Recent progress in small-molecule donors for non-fullerene all-small-molecule organic solar cells

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Abstract
All-small-molecule organic solar cells (all-SM OSCs), with p-type small molecule (p-SM) as donor and n-type small molecule (n-SM) as acceptor, have drawn intensive research interests in recent years. All-SM OSCs show advantages to their polymer counterparts, including well-defined chemical structure, easy purification, and better repeatability in devices. The highest power conversion efficiency (PCE) of all-SM OSCs has increased quickly to over 15% nowadays. In this review, we just summarize the progress of non-fullerene all-SM OSCs (NF all-SM OSCs) in recent five years, by dividing small-molecule donors into four categories based on the molecular segments of oligothiophene, benzo[1,2-b:4,5-b’]dithiophene (BDT) trimer, typical BDT-central unit connected with π-bridges of thiophene or electron deficient acceptor units. We aim to illustrate the relationship of molecular structures, properties, and device performance of small-molecule donors with those different molecular segments. Furthermore, the tendency of molecular design for photo-active materials are also depicted and summarized. Finally, we give our views on the future prospects of NF all-SM OSCs to design the next-generation OSCs.

KEYWORDS
high performance, molecular design strategies, non-fullerene all-small-molecule organic solar cells, small-molecule donors
1 | INTRODUCTION

The consumption of fossil energy (like coal, oil, and gas) has raised serious environment issues and shortage of energy. As a clean and renewable energy, solar energy can be converted into electricity by photovoltaic effects. In contrast with silicon-based solar cells, organic solar cells (OSCs) consume less energy in fabrication and are advantages in light weight and flexible, thus attracting great interest from both industry and academia.\[1\] In particular, bulk heterojunction (BHJ) OSCs that features solution-processed blend active layer of p-type and n-type photovoltaic materials can produce intermixed donor-acceptor network.\[1a,2\] This advantage, together with the chemical functionalization of new photovoltaic materials, has led to high performance device with ever-increasing efficiency during the past decades.

In the device level of OSCs, the conversion of solar light radiation into electricity comprises of five steps: 1) the generation of excitons (bounded electron-hole pairs) from the absorbed photons; 2) the diffusion of excitons to the donor/acceptor (D/A) interfaces; 3) the dissociation of excitons into electrons and holes at the D/A interfaces; 4) the transfer of separated charge-carriers (holes and electrons) along interpenetrating network in the active layer to the anode and metal cathode, respectively; 5) the collection of charge-carriers (holes and electrons) at the anode and the cathode. The performance of OSCs has achieved a great advance during the past two decades,\[3\] being the benefit of the development of new photovoltaic materials, both polymeric and small molecular materials.

Generally, there are four types of BHJ OSCs, including polymer donors with small-molecule (SM) acceptors, polymer donors with polymer acceptors (all-polymer OSCs), as well as SM donor with polymer acceptors, and SM donors with SM acceptors (all-SM OSCs). Specially, SM materials, in contrast with their polymeric counterparts, possess intrinsic advantages of well-defined molecular structure, facile purification, and better batch-to-batch repeatability.\[4\] Therefore, all-SM OSCs are promising candidates for commercializable organic photovoltaics. Despite the aforementioned advantages of all-SM OSCs, however, its performance still lags behind with respect to well-studied polymer solar cells (polymer donors with SM acceptors).

Fullerene derivatives, such as PC_{61}BM and PC_{71}BM (Figure 1A) are the most common acceptors in the solution-processed all-SM OSCs before 2015, due to the
advantages of good solubility property and high electron mobility (~10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}).[8,2,5] To improve the efficiency of fullerene-based all-SM OSCs, researchers have synthesized several high-performance donors, such as p-DTS(DBTTh2)2,[6] DRCN7T,[14] DR3TBDDT,[7] BTR, and BTID-2F,[8] which greatly enriched the system of donor materials. Moreover, the relationship between donor molecular structure and photovoltaic property has also been studied in depth and many design strategies of donors have been put forward and summarized in review papers or research paper.[5b,9] Notably, the great guiding effect not only is on the development of fullerene-based all-SM OSCs, but also on the development of non-fullerene-based all-SM OSCs (NF all-SM OSCs).[3b,10]Thus far, the record PCE for fullerene-based all-SM OSCs has exceeded 11%.[8b,11] However, the weak absorption of fullerene acceptors in the visible region of solar spectrum greatly limited the development of fullerene. Besides, the highly challenging on energy level modulation, the poor mechanical property, rapid molecular diffusion, chemical oxidation, and photoinduced dimerization also limit the efficiency and stability of fullerene-based all-SM OSCs.[1a,2,5] Therefore, it is imperative to develop new non-fullerene acceptors that can overcome above constraints. In the past five years, with the emergence of several new non-fullerene SM acceptors, such as ITIC, IDIC, and Y6 (Figure 1B),[13] the photovoltaic performance of NF all-SM OSCs have boosted remarkably.[14] These acceptors display the merits of strong absorption from the visible light range to the near-infrared, high electron mobility, and appropriate energy levels for device engineering. More importantly, non-fullerene SM acceptors possess a wide structural variability that allows the tuning of bandgap and energy levels for device optimization, while such chemical “flexibility” is constrained in fullerene derivatives. So far, the power conversion efficiency (PCE) of NF all-SM OSCs has developed quickly to exceed 15%,[15] and is approaching to that of polymer-based OSCs.

In this review, we focus on the progress of NF all-SM OSCs in recent five years. We do not focus on the development history of the NF all-SM OSCs, but just discuss the SM donors, by dividing them generally into four categories based on the molecular segments of oligothiophene, benzo[1,2-b:4,5-b’]dithiophene (BDT) trimer, as well as typical BDT-central unit connected with π-bridges of thiophene or electron deficient acceptor units. On this basis, we aim to illustrate the molecular design strategies of SM donors based on different molecular segments from the aspect of modifying of core, π-bridge, side chains, and end group, then explore the structure-property correlation of SM donors. Critically, rational design of novel SM materials presents a shortcut to higher photovoltaic performance of NF all-SM OSCs. Finally, because NF all-SM OSCs have not yet achieved their full potential and are still undergoing rapid development, we give our views on the future prospects of it.

## 2 | OLIGOTHIOPHENE-BASED SMALL-MOLECULE DONORS

Oligothiophene is a kind of SM donor, which possesses advantages of high hole mobility, suitable crystallinity, and simple synthesis. In 2011, Chen et al. designed a series of solution-processable linear A-D-A type oligothiophene-based donor materials DCAE7T, DCA07T, and DCAEH7T.[16] and gained PCEs of 4.46%, 5.08%, and 4.52%, respectively, when combined with PC61BM. These results demonstrated that this series of SM donor materials has great potential for efficient all-SM OSCs.

In 2018, Chen et al. combined an oligothiophene-based SM donor, DRCN5T (Figure 2), with three new non-fullerene acceptors, IDIC8-M, IDIC8-H, and IDIC8-F (Figure 1B).[17] The blend film based on DRCN5T/IDIC8-F showed the best morphology with higher crystallinity, more face-on orientation, and better phase separation, which were beneficial for exciton dissociation and charge transportation, thus led to higher short-circuit current density ($J_{SC}$) and fill factor (FF). The PCE of DRCN5T/IDIC8-F-based device was the highest of 8.42% with $J_{SC}$ of 15.21 mA cm$^{-2}$, an open-circuit voltage ($V_{OC}$) of 0.864 V and an FF of 64.1%. Whereas, when IDIC8-H and IDIC8-M used as acceptor, the PCE was 8.00% and 6.31%, respectively. For further enhancing the absorption and tuning the energy levels, Chen et al. reported a series of fusing SM acceptors F-nCl ($n = 0, 1, 2$) (Figure 1B) with different number of chlorination.[18] The chlorine atoms in end group caused red-shifted absorption, greater crystallinity, and higher electron mobility. When combined with DRCN5T, the PCE for F-0Cl, F-1Cl and F-2Cl were 5.49%, 8.12%, and 9.89%, respectively (Table 1).

In 2020, Lu et al. designed two oligothiophene derivatives 2F7T and 2Cl7T (Figure 2) by introducing halogen atoms (-F and -Cl) into the thienyl center and compared their performances with the that of non-halogenated donor DRCN7T (Figure 2).[19] In comparison to DRCN7T, the film absorption onset of the fluorinated donor 2F7T was slightly blue-shifted with a corresponding bandgap ($E_{g}^{opt}$) of 1.68 eV while that from the chlorinated donor 2Cl7T displayed a wider $E_{g}^{opt}$ of 1.75 eV. A near-infrared acceptor Y6 with complementary absorption was selected to form photovoltaic devices with these three donors. In addition to a deeper HOMO energy level, 2Cl7T has also displayed an exquisite balance between crystallinity and miscibility with Y6 in blend films, with respect to the
FIGURE 2 Chemical structures of oligothiophene-based small-molecule donors

TABLE 1 (Energy levels and device performances of oligothiophene- and BDT trimer-based small-molecule donors.)

| Donor          | HOMO/LUMO (eV/eV) | Active layer      | $J_{SC}$ (mA cm$^{-2}$) | $V_{OC}$ (V) | FF (%) | PCE (%) | Ref   |
|----------------|-------------------|-------------------|--------------------------|--------------|--------|---------|-------|
| DRCN5T         | 5.22/−3.41        | DRCN5T/IDIC8-M    | 10.36                    | 1.002        | 60.7   | 6.31    | [17]  |
| DRCN5T         | 5.22/−3.41        | DRCN5T/IDIC8-H    | 13.44                    | 0.952        | 62.5   | 8.00    |       |
| DRCN5T         | 5.22/−3.41        | DRCN5T/IDIC8-F    | 15.21                    | 0.864        | 64.1   | 8.42    |       |
| DRCN5T/F-0Cl   | 9.64              | 2Cl7T/Y6          | 20.89                    | 0.79         | 54.13  | 9.41    |       |
| DRCN5T/F-1Cl   | 13.07             | 2Cl7T/Y6          | 19.69                    | 0.83         | 68.15  | 11.45   |       |
| DRCN5T/F-2Cl   | 15.97             | 2Cl7T/Y6          | 17.42                    | 0.98         | 65     | 9.08    | [21]  |
| DRTB-T         | −5.51/−3.34       | DRTB-T/IDIC       | 14.25                    | 0.98         | 65     | 9.41    |       |
| DRTB-T         | −5.51/−3.34       | DRTB-T/F-2Cl      | 17.24                    | 0.969        | 64.4   | 10.76   | [25]  |
| DRTB-T         | −5.51/−3.34       | DRTB-T/PC71BM     | 10.02                    | 1.01         | 70     | 7.08    | [22]  |
| DRTB-O         | −5.50/−3.56       | DRTB-O/PC71BM     | 7.49                     | 1.01         | 65     | 4.91    |       |
| DRTB-O         | −5.50/−3.56       | DRTB-O/IDIC       | 0.57                     | 0.99         | 27     | 0.15    |       |
| DRTB-T-C2      | −5.51/−3.34       | DRTB-T-C2/IT-4F   | 16.66                    | 0.893        | 64     | 9.52    | [23]  |
| DRTB-T-C4      | −5.50/−3.32       | DRTB-T-C4/IT-4F   | 18.27                    | 0.909        | 68     | 11.24   |       |
| DRTB-T-C6      | −5.50/−3.32       | DRTB-T-C6/IT-4F   | 19.12                    | 0.929        | 63     | 10.52   |       |
| DRTB-T-C8      | −5.50/−3.33       | DRTB-T-C8/IT-4F   | 16.15                    | 0.928        | 61     | 9.14    |       |
| P2TBR          | −5.36/−3.64       | P2TBR/IDIC        | 17.5                     | 0.94         | 70.1   | 11.5    | [24]  |
| DRTB-FT        | −5.64/−3.61       | DRTB-FT/F-2Cl     | 13.46                    | 1.070        | 53.2   | 7.66    | [25]  |
| 3BDT-4         | −5.15/−3.44       | 3BDT-4/Y6         | 17.0                     | 0.829        | 41.3   | 5.82    | [26]  |
| 3BDT-5         | −5.15/−3.40       | 3BDT-5/Y6         | 21.3                     | 0.840        | 58.1   | 10.4    |       |

Other two donors. With the aforementioned advantages, the devices with 2Cl7T/Y6 delivered an impressive PCE of 11.45% and outperformed the control devices with fluorinated (9.41%) and non-halogenated (2.48%) donors.

Currently, adjusting thiophene backbone, alkyl side chains, and electron-withdrawing end-caps, as well as introducing halogen atoms, are the general methods when researchers enhance the performance of oligothiophene-based all-SM OSC devices. Combined with morphology control, these strategies have achieved good results in both improving the $J_{SC}$ and $V_{OC}$, and reducing the energy loss ($E_{loss} = E_g - qV_{OC}$, where $q$ is elementary charge). Oligothiophene-based SM donor materials have great contribution to the development of this field, and they are promising for developing low-cost SM donors.

3 | BDT TRIMER-BASED SMALL-MOLECULE DONORS

Instead of using oligothiophene as the central backbone, benzo[1,2-b:4,5-b']dithiophene (BDT) trimer was also used
to construct SM donors to take the advantages of BDT units, such as large rigid planar structure and flexible side-chains engineering on the BDT units. With alkoxy substitution on the BDT units, DRBDT$_3$ was synthesized by Chen et al. with 3-ethylrhodamines as the end-caps, showing a PCE of 4.09% with PC$_{71}$BM as acceptor.[20]

With an alkylthienyl-substituted BDT trimer as the backbone, Hou et al. synthesized a BDT trimer based SM donor DRTB-T (Figure 3).[21] The 2D-conjugated donor DRTB-T possessed an $E_g^{opt}$ of 2.0 eV and a low-lying HOMO energy level of $-5.51$ eV. When employing PC$_{71}$BM as the acceptor, the PCEs of DRTB-T-based devices are increased to 7.08%. Encouragingly, with IDIC as acceptor, the photovoltaic device based on DRTB-T achieved a high PCE of 9.08%, with a high $V_{OC}$ of 0.98 V, a $J_{SC}$ of 14.25 mA cm$^{-2}$, and an FF of 65%, while the PCE of DRBDT$_3$ (named as DRTB-O in Hou's paper) is only at 0.15%.[22] Such difference is due to the intense intermolecular interaction between DRBDT$_3$ and IDIC and large size aggregations, resulting in poor charge transport.

In 2018, a series of DRTB-T derivatives with different alkyl chains on the rhodamine end-caps, DRTB-T-CX (X = 2, 4, 6, and 8) (Figure 3), were synthesized.[23] This research was intended to investigate the influence of the length of end alkyl chains on the crystal orientation and molecular packing behavior in solid-state films. Upon the
extension of the end alkyl chain length, the molecular orientation to the substrate converted markedly from edge-on to face-on. Moreover, when organic photovoltaic devices were fabricated with donor DRTB-T-CX and acceptor IT-4F (Figure 1B), the blend thereof afforded a maximum PCE of 11.24% among all the DRTB-T-CX-based devices. In addition, thick film devices based on 300 nm DRTB-T-C4/IT-4F could still retain a high PCE of 10%. The high PCE and its tolerance to film thickness were closely related to the enhancement of charge mobility and extended correlation length of \( \pi-\pi \) stacking that contributed to larger domains in face-on crystallites.

BDT units is a fused aromatic ring of thiophene and benzene. With a non-fused ring structure of thiophene–benzene–thiophene (TBT) to replace the central BDT units in BDT trimer, P2TBR (Figure 3) was synthesized with strong absorption, a low-lying HOMO energy level, high hole mobility.\(^\text{[24]}\) The device based on P2TBR/IDIC exhibited a PCE of 11.5%, with a \( V_{OC} \) of 0.94 V, a \( J_{SC} \) of 17.5 mA cm\(^{-2}\) and a satisfactory FF of 70.1%. Moreover, the optimized P2TBR/IDIC film showed a texture of coexistent face-on and edge-on crystallites and three-dimensional (3-D) charge pathway, which were beneficial to intermolecular charge transfer. Obviously, the performance of P2TBR-based device is better than those of DRTB-T-based devices, which means utilization of non-fused ring structure is a simple and effective molecular design strategy.

In 2020, Chen et al. explored a new BDT trimer-based SM donor DRTB-FT (Figure 3) by introducing fluorine atoms to the thienyl substituent of the central BDT unit and characterized the photovoltaic devices with F-2Cl as acceptor.\(^\text{[25]}\) The introduction of the electron-withdrawing F atom substantially lowers the HOMO level (\(-5.64 \) eV), in contrast to that of DRTB-T (\(-5.51 \) eV). Due to its strong molecular packing and aggregation properties, DRTB-FT based devices show a low the \( J_{SC} \) of 13.46 mA cm\(^{-2}\) and an FF of 53.2%, which limit the efficiency to be increased. To further increase the efficiency, detailed morphology control should be carried out.

This year, Ge et al. designed and synthesized two new BDT trimer-based SM donors, 3BDT-4 and 3BDT-5 (Figure 3).\(^\text{[26]}\) Compared with DRTB-T, 3BDT-4, and 3BDT-5 possessed medium bandgaps of 1.83 and 1.90 eV, and higher HOMO energy levels of \(-5.14 \) and \(-5.15 \) eV, respectively. The result indicated 3BDT-5, with 2-ethylhexyl cyanoacetate as end cap, exhibited lower bimolecular recombination and trap-assisted recombination, higher charge mobility and more ideal morphology of blend film than 3BDT-4 with 3-hexylrhodanine. Therefore, 3BDT-5/Y6-based device achieved higher PCE of 10.4% without any extra treatments, while that of 3BDT-4 was 5.82%.

### 4 TYPICAL BDT-BASED SMALL-MOLECULE DONORS

Small molecular donors with a structure of A-\( \pi \)-D-\( \pi \)-A are more attractive in getting high efficiency in fullerene based OSCs, where D is based on BDT or its derivatives, and \( \pi \)-bridges are based on the thiophenes.\(^\text{[27]}\) With the emerging of non-fullerene acceptors, they are also developed to construct high performance OSCs.

**DR3TBDTT** (Figure 4) is a typical BDT-based SM donor, which was reported by Chen et al. in 2013.\(^\text{[17]}\) It possesses HOMO and LUMO of \(-5.02 \) and \(-3.27 \) eV with an \( E_g^{op} \) of 1.72 eV. When combined with PC\(_{71}BM\), the DR3TBDTT-based device could gain PCE of 9.58% (Table 2). In non-fullerene era, Sano et al. combined DR3TBDTT with an acceptor O-IDTBR (Figure 1B).\(^\text{[28]}\) The devices of DR3TBDTT/O-IDTBR exhibited a low non-radiative recombination energy of 0.21 eV and a low additional radiative recombination loss of 0.06 eV. As a result, a low \( E_{loss} \) of 0.54 eV, a markedly high \( V_{OC} \) of 1.15 V as well as a PCE of 6.36% were realized. Because of its excellent performance and highly adjustable structure, a wide range of BDT-based A-\( \pi \)-D-\( \pi \)-A type SM donors have been extensively exploited until today. Engineering of end groups, side chains as well as BDT cores have been widely used to further optimize the optical absorption, molecular energy level and crystallization property of resultant SM donors.

#### 4.1 End group engineering

For A-\( \pi \)-D-\( \pi \)-A type SM donors, the electron-accepting end groups undertake important impacts on energy levels, absorption property, charge mobility and molecule packing behavior. In the era of fullerene, researchers have made lots of exploration on the end groups, and fortunately, those design rules also can be extensively applied in the design of SM donor in NF all-SM OSCs. But, unlike fullerene-based acceptors, the structure of non-fullerene-based acceptors is more abundant, the selection of end groups in donors must be more accurate. Sometimes, a change of one unit will have great influence on the properties of donor. For example, in 2017, Li et al. synthesized two wide-bandgap BDT-based A-\( \pi \)-D-\( \pi \)-A type SM donors with weak electron-withdrawing ester groups as the end-cap for SM2.\(^\text{[29]}\) In order to explore the influence of cyano group (CN) on end groups, SM1 possessed additional CN group on the ester group was also designed (Figure 4). SM1 displayed stronger absorption, lower-lying HOMO energy level and higher hole mobility in comparison with that of SM2. As a result, the devices
FIGURE 4  (A) Chemical structures of DR3TBDTT. (B) End group engineering, (C) side-chains engineering, and (D) BDT core engineering of typical BDT-based small-molecule donors
| Donor                  | HOMO/LUMO (eV/eV) | Active layer                          | J<sub>SC</sub> (mA cm<sup>-2</sup>) | V<sub>OC</sub> (V) | FF (%) | PCE (%) | Ref  |
|-----------------------|------------------|---------------------------------------|-------------------------------------|-------------------|--------|---------|------|
| DR3TBDTT              | −5.02/−3.27      | DR3TBDTT/PC<sub>71</sub>BM            | 14.21                               | 0.886             | 76.1   | 9.58    | [7]  |
|                       |                  | DR3TBDTT/O-IDTBR                       | 11.06                               | 1.15              | 50.0   | 6.36    |      |
| SM1                   | −5.24/−2.82      | SM1/IDIC                              | 15.18                               | 0.905             | 73.55  | 10.11   | [28] |
| SM2                   | −5.04/−2.70      | SM2/IDIC                              | 10.77                               | 0.768             | 64.40  | 5.32    |      |
| H21                   | −5.38/−3.63      | H21/IDIC                              | 13.00                               | 0.895             | 65.58  | 7.62    | [30] |
| H22                   | −5.39/−3.59      | H22/IDIC                              | 15.38                               | 0.942             | 71.15  | 10.29   |      |
| SM1−S                 | −5.32/−2.81      | SM1-S/IDIC                            | 23.23                               | 0.825             | 67.7   | 12.94   |      |
| SM1−F                 | −5.37/−3.33      | SM1-F/IDIC                            | 23.25                               | 0.866             | 69.9   | 14.07   |      |
| SM1<sup>a)</sup>      | −5.25/−3.33      | SM1-Y6                                | 21.21                               | 0.870             | 61.35  | 11.33   |      |
| SM1−F<sup>b)</sup>    | −5.37/−3.37      | SM1−F/Y6                              | 21.21                               | 0.870             | 61.35  | 11.33   |      |
| BTEC-2F               | −5.39/−3.38      | BTEC-2F/Y6                            | 21.55                               | 0.854             | 72.35  | 13.44   |      |
| BT-2F                 | −5.40/−3.40      | BT-2F/Y6                              | 22.38                               | 0.853             | 72.27  | 13.80   | [34] |
|                       |                  | BT-2F/N3                              | 23.81                               | 0.84              | 70.22  | 14.09   |      |
|                       |                  |                                       | 24.28                               | 0.845             | 75.02  | 15.39   |      |
| BDT(X1)               | −5.29/−3.64      | BDT(X1)/PC<sub>71</sub>BM             | 10.71                               | 0.96              | 69.0   | 7.10    | [36] |
|                       |                  | BDT(X1)/IDIC                          | 13.26                               | 0.92              | 71.0   | 8.69    |      |
| BDT(X2)               | −5.32/−3.63      | BDT(X2)/PC<sub>71</sub>BM             | 12.61                               | 1.00              | 69.0   | 8.72    |      |
|                       |                  | BDT(X2)/IDIC                          | 12.90                               | 0.94              | 58.0   | 7.04    |      |
| BTR                   | −5.34/−3.53      | BTR/Y6                                | 22.25                               | 0.85              | 56.4   | 10.67   | [37] |
| BTR-C1                | −5.46/−3.70      | BTR-C1/Y6                             | 24.17                               | 0.86              | 65.5   | 13.61   |      |
|                       |                  | BTR-C1/BTP-FCI-FCI                    | 24.58                               | 0.8254            | 75.36  | 15.3    | [158]|
|                       |                  | BTR-C1/Y6/PC<sub>71</sub>BM           | 23.75                               | 0.8378            | 77.11  | 15.34   | [38] |
|                       |                  | BTR-C1/Y6/anti-PDFC                   | 23.97                               | 0.837             | 72.6   | 14.56   | [39] |
|                       |                  | BTR-C1/Y6/syn-PDFC                    | 23.41                               | 0.839             | 71.8   | 14.09   |      |
|                       |                  | BTR-C1/Y6/PDFC-Ph                     | 23.62                               | 0.837             | 65.0   | 12.76   |      |
|                       |                  | BTR-C1/Y6/anti-PDFC /PC<sub>71</sub>BM| 25.01                               | 0.836             | 74.9   | 15.67   |      |
| BTR                   | −5.34/−3.52      | BTR/BO-4Cl                            | 17.91                               | 0.83              | 66.0   | 10.4    | [15a]|
| Bi                    | −5.37/−3.51      | Bi/BO-4Cl                             | 25.27                               | 0.83              | 73.0   | 15.3    |      |
|                       |                  | Bi/BO-4Cl/Y7                          | 25.52                               | 0.836             | 76.29  | 16.28   | [41] |
| NDTSR                 | −5.25/−3.50      | NDTSR/ITIC                            | 5.36                                | 1.00              | 32.85  | 1.77    | [42] |
|                       |                  | NDTSR/IDIC                            | 14.13                               | 0.92              | 61.95  | 8.05    |      |
| ZR1                   | −5.32/−3.53      | ZR1/IDIC-4F                           | 18.27                               | 0.776             | 67.96  | 9.64    | [43] |
|                       |                  | ZR1/Y6                                | 24.34                               | 0.861             | 68.44  | 14.34   |      |
| ZR2-C1                | −5.36/−3.55      | ZR2-C1/Y6                             | 21.35                               | 0.848             | 65.12  | 11.79   | [44] |
|                       |                  | ZR2-C1/IDIC-4F                        | 18.15                               | 0.796             | 64.16  | 9.27    |      |
| ZR2-C2                | −5.35/−3.51      | ZR2-C2/Y6                             | 23.03                               | 0.852             | 65.43  | 12.84   |      |
|                       |                  | ZR2-C2/IDIC-4F                        | 18.27                               | 0.783             | 69.29  | 9.91    |      |
| ZR2-C3                | −5.34/−3.50      | ZR2-C3/Y6                             | 24.69                               | 0.854             | 70.06  | 14.78   |      |
|                       |                  | ZR2-C3/IDIC-4F                        | 18.95                               | 0.776             | 70.41  | 10.35   |      |
| DR3TBDTT<sup>c)</sup> | −5.17/−3.43      | DR3TBDTT/Y6                           | 23.64                               | 0.780             | 66.06  | 12.18   | [45] |
| TBFT-TR               | −5.16/−3.46      | TBFT-TR/Y6                            | 24.59                               | 0.784             | 72.78  | 14.03   |      |
| H11                   | −5.31/−3.03      | H11/IDIC                              | 15.21                               | 0.977             | 65.46  | 9.73    | [46] |
| H12                   | −5.38/−3.01      | H12/IDIC                              | 10.51                               | 0.955             | 54.89  | 5.51    |      |
| H13                   | −5.43/−3.39      | H13/IDIC-4F                           | 17.3                                | 0.939             | 63.2   | 10.3    |      |

(Continues)
based on SM1/IDIC exhibited a high PCE of 10.11% with a high $V_{OC}$ of 0.905 V, $J_{SC}$ of 15.18 mA cm$^{-2}$, and FF of 73.55%, while the SM2/IDIC device showed a PCE of 5.32% with a $V_{OC}$ of 0.768 V, $J_{SC}$ of 10.77 mA cm$^{-2}$ and FF of 64.40%.

In 2018, using alkylsilyl-thienyl BDT as central donor unit, Li et al. synthesized H21 with 3-ethylrhodanine as the end-caps, and H22 with cyanocatic acid ester as the end-caps (Figure 4). [30] Compared to H21, H22 displayed more suitable energy levels, higher charge carrier mobility as well as a hypsochromic-shifted and therefore better complementary absorption to IDIC. Encouragingly, the OSCs based on H22 exhibited a high PCE of 10.29% (with a high $V_{OC}$ of 0.942 V, $J_{SC}$ of 15.38 mA cm$^{-2}$, and FF of 71.15%), whereas H21 showed a PCE of 7.62% (with a high $V_{OC}$ of 0.895 V, $J_{SC}$ of 13.00 mA cm$^{-2}$, and FF of 65.58%).

### 4.2 Side-chains engineering

Side-chains engineering is the most common and important method for the optimization of photovoltaic materials. [31] The solubility, crystallinity, molecular packing behaviors, as well as energy levels and absorption spectrum can be efficiently tuned.

Based on SM1, in 2020, Li et al. designed two new SM donors via side-chains engineering, SM1-S with alkylthio and SM1-F with fluorine and alkyl substituents (Figure 4). [32] As a result, combined with Y6, the three corresponding donors displayed efficient photovoltaic performance with high $J_{SC}$. Among them, SM1-F-based all-SM OSCs showed the highest PCE of 14.07%, with an FF of 69.9% and a higher $V_{OC}$ of 0.866 V. Besides, the PCE of SM1-F-based devices is not sensitive to the BHJ thickness. The results revealed side-chains engineering is a feasible strategy to fine-tune the photophysical properties of donor materials.

With two F atoms in the thiophene conjugated side chains, Ge et al. reported BTEC-2F (Figure 4). [33] Compared with SM1 and SM1-F (named as DCAO3TBDTT and BTEC-1F in Ge’s paper, respectively), the HOMO energy levels (-5.39 eV) of BTEC-2F was much deeper benefited from the F atoms. And their enhancement of intermolecular packing and improvement of phase separation in the donor/Y6 blend films were beneficial for better charge carrier transmission and higher domain purity, thus resulting a higher PCE of 13.34% relative to those of SM1-F (11.33%) and SM1 (10.64%) under controlled experiments. Later, through the modulation of alkyl-chain length of the π-bridge, Ge et al. synthesized BT-2F (Figure 4) based on structure of BTEC-2F. [34] BT-2F displayed more ordered molecular arrangement and more compact lamellar stacking due to the less molecule disorder brought by the short alkyl chains. This feature endowed BT-2F with higher hole mobility, more efficient hole extraction and a better phase-separated morphology in blend films with Y6-derivatives acceptors. Photovoltaic devices based on BT-2F/Y6 showed a notably improved PCE of 13.80% as compared to the PCE of 13.34% from BTEC-2F/Y6, which was mainly attributed to the improved $J_{SC}$ from 21.55 to 22.38 mA cm$^{-2}$. Substitution of Y6 with N3 further afforded a higher PCE of 14.09% with an improved $J_{SC}$ of 23.81 mA cm$^{-2}$ and a high FF of over 70% after thermal annealing treatment. Very recently, they further improved PCE of BT-2F/N3-based device to 15.39% by solvent vapor annealing treatment. [35] They found that CS$_2$ solvent vapor annealing treatment can induce stronger molecular interactions, thus better promote molecular mobility, improve molecular $J$-aggregation and molecular interconnection. Moreover, the different solubility of CS$_2$ to donor and acceptor is beneficial to optimize phase structure of donor and inhibits non-radiative recombination.

Side-chains engineering is effective to tune the crystalline of donor materials. Lu et al. synthesized two SM donors, i.e., BDT(X1) with a linear alkyl chain and BDT(X2) with a branched alkyl chain (Figure 4). [36] They found that when combined with IDIC, blend film based on crystalline donor BDT(X1) showed more evident face-on orientation, more compact π-π stacking and larger domain size. In contrast, BDT(X2) with poor crystallinity could form better blend film morphology with fullerene acceptor than BDT(X1). In devices, with fullerene acceptor PC$_{71}$BM, the PCE for BDT(X1) and BDT(X2) were 7.10% and 8.72%, respectively. And with IDIC, the PCE
for BDT(X1) and BDT(X2) were 8.69% and 7.04%, respectively. This research indicated that adjusting the crystallinity of a donor materials could change its compatibility with the acceptors. It offers a shortcut to matching of different acceptors with the same donor.

**BTR** is another typical BDT-based SM donor, which was reported by Ouyang et al. in 2015. Because of the shorter and regular alkyl side chains, BTR exhibited an ideal nematic liquid crystal behavior and a high hole mobility of $1.6 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$. The BTR/PC$_{71}$BM device possessed a high PCE of 9.3%. Recently, to tune its compatibility with non-fullerene acceptors, the optimizing side chains on BTR have attracted more and more attention. Lu et al. designed BTR-Cl (Figure 4), by replacing hexyl groups with Cl atom in BTR in 2019. BTR-Cl exhibited deeper HOMO and LUMO energy levels and stronger absorption. Moreover, BTR-Cl showed a different liquid crystalline pattern, stronger intermolecular interaction and more ordered stacking than BTR. Therefore, an optimized phase separation and more balanced charge transport were achieved, thus the efficiency was finally improved. When combined with Y6 (non-liquid crystalline property), BTR-Cl-based device achieved a PCE of 13.61% with a $J_S$ of 24.17 mA cm$^{-2}$, a $V_{OC}$ of 0.86 V, and an FF of 65.5%, in contrast to the PCE of 10.67% for BTR. These results indicated the difference of the donor and acceptor on crystallinity was significant for the optimization of the morphology of NF all-SM OSCs systems. Recently, Lu et al. reported an asymmetric Y6-type acceptor molecule BTP-FCI-FCI (containing a F and a Cl on the same end-cap, Figure 1B), thus showing a local asymmetric structure. Therefore, the total dipole moment of the molecule is reduced and the average electronic static potential is high. The active layer based on BTR-Cl/BTP-FCI-FCI has more favorable domain size and phase separation, which facilitate faster charge extraction, improves carrier life, and reduces charge recombination rate. The all-SM OSC device based on BTR-Cl/BTP-FCI-FCI realized a significantly high PCE of 15.3% with a $J_S$ of 24.58 mA cm$^{-2}$ and an FF of 75.36%.

In 2020, on the basis of the reported photovoltaic device with BTR-Cl/Y6 blends, Kan et al. chose PC$_{71}$BM as the additive on account of its good miscibility with both BTR-Cl and Y6. When ca. 5 wt% of PC$_{71}$BM was added to the active layer, an increased FF of 77.11% was obtained with retained $V_{OC}$ and $J_S$, leading to a higher PCE of 15.34%, in comparison to the control devices without PC$_{71}$BM (PCE of 13.81% with FF of 69.63%).

In 2021, Zhong et al. designed three new SM acceptors, anti-PDFC, syn-PDFC, and PDFC-Ph (Figure 5), for further optimizing BTR-Cl/Y6 system. Benefitted from the orthogonal 2D sidechains, anti-PDFC and syn-PDFC can not only form their own crystal domains, but also improved the original packing of BTR-Cl and Y6. In contrast, due to the phenyl-hexyl side-chains, PDFC-Ph showed the worst morphology of blend film. Accordingly, the BTR-Cl/Y6/anti-PDFC-based ternary all-SM OSCs achieved the highest PCE of 14.56%. Moreover, the BTR-Cl/Y6/anti-PDFC/PC$_{71}$BM-based triple-acceptor device gained a more excellent PCE of 15.67%.

In 2020, Hou et al. designed and synthesized B1 (Figure 4) based on benzene-substituted BDT unit as the electron-rich core. Compared with BTR, B1 exhibited larger dihedral angle between the BDT core and conjugated side chains and higher rotational barrier, which was beneficial for crystalline and $\pi-\pi$ stacking capabilities. In the blend film with acceptor BO-4Cl (Figure 1B), B1 showed high ratio of face-on orientation. The excellent...
PCE of 15.3% was achieved by B1/BO-4Cl-based device with a high $J_{SC}$ of 25.27 mA cm$^{-2}$ and an FF of 73%, in contrast to 10.4% of BTR-based device.

In ternary OSCs, the introduction of the third component often plays an important role in optimizing the morphology of the blend film.[40] In 2021, An et al. incorporated SM acceptor Y7 (Figure 1B) as a morphology modulator into B1/BO-4Cl film.[41] The great compatibility between Y7 and BO-4Cl1 promoted an orderly arrangement of molecules, while B1 and Y7 showed poor compatibility that can afford driving force to manipulate phase separation. So that the PCE of this optimized ternary device was up to 16.28% with a $J_{SC}$ of 25.52 mA cm$^{-2}$, a $V_{OC}$ of 0.836 V and an FF of 76.29%.

4.3 BDT core engineering

Based on the backbone of DR3TBDDTT, several BDT derivatives have been used as cores for SM donors with favorable results.

In 2018, Wei et al. synthesized a new SM donor NDTSR (Figure 4) with naphtho[1,2-b:5,6-b’]dithiophene (NDT) as the core.[42] Benefitting from the NDT unit, NDTSR showed more edge-on orientation in molecular packings, enhanced crystallinity and better charge transport abilities. Two acceptors ITIC and IDIC were selected to fabricate NF all-SM OSCs, respectively. A high PCE of 8.05% was achieved for NDTSR/IDIC active layers, while an inferior PCE of 1.77% for NDTSR/ITIC, which was attributed to the weaker crystallinity of ITIC versus that of IDIC. By replacing ITIC with IDIC, better morphology and appropriate phase separation were obtained, leading to efficient exciton dissociation, charge transport and less bimolecular recombination.

In 2019, Wei et al. reported a dithieno[2,3-d:2’,3’-d’]BDT (DTBDT)-based SM donor ZR1 (Figure 4) with a medium optical bandgap of 1.84 eV and strong crystallinity.[43] The electron-rich core DTBDT can greatly extend the length of $\pi$-conjugation and strengthen the molecule planarity. Accordingly, shorter bithiophene rather than terthiophene was chosen as a $\pi$ bridge to deepen the HOMO level and to increase the ratio of rigid $\pi$-plane units. Two crystalline acceptor IDIC-4Cl and Y6 with bandgaps of 1.53 eV and 1.33 eV was blended with ZR1. As a result, the ZR1/IDIC-4Cl blend films exhibited a good PCE of 9.64%, with a $V_{OC}$ of 0.776 V, $J_{SC}$ of 18.27 mA cm$^{-2}$ and FF of 68.0%. While, in ZR1/Y6 blend films, the domain size of the co-existing large and small phase area turned out to be 73.9 nm and 10 nm, respectively, and the relative domain purity was calculated to be 0.95. These results suggested that DTBDT unit help the formation of a hierarchical morphology within the ZR1/Y6 blend. The optimized ZR1/Y6-based devices reached a maximum PCE of 14.34% with a $J_{SC}$ of 24.34 mA cm$^{-2}$ and a low $E_{loss}$ of 0.52 eV. Whereafter, Wei et al. synthesized three DTBDT-based SM donors, ZR2-Cn (n = 1, 2, and 3) (Figure 4) with different branching point of alky side chains.[44] The change of side-chain branching position showed great influence on the crystallinities and $\pi-\pi$ stacking interactions of these three molecules. ZR2-C3, which possessed the farthest distance between branching point and backbone, achieved a nanofiber-based hierarchical morphology in ZR2-C3/Y6-based blend film and showed a highest PCE of 14.78% without additives and electron-transporting layer. The PCE of ZR2-C1 and ZR2-C2 were 11.79% and 12.84%, respectively. The similar tendency could be found in the ZR2-Cn/IDIC-4F-based devices.

In 2020, Min et al. synthesized a SM donors TBFFTR (Figure 4) with thiendo[2,3-f]benzofuran (TBFF) as the core units and fabricated photovoltaic devices with acceptor Y6.[45] In comparison to DR3TBDDTT (named as BDTT-TR in Min’s paper) with BDT as a centrosymmetric core, TBFF-TR with TBFF as an asymmetric core showed red-shifted absorption, higher and more balanced charge carrier mobility, highly ordered molecular packing and therefore faster charge transport pathway in the blend films. A high PCE of 14.03% for the TBFF-TR/Y6-based devices was achieved with a $J_{SC}$ of 24.59 mA cm$^{-2}$ and FF of 72.78% compared to the BDTT-TR/Y6 system (PCE of 12.18% with $J_{SC}$ of 23.64 mA cm$^{-2}$ and FF of 66.06%).

5 BDT-FBTA-BASED SMALL-MOLECULE DONORS

Li et al. previously developed a series of two-dimension (2-D)-conjugated D-A copolymers based on bithienylbenzodithiophene (BDTT) as donor unit and fluorobenzotriazole (FBTA) as acceptor unit.[50] Resultant polymers possess medium bandgaps (1.93~1.96 eV),[46] suitable HOMO levels for hole extraction, as well as high crystallinity and hole mobilities. They afforded efficiency up to 9~14% in non-fullerene polymer solar cells when combined with low-bandgap SM acceptors. In 2017, based on the BDTT-alt-FBTA D-A copolymers, Li et al. designed an A-\pi-D-\pi-A type small molecule H11 (Figure 6) that was based on electron-rich BDT core sandwiched by two adjacent electron-weak FBTA units as the $\pi$-bridge.[51] Meanwhile, for investigating the influence of the thiienyl conjugated side chains on the photovoltaic performance, a control molecule H12 (Figure 6) with alkoxy substituents on BDT unit was also synthesized. In comparison to H12, the 2-D conjugated H11 displayed a higher extinction coefficient, relatively lower HOMO and LUMO energy levels, higher charge carrier mobility and better 3-D charge-transport pathways in blend films. Photovoltaic performance of
these two small molecule donors was quantified by OSCs thereof with IDIC as acceptor. Encouragingly, the OSCs based on H11 exhibited a high PCE of 9.73% (with a high $V_{OC}$ of 0.977 V, $J_{SC}$ of 15.21 mA cm$^{-2}$, and FF of 65.46%), whereas H12 showed a PCE of 5.51% (with a high $V_{OC}$ of 0.955 V, $J_{SC}$ of 10.51 mA cm$^{-2}$, and FF of 54.89%). This result as well as the case of DRTB-O/DRTB-T motioned above both imply that chemical functionalization of the side chains on conjugated molecules is an effective strategy for optimizing the performance of NF all-SM OSCs.

Stimulated by the favorable photovoltaic performance of H11, thus a variety of exploration to optimize this BDT-FBTA-based SM donors by side-chains engineering has been made, and all achieved good results.

Later, Li et al. designed two novel small molecules, H13 and H14 (Figure 6), by fluorine and chlorine substitution of H11. The introduction of halogen atoms decreased the HOMO energy levels of H13 and H14, which were -5.43 eV and -5.46 eV, respectively, compared with -5.27 eV for H11. After thermal annealing treatment, the optimized H14/IDIC-based device shows appropriate size of aggregated domains and high domain purity in the blend film, so the charge collection was increased and the bimolecular recombination was suppressed. Finally, H14-based device achieved a high PCE of 12.1% with a $J_{SC}$ of 18.3 mA cm$^{-2}$, a $V_{OC}$ of 0.943 V, and FF of 70.2%, after thermal annealing treatment. And the PCE for H13 was 10.3%.

In 2018, Min et al. reported a new alkylthiethienylenevinylene thiophene (TVT-SR)-substituted BDT-FBTA-based small molecule, BDT(TVT-SR)$_2$ (Figure 6). Compared with H11, BDT(TVT-SR)$_2$ possessed extended molecular conjugation length as well as more ordered intermolecular stacking, thus it showed red-shifted and stronger absorption and higher hole mobility in the film. After the thermal annealing, the blend film based on BDT(TVT-SR)$_2$ and IDIC exhibited attractive bi-continuous interpenetrating networks with suitable domain size. The optimized PCE for BDT(TVT-SR)$_2$ was as high as 11.10% with higher $J_{SC}$ and FF of 15.92 mA cm$^{-2}$ and 71.15%. In addition, BDT(TVT-SR)$_2$ possessed stronger thermal stability and photo-stability than H11, due to the TVT-SR side chains.

In the same year, Li et al. replaced FBTA unit with benzothiadiazole (BT) unit and reported two SM donors, SM-BT-2OR with alkoxy substitution and SM-BT-2F with fluorine atom on the BT unit (Figure 6), for investigating the influence of side-chains engineering on the morphology tuning and photovoltaic performance. Compared to SM-BT-2OR, SM-BT-2F showed bathochromic-shifted absorption, deeper HOMO energy level, and reduced bandgap. After thermal annealing at 120°C for 10 minutes, SM-BT-2OR/IDIC-based devices achieved an enhanced PCE of 7.20% and a reduced $V_{OC}$, however, the SM-BT-2F/IDIC-based device presented a lower PCE of 1.60% but slightly higher $V_{OC}$, which should be ascribed to the undesirable morphology and molecular orientation.

6 | SUMMARY AND OUTLOOK

The first working D/A junction-type OSC was proposed by Tang, comprising a bilayer of Copper(II) phthalocyanine donor and perylenetetracarboxylic derivative as acceptor, and showing a PCE of nearly 1%. Up to now, with the superior absorption of visible range photons and impressive structural adjustability enabled by low-bandgap IDIC- and Y6-based acceptors, NF all-SM OSCs is developing rapidly, and the PCE of a state-of-the-art device has exceeded 15%. In spite of these achievements, photovoltaic performance of NF all-SM OSCs still remain inferior to that of polymer solar cells (polymer donors with SM acceptors) over the past decades. Considering that SM materials possess the intrinsic advantages of well-determined molecular structure, facile purification, and higher batch-to-batch repeatability, however, the
academic community need pay more efforts to enhance the performance of NF all-SM OSCs.

Thus far, Hou et al., Lu et al., and Ge et al. all hold the record PCE over 15% for NF all-SM OSCs based on typical BDT-based SM donors. It shows that this kind of BDT-based SM donors possesses a wider structural variability due to the A-π-D-π-A structure. It is easy to enhance photoelectric performance and improve miscibility with various kinds of acceptors by chemical modification.

On the basis of these four categories of donors, strategies of core, π-bridge, side chains, and end group engineering have been devoted to meet the demand of non-fullerene acceptors and boost the performance of device. The following suggestions for optimization of SM donors are put forward.

(1) Because of the advantages of relatively larger planar aromatic ring, high carrier mobility, easy-modified chemical structure, BDT unit is still one of the best choice for SM donors. The core groups with better planarity and bigger conjugated frame like DTBDT unit and NDT unit can effectively strengthen photon-absorption, hole mobility, and crystallinity. In addition, sometimes the core group that possesses an asymmetric structure such as TBF unit was also used in donor material. The research indicated that the design of asymmetric core could tune energy levels and crystallinity of SM donors effectively.

(2) Terthiophene is the most common unit used for π-bridge. Its functions are as follows: (a) Extending the length of molecular conjugated backbone, thus improving the solar absorption capability. (b) Adjusting the molecular packings and optimizing the morphology of blend film. In addition, electron deficient units, such as FBTA, 1,3-dithiophene-4,8-dione (BDD) and thiazolo[5,4-c]c-[2,1,3]thiadiazole (TTz) are also used to build π-bridges to increase the diversity, and effectively improved the photovoltaic performance of small molecular donors.[54]

(3) The functions of electron-accepting end groups mainly cover down-shifting the LUMO energy level and forming a strong electron push-pull effect with electron-donating core groups that could help to tune the band gap and promote the intramolecular charge transfer. Besides, researchers sometimes would introduce cyano and fluorine and so on units into end-caps not only because of their strong ability of electron-accepting, but they also can enhance π-π stacking and improve the miscibility with acceptor molecule. Currently, 3-ethylrhodanine and cyanoacetic acid ester are most commonly used end groups.

(4) Side-chains engineering could tune the solubility, crystallinity, and crystal orientation of the solution-processed photovoltaic materials. Despite the adjustment of length and branching of alkyl side chains, introducing conjugated side chains and heteroatom (sulfur, silicon, fluorine, and chlorine on side chains) as the linker are also common design. Facilitated by suitable side chains, donor and acceptor can self-assemble to form a nanoscale phase separation, and it is beneficial for charge dissociation and transport. Furthermore, tuning the molecular orientation of donor to from 3-D charge carrier transport pathway with acceptor is an efficient way to improve hole and electron mobility.

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