Narrowing the Band Gap: The Key to High-Performance Organic Photovoltaics

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CONSPECTUS: Organic photovoltaics (OPVs) have attracted considerable attention in the last two decades to overcome the terawatt energy challenge and serious environmental problems. During their early development, only wide-band-gap organic semiconductors were synthesized and employed as the active layer, mainly utilizing photons in the UV−visible region and yielding power conversion efficiencies (PCEs) lower than 5%. Afterward, considerable efforts were made to narrow the polymer donor band gap in order to utilize the infrared photons, which led to the enhancement of the PCE from 5% to 12% in about a decade. Since 2017, the study of narrow-band-gap non-fullerene acceptors helped usher in a new era in OPV research and boosted the achievable PCE to 17% in only 3 years. In essence, the history of OPV development in the last 15 years can be summarized as an attempt to narrow the band gap of organic semiconductors and better position the energy levels. There are multiple benefits of a narrower band gap: (1) considerable infrared photons can be utilized, and as a result, the short-circuit current density can increase significantly; (2) the energy offset of the lowest unoccupied molecular orbital energy levels or highest occupied molecular orbital energy levels between the donor and acceptor can be reduced, which will reduce the open-circuit voltage loss by minimizing the loss caused by the donor/acceptor charge transfer state; (3) because of the unique molecular orbitals of organic semiconductors, the red-shifted absorption will induce high transmittance in the visible region, which is ideal for the rear subcells in tandem-junction OPVs and transparent OPVs.

In this Account, we first summarize our work beginning in 2008 on the design and synthesis of narrow-band-gap polymer donors/non-fullerene acceptors. Several strategies for constructing these materials, including enhancing the intramolecular charge transfer effect and steric hindrance/energy level engineering are discussed. In this part, in addition to systematic analyses of the design of narrow-band-gap polymer donors based on BDT/TT or BDT/DPP, donors/acceptors based on the new donor moieties DTP or BZPT are discussed as well. Especially, we highlight our work on the first report on the narrow-band-gap acceptor Y1 (based on the new donor moiety BZPT), which pioneered the future development and usage of acceptors belonging to the Y1 family (or series). Subsequently, we analyze several reported certified world record single-junction or tandem-junction OPVs that use these narrow-band-gap donors or acceptors. We share our experiences and insights from a device perspective in terms of donor/acceptor selection, energy level alignment management, film morphology control, current matching of subcells, interconnecting layer construction, interface engineering, and device geometry selection. In this part, the construction of high-performance ternary-blend OPVs and transparent OPVs based on these narrow-band-gap donors/acceptors is also discussed. Finally, in order to push the field into the 20−25% high-efficiency era in the next few years, some suggestions to further develop narrow-band-gap donors/acceptors and related device technologies are proposed.

1. INTRODUCTION

Organic photovoltaics (OPVs), with unique advantages such as light weight, flexibility, large area, and low-cost fabrication, have attracted considerable attention in the last two decades to overcome the terawatt energy challenge and serious environmental problems.1−6

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At the early stage of OPV development (before 2005), only large optical band gap ($E_g > 1.9$ eV) organic semiconductors (e.g., poly(2-methoxy-5-(2′-ethylhexoxy)-1,4-phenylenevinylene) (MEH-PPV), poly(3-hexylthiophene) (P3HT), and phenyl-C$_{61}$-butyric acid methyl ester (PCBM)) were synthesized and employed as the active layer. These wide-band-gap materials can only utilize photons in the UV−visible region (i.e., only 57% energy in the AM 1.5G solar spectrum), yielding power conversion efficiencies (PCEs) lower than 5% for the OPVs. According to the Shockley−Queisser model, $E_g$ should be around 1.1−1.3 eV to match the AM 1.5G solar spectrum well. Therefore, considerable efforts (e.g., utilizing donor−acceptor (D−A) interactions) to narrow the band gap of p-type organic semiconductors (donors) were made, and the PCEs were increased from 5% to 12% in a decade. In 2017, the study of narrow-band-gap n-type organic semiconductors (new non-fullerene acceptors) became a new wave, and the PCEs were boosted to 17% in only 3 years.

In essence, the history of OPV development in the last 15 years is a history of narrowing the band gap of organic semiconductors. The benefits of narrowing the band gap are multiple: (1) considerable infrared (IR) photons can be utilized, and as a result, the short-circuit current density ($J_{SC}$) can increase significantly; (2) the energy offset of the lowest unoccupied molecular orbital (LUMO) energy levels or the highest occupied molecular orbital (HOMO) energy levels between the donor and acceptor can be reduced, and this will reduce the open-circuit voltage ($V_{OC}$) loss by minimizing the loss caused by the donor/acceptor charge transfer state; (3) because of the unique molecular orbitals of organic semiconductors, the red-shifted absorption will induce high transmittance in the visible region, which is ideal for the rear subcells in tandem-junction OPVs and transparent OPVs.

In this Account, we first summarize our work starting from 2008 on narrow-band-gap polymer donors. Research experiences and insights on enhancing the intramolecular charge transfer effect as well as steric hindrance/energy level engineering of these materials are shared in this part. Second, we focus on our recent work on the design and synthesis of a new narrow-band-gap non-fullerene acceptor, Y1, which launched the exciting journey of the Y1 family of acceptors (e.g., Y6). Third, we analyze several examples of making certified world record single-junction or tandem-junction OPVs that use these narrow-band-gap donors/acceptors. Afterward, unique applications of narrow-band-gap donors/acceptors (employed as the third component or making transparent OPVs) are discussed. Finally, some suggestions for the further development of narrow-band-gap donors/acceptors and the related device technology are
proposed to potentially push the field into the 20–25% high-efficiency era in the next few years.

2. NARROW-BAND-GAP DONORS

First and foremost, large \( \pi \) conjugation is a critical and fundamental requirement to enable narrow-band-gap polymer donors. Fusing more aromatic rings in the repeat unit and/or increasing the degree of polymerization can help enlarge the \( \pi \) conjugation to some extent. In order to further narrow the band gap and push the absorption edge to 800–1000 nm, two important strategies were proposed: (1) stabilizing the quinoid resonance structure, since this resonance structure usually has a narrower band gap; (2) utilizing alternating D–A interactions in copolymerization, since the HOMO/LUMO of the donor (electron-donating) moiety will interact with the HOMO/LUMO of the acceptor (electron-withdrawing) moiety, resulting in a higher HOMO energy level and a lower LUMO energy level of the polymer donor. Some strong donor moieties (e.g., thiophene, bithiophene, benzodithiophene (BDT), dithienosilole (DTS), cyclopentadithiophene (CPDT), etc.) and acceptor moieties (e.g., benzothiazole (BT), diketopyrrolopyrrole (DPP), isoindigo, etc.) are usually employed to construct D–A copolymers. Taking these into account, began on 2008, our group designed and synthesized some representative narrow-band-gap polymer donors (Figure 1) via four specific strategies: (1) constructing D–A copolymers based on strong donor moieties and strong acceptor moieties; (2) modifying D–A copolymers based on BDT and thieno[3,4-b]thiophene (TT); (3) substituting sulfur atoms by selenium atoms on strong acceptor moieties; and (4) introducing an asymmetric donor moiety, dithienopyrrole (DTP). The details are provided in the following paragraphs.

(1) In 2008, we demonstrated a narrow-band-gap polymer donor, PSBT-BT, which is based on DTS and BT.\(^{15}\) Thanks to the strong electron-donating and electron-withdrawing abilities of DTS and BT, respectively, PSBT-BT exhibits a narrow \( E_g \) of 1.45 eV. At the same time, the hole mobility of PSBT-BT (\( 3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \)) is higher than that of PCPDT-BT\(^\text{16}\) (a prototype polymer based on CPDT and BT) because of the enhanced molecular planarity and packing of DTS compared with CPDT.\(^\text{17}\) In addition to CPDT/DTT, the strong moiety BDT with good planarity and small steric hindrance is a good candidate for constructing narrow-band-gap polymer donors. Combined with diphenylquinonoxaline (Qu) or thienopyrazine (TP) as the acceptor moiety, the narrow-band-gap donors PBDDT-Qx (\( E_g \) of 1.50 eV) and PBDDT-TP (\( E_g \) of 1.19 eV) were designed and synthesized.\(^\text{18}\) In 2009, still based on the BDT donor moiety, we incorporated another strong acceptor moiety, DPP, to construct a narrow-band-gap polymer donor.\(^\text{19}\) Because of the strong \( \pi–\pi \) interaction and electron-withdrawing ability of the DPP moiety and the features of the BDT moiety mentioned above, the new polymer donor PBDDT-DPP exhibits a narrow \( E_g \) of 1.31 eV with a HOMO energy level of −5.16 eV. Three years later, by utilizing the strategy of two-dimensional conjugation,\(^\text{19}\) we tried to further improve the performance of the polymer donor PBDDT-DPP.\(^\text{20}\) Alkylphenyl and alkylthienyl groups were attached to BDT to construct the new donor moieties alkylphenylbenzodithiophene (BDTP) and alkylthienylbenzodithiophene (BDTT) with enhanced two-dimensional conjugation. Then two polymer donors, PBDDTP-DPP and PBDDTT-DPP, with similar band gaps of 1.44 and 1.46 eV, were synthesized by the polymerization of BDTP/BDTT and DPP moieties. Compared with PBDDT-DPP, the modified polymer donors PBDDTT-DPP and PBDDTP-DPP show deeper HOMO energy levels (−5.30 and −5.35 eV, respectively), a characteristic for a potentially higher \( V_{OC} \).

(2) In addition to constructing D–A copolymers based on strong donor moieties and strong acceptor moieties, we made some efforts to modify copolymers based on BDT and TT. In 2008, Yu et al. reported a very important BDT/TT-based polymer donor, PTB1.\(^\text{21}\) The TT moiety has weak electron-donating ability but is able to stabilize the quinoidal structure of the polymer backbone, a feature showing benefits in narrowing the band gap. As a result, the polymer donor PTB1 exhibits an \( E_g \) of 1.6 eV, but it has a high HOMO energy level of −4.90 eV. In order to achieve a high \( V_{OC} \) and a high \( j_{SC} \) of OPVs, it is important to shift the HOMO energy level of polymer donor downward without enlarging the band gap. On the basis of this principle, we employed an alkyl group and fluorine atom on the TT moiety step-by-step to modify the BDT/TT polymer donor. First, the alkoxyl group on the TT moiety was substituted by an alkyl group, which has a much weaker electron-donating activity.\(^\text{22}\) As a result, the modified polymer donor PBDDT-TTC shows a deeper HOMO energy level (−5.12 eV) than PTB1 without any change in band gap. Second, PBDDT-TTC was modified with an electron-withdrawing F atom on the TT moiety to further shift the HOMO energy level downward.\(^\text{23}\) As a result, the new polymer donor PBDDT-TTCF exhibits the same band gap as PTB1 and PBDDT-TTC but has a much deeper HOMO energy level of −5.22 eV, which is a feature for potentially higher \( V_{OC} \).

(3) Furthermore, the strategy of substituting the S atom by the Se atom on the strong acceptor moieties was carried out. Compared with the S atom, the larger Se atom not only has a bigger/looser outermost electron cloud, which improves the \( \pi \)-electron delocalization and results in a narrower band gap, but also presents a large frontier orbital contribution, which is helpful for intermolecular charge transport.\(^\text{24}\) We used this strategy on the two polymer donors PCPDT-BT and PBDDT-DPP. For the polymer donor PCPDT-BT, a benzoselenadiazole (BSe) moiety was employed to replace the BT moiety.\(^\text{25}\) The modified polymer donor PCPDT-BSe shows a narrow \( E_g \) of 1.35 eV, which is 0.1 eV smaller than that of PCPDT-BT. For the polymer donor PBDDT-DPP, the DPP moiety was substituted by the bis(selenophenyl)diketopyrrolopyrrole (SeDPP) moiety.\(^\text{26}\) As a result, the new polymer donor PBDDT-SeDPP exhibits a narrower band gap (1.38 eV) and a higher hole mobility (6.9 × 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}) compared with PBDDT-DPP (1.46 eV and 2.5 × 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}).

(4) In addition to widely used donor moieties (e.g., CPDT, BDT etc.), in 2013 we introduced an asymmetric DTP moiety by inserting an oxygen atom on the cyclopentane ring of the CPDT moiety.\(^\text{27}\) For comparison, three polymer donors were synthesized with different donor moieties (DTP, CPDT, BDT) and the same acceptor moiety, difluorobenzothiadiazole (DFBT). The results showed that the polymer donor PDTNP-DFBT exhibits the highest HOMO energy level, a result signifying the DTP moiety’s very strong electron-donating ability. Finally, the \( E_g \) of this new polymer donor PDTNP-DFBT is 1.38 eV.

3. NARROW-BAND-GAP ACCEPTORS

The introduction of PCBM as the acceptor in the active layer was a great progress in OPV development. However, PCBM has a restricted chance of band gap variation because the C\textsubscript{60}/C\textsubscript{70} core dominates its band gap. Therefore, the concept of non-
fullerene acceptors was developed in view of the infinite possibilities for chemical modifications to narrow the band gap. In the early stage of non-fullerene acceptors (before 2015), almost all non-fullerene acceptors were based on the acceptor moieties perylene diimide (PDI) and naphthalene diimide (NDI).28,29 In 2015, a novel type of non-fullerene acceptor, ITIC (Eg of 1.6 eV), based on the donor moiety indacenodithiophene (IDT) and the acceptor moiety 2-(3-oxo-2,3-dihydroinden-1-ylidene)malononitrile (INCN), was reported by Zhan et al.30 Because chemical modifications of the core, π bridge, or end groups of ITIC can easily vary its band gap, the new ITIC-type structure provided a great platform for developing new narrow-band-gap acceptors.

In 2019, we designed and synthesized Y1, a non-fullerene acceptor based on the acceptor moiety INCN with an Eg of 1.44 eV (Figure 2), by incorporating a new donor moiety, dithienothiophen[3,2-b]pyrrolobenzotriazole (BZPT).13 In the design of BZPT, the covalent nitrogen bridges the adjacent thiieno[3,2-b]thiophene and benzotriazole (BZ) to form a thiieno[3,2-b]thiophene-BZ-thieno[3,2-b]thiophene donor—acceptor—donor (D–A–D) structure. This D–A–D donor moiety offers a relatively planar structure that facilitates intramolecular charge transfer because of the enhanced π-electron delocalization. In addition, the introduction of the nitrogen atoms serving as heteroatomic bridges for covalent planarization provides stronger electron-donating ability that shifts the LUMO and HOMO energy levels of the acceptor Y1 upward to −3.95 and −5.45 eV, respectively. Furthermore, the existence of the weak electron-withdrawing BZ group in the middle of the D–A–D donor moiety enhances the electroluminescence yield, which potentially has the benefit of smaller Voc loss of OPVs since the nonradiative charge recombination may be reduced. In the same year, in order to further narrow the band gap of Y1 to match the AM 1.5G solar spectrum well, Y2 and Y3 were designed and synthesized by changing the benzenes of INIC into thiophenes and by incorporating F atoms on the benzenes of INIC, respectively. With no change in the donor moiety BZPT, the stronger electron-withdrawing abilities of the modified acceptor moieties shift the LUMO energy level down by 0.09 and 0.16 eV, respectively, relative to Y1. As a result, the modified acceptors Y2 and Y3 exhibit red-shifted absorption onsets of 25 and 43 nm compared with Y1.

Based on the ITIC skeleton (strong acceptor–fused ring donor–strong acceptor), our new acceptor Y1 launched the exciting journey of the Y1 family of acceptors, which have drawn a lot of attention in the last 2 years. The relatively high LUMO energy levels and narrow band gaps of the Y1-family acceptors significantly contributed to the reported high Voc and high Jsc, respectively. For example, Y6 (a member of the Y1 family of acceptors) has a narrow band gap of 1.33 eV, which is very attractive to the OPV community.

4. HIGHLY EFFICIENT SINGLE-JUNCTION OPVs

To design highly efficient single-junction OPVs, some important aspects should be taken into consideration: (1) selecting the donor and acceptor with broad and complementary absorption to maximize the photon utilization; (2) managing the donor/acceptor energy level alignment to minimize the Voc loss while still ensuring sufficient driving force for charge transfer; (3) controlling the film morphology in terms of molecular packing and donor/acceptor phase separation to guarantee efficient charge transfer and transport; (4) constructing the device structure by inserting suitable hole/electron-transport layers and employing conventional/inverted geometry to increase the charge extraction efficiency. In this part, from a device perspective, we analyze several examples of the construction of highly efficient single-junction OPVs that use these narrow-band-gap donors/acceptors.

In 2009, OPVs in the conventional geometry (indium tin oxide | (ITO) / poly-(ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS)/active layer/calcium/aluminum) were fabricated using PBDTT-TTCF as the donor and PCBM as the acceptor.25 Thanks to the downshifted HOMO energy level of PBDTT-TTTF, the offset between the HOMO energy level of the donor and the LUMO energy level of the acceptor was increased to 0.92 eV. As a result, a relatively high Voc of 0.76 V and PCE of 7.7% were achieved, which were attractive at that time. More importantly, the devices were tested by the National Renewable...
Energy Laboratory (NREL), and a certified PCE of 6.8% (Figure 3a) was recognized on the NREL “Best Research-Cell Efficiencies” chart.\(^{12}\)

In contrast to the narrow-band-gap donor/wide-band-gap acceptor combination, the wide-band-gap donor/narrow-band-gap acceptor pair became much more promising because of the rapid developments of non-fullerene acceptors. In 2019, OPVs consisting of the polymer donor PBDB-T\(^{32}\) and the non-fullerene acceptor Y1 were constructed with an inverted geometry of ITO/zinc oxide (ZnO)/active layer/molybdenum oxide (MoO\(_3\))/silver.\(^{13}\) The selection of PBDB-T as the donor was considered from two aspects: (1) PBDB-T has a wide band gap (1.8 eV) that exhibits an absorption region complementary to that of Y1 (E\(_g\) of 1.44 eV), potentially enabling a high J\(_{SC}\); (2) PBDB-T has a slightly higher HOMO energy level (−5.39 eV) than Y1 (−5.45 eV), potentially enabling a high V\(_{OC}\) due to the possibly reduced radiative recombination related to the donor/acceptor charge-transfer state. As a result, the champion device showed a high J\(_{SC}\) of 22.4 mA/cm\(^2\) and a high V\(_{OC}\) of 0.87 V, which pushed the PCE to 13.4%. The devices were tested by the Newport Corporation, and a certified PCE of 12.6% (Figure 3b) was recognized on the NREL Best Research-Cell Efficiencies chart. The V\(_{OC}\) loss of PBDB-T/Y1 devices is as low as 0.57 V, which is mainly caused by the reduced radiative recombination below the band gap. As shown in Fourier transform photocurrent spectroscopy external quantum efficiency (EQE) measurements (Figure 3c), the absorption onset of the PBDB-T/Y1 devices is sharp, indicating that the V\(_{OC}\) loss due to radiative recombination below the band gap (i.e., the donor/acceptor charge-transfer state) is estimated to be as low as 0.04 V, a value that is significantly smaller than that observed in typical OPVs (up to 0.7 V).

In addition to being directly used as a donor or acceptor, the narrow-band-gap organic semiconductor can also be employed as the third component in a ternary-blend active layer to broaden the absorption region.\(^{33–35}\) To maximize contributions of the narrow-band-gap third component, two aspects are considered: (1) the band gap of the third component should be as narrow as possible while still avoiding potential charge recombination in the narrow-band-gap material, and (2) the compatibility between the third component and the donor/acceptor should be good. In 2015, the polymer donor PBDTT-SeDPP\(^{26}\) with a narrow E\(_g\) of 1.38 eV was employed as the third component in the PTB7 (E\(_g\) of 1.6 eV)/PCBM active layer.\(^{37}\) Compared with the polymer donor PTB7, the third component, the polymer PBDTT-SeDPP, exhibits a similar HOMO energy level but a much lower LUMO energy level, which broadens the absorption region from 775 to 900 nm. In addition, the molecular structures of PTB7 and PBDTT-SeDPP are similar to some extent because both of them have a BDT unit. As a result, the PTB7/PBDTT-SeDPP/PCBM ternary-blend devices produce a best PCE of 8.7%, which is higher than that of binary-blend devices made from PTB7/PCBM (PCE of 7.2%) or PBDTT-SeDPP (PCE of 7.2%). The J\(_{SC}\) of the ternary-blend devices (18.7 mA/cm\(^2\)) is significantly higher than that of PTB7/PCBM binary-blend devices (15.1 mA/cm\(^2\)) because of the additional photon utilization in the IR region (Figure 3d). Three years later, we proposed the design of a “unique energy level alignment”: a third component with a LUMO energy level similar to that of the acceptor and a HOMO energy level similar

Figure 3. (a) J–V curve for the PBDT-TTCF/PCBM device certified by NREL. (b) J–V curve for the PBDB-T/Y1 device certified by Newport Corporation. (c) Fourier transform photocurrent spectroscopy EQE spectra of the PBDB-T/Y1 and PBDB-T/Y2 devices. (d) EQE spectra of PTB7/PCBM, PTB7/PBDTT-SeDPP/PCBM, and PBDTT-SeDPP/PCBM devices. The PTB7/PBDTT-SeDPP/PCBM device shows significantly enhanced EQE compared with the PTB7/PCBM device in the 700–900 nm range. (e) 2D GIWAXS patterns of FTAZ/IDIC and FTAZ/ITIC-Th-O/IDIC films, indicating similar molecular packing behaviors. (a) Reproduced with permission from ref 23. Copyright 2009 Macmillan Publishers Ltd. (b, c) From ref 13. CC BY 4.0. (d) Reproduced with permission from ref 37. Copyright 2015 Macmillan Publishers Ltd. (e) Reproduced with permission from ref 38. Copyright 2018 Wiley-VCH.
to that of the donor was introduced. In this design, the absorption region can be maximally broadened without inducing charge recombination in the narrow-band-gap material.38 In this work, we designed and synthesized a narrow-band-gap third component, ITIC-Th-O (E_g of 1.4 eV), which has a chemical structure and LUMO energy level similar to those of the acceptor IDIC (E_g of 1.6 eV)39 and a HOMO energy level similar to that of the donor FTAZ (E_g of 2.0 eV).40 Compared with the FTAZ/IDIC binary blend, the broadened absorption and enhanced charge transfer of the FTAZ/ITIC-Th-O/IDIC ternary blend exhibited an enhanced J_SC. The good compatibility of ITIC-Th-O and IDIC induces similar molecular packing behavior in terms of molecular crystallite orientation and aggregation in the FTAZ/IDIC binary blend and FTAZ/ITIC-Th-O/IDIC ternary blend, as indicated by 2D grazing-incidence wide-angle X-ray scattering (GIWAXS)41,42 results (Figure 3e).

The retained optimized film morphology keeps the high fill factor (FF). Finally, the ternary-blend devices that incorporated ITIC-Th-O exhibited higher a PCE (11.6%) than the binary-blend devices (10.4%).

5. HIGHLY EFFICIENT TANDEM-JUNCTION OPVs

Tandem-junction OPVs, comprising two or more subcells stacked together, were invented to overcome the limitations of single-junction OPVs through their advantages of enhanced photon utilization efficiency and reduced thermal loss.43−45 Compared with single-junction OPVs, tandem-junction OPVs are more complicated. In addition to donor/acceptor selection, energy level alignment management, and film morphology control of the subcells, three new issues of tandem-junction OPVs should be taken into account: (1) current matching of the subcells to maximize the J_SC of the tandem-junction device; (2) construction of the interconnecting layer (ICL) with minimized electrical and optical losses; and (3) modification of the two new active layer/ICL interfaces to ensure good film coverage and efficient charge recombination in the ICL. In this part, from a device perspective, we analyze several examples of the construction of highly efficient tandem-junction OPVs that use these narrow-band-gap donors/acceptors.

In 2012, we constructed a tandem-junction OPV based on an inverted geometry (Figure 4a).46 The front subcell was based on P3HT/indene−C_60 bisadduct (ICBA),47 while the rear subcell was based on PBDTT-DPP20/PCBM. The band gaps of P3HT and PBDTT-DPP are 1.9 and 1.46 eV, respectively, which means that the absorption onsets of the front and rear subcells are at 650 and 850 nm, respectively. The ICL consisted of MoO_3 (hole-transport layer), ZnO (electron-transport layer), and PEDOT:PSS PH 500 (charge recombination layer). MoO_3 and ZnO were employed as the transport layers because of their high transmittances in the visible−IR region, relatively high mobilities, and suitable work functions. In addition, the thermally evaporated MoO_3 layer also can prevent solvent penetration during processing of the PEDOT:PSS layer. The EQE spectra of the front and rear subcells in the optimized tandem-junction OPV are shown in Figure 4b. In view of the different structures of single-junction and tandem-junction devices, bias light and bias voltage are employed to exclude the influences of the other subcell when EQE measurements are
carried out on a subcell of a tandem-junction device. The front subcell has a photoresponse from 300 to 600 nm with an integrated $J_{SC}$ of 8.2 mA/cm$^2$, while the main contribution of the rear subcell can be found between 600 and 850 nm with a similar integrated $J_{SC}$ of 8.1 mA/cm$^2$. Thanks to the well-matched $J_{SC}$ of the front and the rear subcells, the tandem-junction OPVs achieved a $J_{SC}$ of 8.3 mA/cm$^2$, a value that was very promising at the time. The $J-V$ measurements of tandem-junction OPVs were accomplished by NREL, and a certified PCE of 8.6% (Figure 4c) was recognized on the NREL Best Research-Cell Efficiencies chart. One year later, we demonstrated another tandem-junction OPV based on the same front subcell and ICL that incorporated the narrower-band-gap polymer donor PDTP-DFBT. The substitution of PBDTT-DPP by PDTP-DFBT resulted in a red shift of the absorption onset by 50 nm, which enhanced the photon utilization efficiency and contributed to higher $J_{SC}$. As a result, the tandem-junction devices (as measured by NREL) showed a $V_{OC}$ of 1.53 V, $J_{SC}$ of 10.1 mA/cm$^2$, FF of 68.5%, and PCE of 10.6% (Figure 4d). The certified PCE of 10.6% was the first report to break the 10% efficiency barrier and was also recognized on the NREL Best Research-Cell Efficiencies chart.

In the following years, although researchers have made some progress on tandem-junction OPVs, the trade-off between the $V_{OC}$ and $J_{SC}$ is still challenging to balance. In 2019, instead of performing rational and careful synthesis of new materials with only a slight difference in band gaps, we introduced a simple strategy to balance the trade-off between the $V_{OC}$ and $J_{SC}$ in tandem-junction OPVs by employing mixed non-fullerene acceptors (FOIC/F8IC) in the rear subcell. In the rear subcell, the $V_{OC}$ and $J_{SC}$ can be tuned because of the different energy levels and different band gaps of the two acceptors, FOIC and F8IC. At the same time, the good compatibility of these two structurally similar acceptors guarantees that the tuning is applicable over a wide range of FOIC/F8IC mixing ratios. As a result, by the use of different rear subcells (with different FOIC/F8IC ratios), the $V_{OC}$ and $J_{SC}$ of tandem-junction devices can be easily tuned ($V_{OC}$ of 1.57–1.66 V, $J_{SC}$ of 11.1–9.9 mA/cm$^2$).
Finally, tandem-junction devices based on 1:1 FOIC/F81C exhibited the best performance (the EQE spectra of the corresponding front and rear subcells are shown in Figure 4e), and a PCE of 13.3% was achieved in our lab. Afterward, these devices were certified by NREL under the new protocols (asymptotic scans, which are much tougher than regular fast scans), and a PCE of 11.5% (Figure 4f) was achieved and recognized on the NREL Best Research-Cell Efficiencies chart.

6. HIGH-PERFORMANCE TRANSPARENT OPVs

Because of the nature of their molecular orbitals, the absorption spectra of organic semiconductors are not continuous, in contrast to those of traditional inorganic semiconductors, and this feature offers a unique application—transparent OPVs (TOPVs). Especially for narrow-band-gap organic semiconductors, their absorption region is red-shifted, meaning that high absorption occurs in the IR region and relatively low absorption occurs in the visible region, providing great potential for high-performance TOPVs. The schematic structure of TOPVs is shown in Figure 5a.

In 2012, we demonstrated a TOPV based on the donor PBDBT-DPP and the acceptor PCBM. Figure 5b shows the absorption spectra of PBDBT-DPP and PCBM films and the transmission spectrum of the PBDBT-DPP/PCBM blend film. The broad-band-gap polymer donor PBDBT-DPP (Eg of 1.46 eV) shows strong photosensitivity in the range of 650–850 nm, while the absorption region of PCBM is below 400 nm. As a consequence, the PBDBT-DPP/PCBM active layer shows high transmittance in the visible region with a maximum peak of 73% at ~550 nm. To construct TOPV devices, a spray-coated Ag nanowire-based composite, with an average transmittance of ~87% from 400 to 1000 nm and a sheet resistance of ~30 Ω/□, was applied as the transparent back electrode. As a result, TOPV devices with a PCE of 4.0% and an average visible transmittance (AVT) of 61% over the 400–650 nm range were enabled. Figure 5c shows a photograph of the corresponding TOPV device. One year later, TOPV devices with improved performance were developed using the narrower-band-gap polymer donor PBDBT-SeDPP. With no change in the device structure and the acceptor material, the replacement of PBDBT-DPP by PBDBT-SeDPP red-shifts the absorption region of the active layer by 50 nm, resulting in a higher PCE of 4.5%. The AVT of the PBDBT-SeDPP/PCBM TOPV device within the 400–700 nm range is 58%, and the transmission spectrum and a photograph of this device are shown in Figure 5d. Comparison shows that the transmission spectra of the PBDBT-DPP-based and PBDBT-SeDPP-based TOPVs are similar in the visible region. The higher PCE of the PBDBT-SeDPP-based TOPVs is attributed to the enhanced photon utilization efficiency in the IR region. In addition, the PCE of PBDBT-SeDPP-based TOPVs can be further enhanced by employing a tandem-junction structure. A higher PCE of 6.4% with an AVT of 43% over the 400–650 nm range was realized.

In the following years, the rapid development of narrow-band-gap non-fullerene acceptors has significantly promoted the TOPV field. In 2019, we produced high-performance flexible TOPVs based on the polymer donor PTB7-Th (Eg of 1.6 eV) and three different narrow-band-gap non-fullerene acceptors, FOIC (Eg of 1.32 eV), F81C (Eg of 1.27 eV), and IEICO-4F (Eg of 1.24 eV). Constructed on a flexible substrate (poly(ethylene terephthalate)/Ag mesh/PEDOT:PSS PH 1000/ZnO), TOPVs based on these three different active layers exhibited good performance (PCEs of 8.9–10.0% and AVTs of 31–34% within 400–700 nm region). The transmission spectra of the three flexible TOPVs and a photograph of the PTB7-Th/IEICO-4F-based flexible TOPV are shown in Figure 5e, respectively. More importantly, a potential agricultural application of these high-performance flexible TOPVs was demonstrated (Figure 5g), utilizing the visible light for plant growth and the IR light for power generation. For the plant growth, the required transmittance in the visible region (400–700 nm) is typically 10–50%. On the basis of the absorption peaks of chlorophyll a, plants usually require relatively higher transmittance in the region of 400–450 nm and 650–700 nm. In this work, the side-by-side comparison of plant growth is shown in Figure 5h. Mung beans grown under the light filtered by PTB7-Th/IEICO-4F TOPVs and those under normal sunlight give very similar results, indicating that these TOPVs have great potential to be used to equip greenhouses for power generation without influencing the plant growth under them.

7. CONCLUSIONS AND OUTLOOK

In this Account, we first shared our experiences and insights on the design of narrow-band-gap polymer donors and non-fullerene acceptors. Several strategies for constructing these materials were discussed, including enhancing the intra-molecular charge transfer effect and steric hindrance/energy level engineering. In that part, in addition to systematic analyses of the design of narrow-band-gap polymer donors based on BDT/TT or BDT/DP, donors/acceptors based on the new donor moieties DTP or BZPT were discussed as well. Especially, we highlighted our work on the narrow-band-gap acceptor Y1 (based on the new donor moiety BZPT), which pioneered the future development and usage of acceptors belonging to the Y1 family. Subsequently, we analyzed several examples of making certified world record single-junction or tandem-junction OPVs that use these narrow-band-gap donors (PBDBT-TTCE, PBDBT-DPP, PDTP-DDBT) or narrow-band-gap acceptors (Y1). Experiences and insights from a device perspective were shared in terms of donor/acceptor selection, energy level alignment management, film morphology control, current matching of subcells, interconnecting layer construction, interface engineering, and device geometry selection. In that part, the construction of high-performance ternary-blend OPVs and transparent OPVs based on these narrow-band-gap donors/acceptors was also discussed.

In order to push the field into the 20–25% high-efficiency era in the next few years, some suggestions for the further development of narrow-band-gap donors/acceptors and related device technologies are proposed: (1) New donor/acceptor moieties with strong electron-donating/electron-withdrawing abilities to further narrow the band gaps of polymer donors and non-fullerene acceptors to 1.1 eV (to better match the AM 1.5 G solar spectrum) should be designed. For instance, heteroatoms could be inserted onto the aromatic rings to form new donor/acceptor moieties. (2) Donor/acceptor moieties with strong luminescence should be incorporated, which may reduce the nonradiative recombination in the corresponding devices. (3) Machine learning methods can be used to discover combinations of donor and acceptor moieties to construct new narrow-band-gap materials. (4) The intermolecular packing can be enhanced to further broaden the film absorption region. A planar and rigid molecular backbone can help the intermolecular packing. Moreover, new strategies from a device perspective (beyond the methods of annealing and solvent additives) to...
enhance the intermolecular packing are desired. (5) The basic optoelectronic properties of new narrow-band-gap donors/acceptors should be studied to figure out the exciton generation and dissociation mechanisms of the new materials, especially in the aspect of the band structure (molecular orbitals) when the band gap is ultranarrow and the electron delocalization is effective as a result of the large π conjugation. (6) The donor/acceptor energy level alignment must be managed carefully to further reduce the radiative recombination related to the donor/acceptor charge transfer state. (7) New strategies to control the film morphology of narrow-band-gap non-fullerene acceptor-based active layers should be developed since the well-used morphology control strategies were developed for polymer/PCBM blends. New ideas may be generated by taking advantage of heteroatoms (e.g., fluorine, chlorine, etc.) or functional groups (e.g., cyano) on the non-fullerene acceptors. (8) Suitable electron-transport layers for narrow-band-gap non-fullerene acceptors, which usually exhibit downshifted LUMO energy levels compared with PCBM, should be explored. In addition, some (weak) chemical interactions can be formed between the heteroatoms or cyano groups on non-fullerene acceptors and the electron-transport layer. (9) Triple (or more)-junction tandem OPVs could be constructed to further enhance the photon utilization and reduce the thermalization loss. (10) New strategies, in both the active layer and device optical structure (e.g., photonic crystals) should be developed to further improve the performance (both PCE and AVT) of transparent OPVs and explore various applications.

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#### Author Contributions

Both authors contributed to the manuscript and approved the final version of the manuscript.

#### Notes

The authors declare no competing financial interest.

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