. Met.* 2019, 257, 116182.

65 Li, X.; Huang, G.; Zheng, N.; Li, Y.; Kang, X.; Qiao, S.; Jiang, H.; Chen, W.; Yang, R. High-efficiency polymer solar cells over 13.9% with a high Voc beyond 1.0 V by synergistic effect of fluorine and sulfur. *Solar RRL* 2019, 3, 1900005.

66 Mori, D.; Benten, H.; Okada, I.; Okita, H.; Ito, S. Highly efficient charge-carrier generation and collection in polymer/polymer blend solar cells with a power conversion efficiency of 5.7%. *Energy Environ. Sci.* 2017, 10, 15181–15185.

67 Liu, X.; Rand, B. P.; Forrest, S. R. Engineering charge-transfer states for efficient, low-energy-loss organic photovoltaics. *Trends Chem.* 2019, 1, 815–829.

68 Hou, J.; Inganäs, O.; Friend, R. H.; Gao, F. Organic solar cells based on non-fullerene acceptors. *Nat. Mater.* 2018, 17, 119.

69 Wang, T.; Kupgal, G.; Brédas, J. L. Organic photovoltaics: relating chemical structure, local morphology, and electronic properties. *Trends Chem.* 2020, 2, 535–554.

70 Yu, L.; Li, Y.; Wang, Y.; Wang, C.; Cui, W.; Wen, S.; Zheng, N.; Sun, M.; Yang, R. Fuse the π-bride to acceptor moiety of donor-π-acceptor conjugated polymer: enabling an all-round enhancement in photovoltaic parameters of nonfullerene organic solar cells. *ACS Appl. Interfaces* 2019, 11, 31087–31095.

71 Lan, L.; Chen, Z.; Hu, Q.; Ying, L.; Zhu, R.; Liu, F.; Russell, T. P.; Huang, F.; Gao, Y. High-performance polymer solar cells based on a wide-bandgap polymer containing pyrrolo[3,4-f]benzothiadiazole-5,7-dione with a power conversion efficiency of 8.63%. *Adv. Sci.* 2016, 3, 1600332.

72 Fan, B.; Zhang, D.; Li, M.; Zhong, W.; Zeng, Z.; Ying, L.; Huang, F.; Gao, Y. Achieving over 16% efficiency for single-junction organic solar cells. *Sci. China Chem.* 2019, 62, 746–752.

73 Fan, B.; Du, X.; Liu, F.; Zhong, W.; Ying, L.; Xie, R.; Tang, X.; An, K.; Xin, J.; Li, N.; Ma, W.; Brabec, C. J.; Huang, F.; Gao, Y. Fine-tuning of the chemical structure of photovoltaic materials for highly efficient organic photovoltaics. *Nat. Energy* 2018, 3, 1051–1058.

74 Li, Z. Y.; Zhong, W. K.; Ying, L.; Li, N.; Liu, F.; Huang, F.; Gao, Y. Achieving efficient thick film all-polymer solar cells using a green solvent additive. *Chinese J. Polym. Sci.* 2020, 38, 323–331.

75 Zhu, L.; Zhong, W.; Qiu, C.; Lyu, B.; Zhou, Z.; Zhang, M.; Song, J.; Xu, J.; Wang, H.; Ali, J.; Feng, W.; Shi, Z.; Gu, X.; Ying, L.; Zhang, Y.; Liu, F. Aggregation-induced multilength scaled morphology enabling 11.76% efficiency in all-polymer solar cells using printing fabrication. *Adv. Mater.* 2019, 31, 1902899.

76 Jiang, X.; Wang, J.; Wang, W.; Yang, Y.; Zhan, X.; Chen, X. Impact of an electron withdrawing group on the thiophene-fused benzothiazole unit on the photovoltaic performance of the derived polymer solar cells. *Dyes Pigments* 2019, 166, 381–389.

77 Dong, Y.; Hu, X.; Duan, C.; Liu, P.; Liu, S.; Lan, L.; Chen, D.; Ying, L.; Su, S.; Gong, X.; Huang, F.; Cao, Y. A series of new medium-bandgap conjugated polymers based on naphto[1,2-c,5,6-c]bis(2-oxyl-[1,3]triazole) for high-performance polymer solar cells. *Adv. Mater.* 2013, 25, 3683–3688.

78 Feng, K.; Yuan, J.; Bi, Z.; Ma, W.; Xu, Z.; Zhang, G.; Peng, Q. Low-energy-loss polymer solar cells with 14.52% efficiency enabled by wide-band-gap copolymers. *Science* 2019, 1, 1–12.

79 Fu, H.; Wang, Z.; Sun, Y. Polymer donors for high-performance non-fullerene organic solar cells. *Angew. Chem. Int. Ed.* 2019, 58, 4442–4453.

80 Zheng, B.; Huan, L.; Li, X. Benzothiadiazinedione-based polymers: recent advances in organic photovoltaics. *NPJ Asia Mater.* 2020, 2, 13.

81 An, C.; Zheng, Z.; Hou, J. Recent progress in wide-bandgap conjugated polymer donors for high-performance nonfullerene organic solar cells. *Chem. Commun.* 2020, 56, 4750–4760.

82 Zheng, Z.; Yao, H.; Ye, L.; Xu, Y.; Zhang, S.; Hou, J. PBDB-T and its derivatives: a family of polymer donors enables over 17% efficiency in organic photovoltaics. *Mater. Today* 2020, 35, 115–130.

83 Cui, C.; Li, Y. High-performance conjugated polymer donor materials for polymer solar cells with narrow-bandgap nonfullerene acceptors. *Energy Environ. Sci.* 2019, 12, 3225–3246.

84 Sun, C.; Fan, B.; Bin, H.; Zhang, J.; Xue, L.; Qiu, B.; Wei, Z.; Zhang, Z. G.; Li, Y. A low cost and high performance polymer donor material for polymer solar cells. *Nat. Commun.* 2019, 10, 743.

85 Yuan, J.; Guo, W.; Xia, Y.; Ford, M. J.; Jin, F.; Liu, D.; Zhao, H.; Inganäs, O.; Bazan, G. C.; Ma, W. Comparing the device physics, dynamics and morphology of polymer solar cells employing conventional PCBM and non-fullerene polymer acceptor N2200. *Nano Energy* 2017, 35, 251–262.

86 Li, B.; Zhang, Q.; Dai, G.; Fan, H.; Yuan, X.; Xu, Y.; Cohen-Kleinstein, B.; Yuan, J.; Ma, W. Understanding the impact of side-chains on photovoltaic performance in efficient all-polymer solar cells. *J. Mater. Chem. C* 2019, 7, 12641–12649.

87 Jiang, K.; Wei, Q.; Lai, J. Y.; Peng, Z.; Kim, H. K.; Yuan, J.; Ye, L.; Ade, H.; Zou, Y.; Yan, H. Alkyl chain tuning of small molecule acceptors for efficient organic solar tuning. *Joule* 2019, 3, 3020–3033.

88 Jia, T.; Zhang, J.; Zhong, W.; Liang, Y.; Zhang, K.; Dong, S.; Ying, L.; Liu, F.; Wang, X.; Huang, F.; Gao, Y. 14.4% Efficiency all-polymer solar cell with broad absorption and low energy loss enabled by a novel polymer acceptor. *Nano Energy* 2020, 12, 104718.

89 Wu, Q.; Wang, W.; Wang, T.; Sun, R.; Guo, J.; Wu, Y.; Jiao, X.; Brabec, C. J.; Li, Y.; Min, J. High-performance all-polymer solar cells with only 0.47 eV energy loss. *Sci. China Chem.* 2020, 63, 1449–1460.

90 Du, J.; Hu, K.; Meng, L.; Angunawela, I.; Zhang, J.; Qin, S.; Liebman-Pelaez, A.; Zhu, C.; Zhang, Z.; Ade, H.; Li, Y. High performance all-polymer solar cells with the polymer acceptor synthesized via a random ternary copolymerization strategy. *Angew. Chem. Int. Ed.* 2020, 59, 15181–15185.