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# Challenges and recent advances in photodiodes-based organic photodetectors

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Organic photodetectors (OPDs) have drawn extensive research efforts due to their tailorable spectral response, ease of processing, compatibility with flexible devices and cooling-free operations. In this review, we outline the promising strategies for constructing high-performance and highly stable photodiodes-based OPDs from the perspectives of molecular engineering, morphology control, and device structure design. Firstly, the impact of molecular design and morphology control on OPD performance is clearly underlined and the molecular design rules and quantitative analysis methods are presented for high-performance OPDs. Subsequently, some striking device designs for multifunctional applications are discussed to elucidate the corresponding mechanism for various responses. What follows are the research efforts of boosting OPD stability for commercial applications. This review not only presents the detailed discussion on various OPD strategies aiming at simultaneously enhancing performance and stability but also provides some insights for the remaining challenges to make further breakthrough of OPDs.

Keywords: Organic photodetectors; Molecular engineering; Morphology control; Novel device design; Device stability

## Introduction

Photodetector (PD) has become one of the vital technologies in modern life with wide applications, including image sensing, optical communication and health/environmental monitoring. To date, inorganic PDs still lead the market due to their mature fabrication technology and stable performance in terms of desirable sensitivity, responsivity/external quantum efficiency (EQE), detectivity and fast response speed, owing to their high mobility and small exciton binding energy [1–3]. However, there are inevitable drawbacks for inorganic PDs such as complex process-

As promising alternatives, organic photodetectors (OPDs) can address these issues due to their tailorable spectral response, ease of processing, compatibility with flexible devices and coolingfree operation [7–11]. OPDs can achieve spectral selective response via the modulation of organic semiconductor materials and device structure, rather than with optical filters, which can simplify OPD structures and advance commercial applications [12–16]. Moreover, flexible and cooling-free OPDs have great application potential in wearable electronics for real-time health monitoring and electronic eyes, *etc.* [17–22]. With these benefits, OPDs have drawn extensive research efforts and progressed

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ing and high brittleness. These undesirable properties place some restrictions on the applications of inorganic PDs [4-6].

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greatly in the past decade [23,24]. However, the intrinsic properties of organic semiconductors, including low carrier mobility, high exciton binding energy and disordered molecular alignment, still limit the OPD performance with their inorganic PD counterparts. To address such issues, many strategies have been developed to improve the OPD performance with different structures in many prior reports [25–31].

OPDs can be classified into photoconductors-based OPDs (PCphototransistors-based OPDs), OPDs (PT-OPDs) and photodiodes-based OPDs (PD-OPDs) [24,32,33]. Generally, PC-OPDs are based on the photoconductive phenomenon. Such a device shows large resistance in the dark condition and exhibits conductive behavior under illumination (the corresponding structures are plotted in Fig. 1. PC-OPDs can achieve high responsivity/EQE via multiple carrier recirculation, with a low response speed and high dark current density. As a comparison, PT-OPDs generally have three electrodes, including the source, drain, and gate electrodes, where the channel resistance between the source and drain electrodes can be tuned via the gate electrode, i.e., the photoconductive gain modulated by the additional bias (Fig. 1). Thus, PT-OPDs can simultaneously achieve high performance, including high responsivity, detectivity and response speed. Nevertheless, PT-OPDs still suffer from high dark current density, mainly due to the relatively high bias in operation. Therefore, a balance needs to be weighed in the device design process between the responsivity/EQE and response speed against the dark current density.

Moreover, PD-OPDs have a device structure similar to that of organic solar cells (OSCs), which attach the active layer between the two asymmetrical electrodes (Fig. 1). The active layer absorbs photons and generate excitons, which subsequently diffuse to the donor: acceptor interface. Then, generated excitons dissociate into free charge carriers via the built-in voltage/extra reverse bias. Finally, the free charge carriers are collected by the corresponding electrodes. Based on the above mechanism, PD-OPDs can derive low dark current density and high response speed, but low responsivity/EQE rate due to the intrinsic restrictions of PD structure [24,32,33]. Nevertheless, the responsivity/ EQE limit of PD-OPDs can be broken by introducing the photomultiplication effect due to the trap-assisted charge tunneling injection in the interface [34-39]. With these benefits, PD-OPDs can achieve high performance with a striking detectivity over 10<sup>14</sup> Jones [40,41]. Therefore, the promising PD-OPDs (PD-OPDs are simplified into OPDs for the following content) are



#### **FIGURE 1**

OPD structures and schematic illustration of this review. There exist three kinds of OPDs, including photoconductors-based OPDs, phototransistors-based OPDs and photodiodes-based OPDs. The structure illustration of three OPDs is shown in the top of the figure. Additionally, the review mainly discusses various strategies from four parts, *i.e.*, molecular engineering, morphology control, device structure design and device stability. Among them, molecular engineering section mainly includes donor design, nonfullerene acceptor design and polymer acceptor design. Morphology control section mainly includes morphology for low-bias OPDs, morphology for photomultiplication-type OPDs and miscibility for high-performance OPDs. The section of device structure design mainly includes structure for color-selective OPDs and tandem structure for multifunctional OPDs. Device stability includes stability with fullerene acceptors.

highlighted here due to the desirable device performance in prior reports.

In this review, we firstly summarized the recent advances of critical OPD metrics, including the detectivity, dark current density, linear dynamic range (LDR) and response speed. Subsequently, the molecular design strategies for the performance improvement of OPDs are discussed in detail and the corresponding design rules of donors, nonfullerene acceptors and polymer acceptors are provided. Moreover, we discuss the morphological control of OPDs with low bias and photomultiplication, and then introduce a quantitative analysis method to provide a better understanding of OPD morphology control. Afterwards, some striking device structure designs for multifunctional applications are further discussed to elucidate the corresponding mechanism for color selectivity, narrowband response, photomultiplication response, two-terminal response, dual-wavelength response and dual-mode response. More importantly, we overviewed the research efforts of OPD stability for commercial applications and highlighted the great potential of achieving highly stable OPD with nonfullerene acceptors.

# Working principles and performance metrics

## Working principles

The working principle of OPDs is similar to that of OSCs [24,33]. Firstly, organic semiconductor layers absorb the incident photon energy and produce excitons *i.e.*, bounded electron-hole pairs. Then, these excitons diffuse to the donor–acceptor interface and turn to the lower energy state (charge transport state). Subsequently, these excitons dissociate into free carriers (electrons and holes) via the built-in potential or the extra reverse bias and the electrons and holes transport through the organic semiconductors toward the electron/hole transport layers, respectively. Finally, the free charges are collected by the cathode and the anode. For photomultiplication-type OPDs, the working principle is similar and the main difference is that they generally employ the extremely few acceptors/donors (~1%) to trap electrons/holes and induce the secondary charge injection with the help of reverse bias.

In summary, the working principle of OPDs generally include exciton production and dissociation, carrier transport and extraction. Therefore, we discuss the various strategies to advance OPD performance from molecular engineering, morphology control and device design. For molecular engineering, we mainly focus on the reasonable donor and acceptor design to broad the detection range and accelerate the exciton dissociation of OPDs via the suitable highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) offsets. Furthermore, it is essential to develop the favorable morphology to advance carrier transport and extraction for high-performance OPDs. For instance, OPDs with low bias generally require the suitable miscibility of the donor: acceptor (D: A) blend to achieve the favorable phase separation. Instead, photomultiplication-type OPDs generally require significantly higher miscibility, which can enhance the D: A interfacial area. Additionally, device design not only has great impact on OPD performance, but also can realize some special OPDs via carrier extraction, e.g., colorselective OPDs and multifunctional OPDs.

## Performance metrics

The key performance metrics of OPDs include dark current density, external quantum efficiency (EQE)/spectral responsivity, noise equivalent power/specific detectivity, LDR and response speed.

- (1) **Dark current density**  $(J_{dark})$ : It is defined as the current flowing through the OPDs under an applied reverse bias in the dark. Dark current density has a negative impact on the OPD performance, including sensitivity, linear dynamic range and specific detectivity, *etc.* Therefore, a large number of strategies have been developed to reduce  $J_{dark}$  for high-performance OPDs.
- (2) **External quantum efficiency (EQE)/spectral responsivity**: EQE is described as the ratio of the number of charge carriers collected to the number of incident photons [42]. It can be expressed as

$$EQE = (J_{ph}/L_{in}) \times (hc/q\lambda)$$
<sup>(1)</sup>

where  $J_{ph}$  is the photocurrent density,  $L_{in}$  is incident light intensity, c is light speed, h is Planck's constant, q is the elementary charge and  $\lambda$  is the corresponding wavelength.

Spectral responsivity (R) is defined as the ratio of photocurrent generated to the incident light intensity, which can be expressed as

$$R = J_{ph}/L_{in} = EQE \times \frac{q\lambda}{hc}$$
(2)

## (3) Noise current/Noise equivalent power (NEP)/ specific detectivity:

Typically, noise current  $(i_{noise})$  is distinguished into three parts including 1/f noise, thermal noise and shot noise.1/f noise (flicker noise) is frequency dependent and is mostly dominant for low frequencies, thermal and shot noise are frequency independent and scale with the device shunt resistance and dark current density, respectively. Moreover, shot noise caused by dark current density was considered as the main noise in the OPDs operated under the external bias.

NEP stands for the power of the light signal that generates a signal-to-noise (S/N) ratio of unity and it can be given by

$$NEP = \frac{i_{noise}}{R\sqrt{B}}$$
(3)

where *B* is the normalized detection bandwidth. It is accepted that experimental measurements of  $i_{noise}$  are challenging and not always performed. For sake of simplicity, the shot noise from dark current density is often used to assume the dominant contribution to  $i_{noise}$ . Therefore, specific detectivity (*D*\*) is obtained by normalizing the NEP to the OPD area and it can be expressed as

$$D^* = \frac{\sqrt{A}}{NEP} \cong \frac{R}{\sqrt{2qJ_{dark}}} \tag{4}$$

Under this assumption, Eq. (4) indicates that  $J_{dark}$  is dominated by shot noise which places restrictions on  $D^*$ , while 1/f noise and thermal noise are ignored. It is worth noting that the assumption can overestimate specific detectivity and the general use of Eq. (4) is thus questionable. Nevertheless, Eq. (4) is widely used in a lot of OPD reports and thus provides a fair comparison

between the reported OPD performances. Therefore, we employ this assumption to discuss the specific detectivity of OPDs in this review.

(4) **Linear dynamic range (LDR):** it describes the response range, where photocurrent  $(I_{ph})$  is linearly proportional to the incident light intensity  $(L_{in})$ . It can be given by

$$LDR = 20\log\left[\frac{J_{ph}(max)}{J_{ph}(min)}\right]$$
(5)

(5) **Response speed:** it can be expressed by two metrics, frequency response with the cutoff frequency reduced by -3 dB ( $f_{-3dB}$ ) and response time with the rise time for response from 10% to 90% or decay time as that from 90% to 10%.

As summarized in Fig. 2a, most of OPDs still have high  $J_{dark}$ , which is even six orders of magnitude higher than that of silicon PDs. Only a few OPDs can achieve superior dark current density lower than that of silicon PDs [43]. For specific detectivity, some reported OPDs can achieve high detectivity close to or even over that of silicon and InGaAs PDs [44,45]. However, most OPDs still suffer from the low detectivity with a value below  $10^{12}$  Jones, especially for the OPDs working at the near-infrared band (Fig. 2b). Additionally, most OPDs can achieve high linear dynamic range (LDR) over 100 dB and some can even exceed that of silicon and InGaAs PDs (Fig. 2c) [44,45]. Last but not least,

most OPDs achieve a low cutoff frequency below 100 kHz and none can achieve a lower response time than that of commercial silicon PDs (blue star in Fig. 2d) [43].According to the above discussion, we take the view that despite these promising advances, there remains great room for OPD performance improvement for their commercial applications. Thus, it is exceedingly essential to presents a timely and critical review of the recent advances and promising strategies for high-performance OPDs.

## Molecular engineering

In this section, we summarize the main donor materials and the corresponding design guidelines for high-performance OPDs. Subsequently, we outline the great advantages of nonfullerene acceptor materials over the conventional fullerene derivatives and discuss the design of nonfullerene acceptors in depth. Finally, we proceed to offer more details of the polymer acceptor design for all-polymer OPDs and highlight their great potential for commercial applications.

## Donor design

To develop high-performance OPDs, continuous efforts have been devoted to the design of donor materials. Here, we first summarize the recent advances in donor design in the OPD field. It is worth noting that we mainly focus on the most used conjugated polymers and the corresponding chemical structures are shown in Fig. 3.



#### FIGURE 2

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Recent advances of PD-OPDs including dark current density, detectivity, LDR and response speed. (a) Dark current density, (b) detectivity, (c) LDR and (d) response speed as a function of wavelength, as compared to silicon PDs and InGaAs PD [43–45]. Note that dark current density and detectivity are the peak value at the corresponding wavelength in (a and b). Silicon PD1 and Silicon PD2 are OSI UV enhanced Si photodiode (OSD35-7Q) and Hamamatsu Si photodiode for photometry (S1336-44BQ) from Ref. [44], while Silicon PD3 is from Ref. [45] Additionally, the LDRs of the two silicon PDs and InGaAs PD are 160 dB, 120 dB and 66 dB, respectively in Fig. 2c. Moreover, response time is used to character the response speed of silicon PD. We screen 35 recent OPD reports shown in Table 1.

Due to low cost and high scalability, poly(3-hexylthiophene) (P3HT) is the most widely-used donor material for OPDs with a high potential for commercialization [35,38,76–78]. Park et al. [10] employed extrusion-based 3D printing to produce the organic photodetector with the blend of P3HT and [6,6]- phenyl C<sub>61</sub>-butyric acid methyl ester (PC<sub>61</sub>BM). The developed OPD can achieve a high EQE of 25.3% and a high specific detectivity of ~8 × 10<sup>11</sup> Jones at a reverse bias of -1 V ( $\lambda = 510 \text{ nm}$ ). Recently, Fuentes-Hernandez et al. [43] reported a large-area and flexible OPD with high performance, which can rival silicon photodiodes. They used the blend of P3HT and indene-C<sub>60</sub> bis-adduct

(ICBA) as the photoactive layer, which can enable a high detectivity of ~2 × 10<sup>12</sup> Jones and a low  $J_{dark}$  of ~10<sup>-10</sup> A/cm<sup>2</sup> (-1.5 V and 600 nm). Impressively, the 1-cm<sup>2</sup> ring-shaped OPD can yield photoplethysmography (PPG) signals closed to that of silicon photodiodes with an area of 0.07 cm<sup>2</sup>. More strikingly, P3HT has great application potential in OPDs with photomultiplication, due to the high-lying LUMO energy level, which can effectively reduce the  $J_{dark}$  via preventing electron tunneling [39,54,79–83]. Wu et al. [40] reported a highly responsive OPD for image sensors with the blend of P3HT and PC<sub>61</sub>BM (100:1). The developed OPD can achieve an extremely high responsivity



## FIGURE 3

Chemical structures of some representative donors in this review.

of ~42 A/W at 450 nm and a low  $J_{dark}$  of 2.53 × 10<sup>-7</sup> A/cm<sup>2</sup>, resulting in a significantly high detectivity of 1.48 × 10<sup>14</sup> Jones at a reverse bias of -20 V.

Despite these great achievements, P3HT still suffers from pronounced limitations, including the large bandgap (~2 eV), the high-lying HOMO energy level and the relatively low hole mobility [84,85]. More specifically, the large bandgap leads to the small absorption spectra (up to ~600 nm) of the OPDs paired with fullerene derivatives [47,82]. The high-lying HOMO energy level is not enough to hold back hole tunneling, thus leading to the high J<sub>dark</sub> for the OPDs working at low reverse bias. Additionally, the low hole mobility places great restrictions on carrier transport, resulting in the low EQE and responsivity of P3HTbased OPDs [81,82]. To address these issues, one can finely tune the structure of P3HT via molecular engineering. For instance, fluorination strategy can be used to deepen the HOMO energy level of P3HT. Moreover, we can simultaneously reduce the bandgap and improve the hole mobility of P3HT via introducing the proper electron acceptor units, e.g., diketopyrrolopyrrole (DPP). However, few research efforts so far have been devoted to the structure modification of polythiophene and its derivatives in the OPD field. The detailed strategies of polythiophene modification can refer to our recent reports on polythiophenebased solar cells [84,85].

Besides the polythiophene-based materials, many other donor-acceptor (D-A) conjugated polymers have been used for high-performance OPDs, including benzo[1,2-b:4,5-b']dithio phene (BDT)-based polymers [89,90], [1,2,5]thiadiazolo[3,4-g]qui noxaline (TQ)-based polymers [73,91] and DPP-based polymers [71,92], etc. Here, we discuss the impact of polymer structure modification on OPD performance in detail, mainly including D-unit tuning, A-unit tuning and side chain tuning. As discussed above, DPP unit has great potential in broadening absorption spectra and improving hole mobility. Nevertheless, different Dunits still play a great role in the performance of OPDs. Simone et al. [86] investigated the origin of dark current in OPDs with different donor polymers paired with  $PC_{61}BM$  (Fig. 4a–c). They found that even with the same A-unit, different donor polymers still achieve the significantly different  $J_{dark}$  with a difference of about three orders of magnitude. The great difference can be attributed to the distinct open-circuit voltage (under AM 1.5G solar radiation), which mainly depends on the difference between donor HOMO and acceptor LUMO energy levels. More specifically, it is accepted that the open-circuit voltage of photovoltaic devices is known to vary linearly with the difference between the acceptor LUMO and donor HOMO, here the slope of the linear fit reaches ~1. Moreover, the origin of  $J_{dark}$  can be attributed to the dark current thermal activation energy. With the increase of thermal activation energy, the  $J_{dark}$  gradually reduces and the activation energy of  $J_{dark}$  is very similar for the above OPDs (~0.25 ± 0.03 eV). (Fig. 4b and c). Similarly, the Dtuning reports on TQ-based polymers by Gielen et al. [28] and Verstraeten et al. [73] also present evidence on the relevance between J<sub>dark</sub> and donor HOMO energy level. Additionally, the reports on the D-tuning of donor polymers by Han et al. [75], Verstraeten et al. [73] and Eom et al. [93] revealed that the great drop of J<sub>dark</sub> and the improving responsivity can be ascribed to

the different molecular ordering and orientation induced by D-tuning strategy.

The A-unit tuning can also affect the performance of OPDs. BDT unit has been widely used in designing  $\pi$ -conjugated polymers for high-performance optoelectronic devices. Zhang et al. [87] explored the performance of BDT-based OPDs via introducing the A-units of Thieno[3,4-c]pyrrole-4,6-dione (TPD) and DPP (Fig. 4d-f). DPP unit can broaden the light- absorption to ~850 nm, but the corresponding polymers (PBD(EDOT) and PBD(TH)) have the relatively high-lying HOMO energy level, leading to slightly higher  $J_{dark}$ , compared with that of the polymers with TPD unit (PBT(EDOT) and PBT(TH)). More strikingly, the authors further introduced 3,4-ethylenedioxythiophene (EDOT) side chain conjugated to the polymer backbone and the corresponding OPD can achieve an exceedingly low  $J_{dark}$  of  $\sim$ 5.9  $\times$  10<sup>-9</sup> A/cm<sup>2</sup> at -2 V, more than three orders of magnitude lower than that with thiophene side chain. The great  $J_{dark}$  difference can be attributed to the distinct surface energies between the EDOT-polymer and TH-polymer. EDOT unit can interact with PEDOT: PSS layer, resulting in the favorable vertical phase separation, thus effectively blocking the electron injection from the anode (Fig. 4f). Moreover, other A-tuning reports based on exocyclic olefin substituted cyclopentadithiophene (CPDT) [69] and carbazole (PC) [94] units also demonstrated the great impact of A-unit tuning on the J<sub>dark</sub>, responsivity and response speed of OPDs.

The side-chain tuning of donor polymers is another effective strategy to improve the overall performance of OPDs (Fig. 4g). Side-chain tuning can not only modify the energy level but also can tune the aggregation of donor polymers, when paired with acceptor materials. Yoon et al. [88] employed sp<sup>2</sup>-hybridized olefinic bis(alkylsulfanyl)-methylene side chains (strong electronwithdrawing) to replace alkyl side chains, thus broadening the light-absorption of the corresponding OPDs. The modified polymer showed a typical face-on orientation and significantly lower paracrystalline disorder, which can substantially reduce charge trapping sites and accelerate charge transport. Thus, the modified polymer can achieve markedly lower J<sub>dark</sub>, much higher photocurrent (responsivity) and detectivity, compared with that of the counterpart (Fig. 4h and i). Additionally, Ko et al. [60] reported that long alkyl side chain may have a negative effect on the molecular orientation of donor polymers. Thus, the polymer with the long alkyl side chain (BDT-Th-3AT) can achieve a detectivity of ~7  $\times$  10  $^{12}$  Jones, much lower than that of the counterpart. Other strong electron-withdrawing side chains, e.g., alkoxy side chain, alkylthio side chain, and halogen atom (F and Cl), also have the similar effect on the optical and electrical properties of donor polymers. We can draw a lot of design insights from the well-developed OSCs [95,96].

On the basis of the above discussion, we further summarize the design guidelines of donor polymers for high-performance OPDs, generally including: (a) Broad absorption spectra, up to 2000 nm for the effective function of PPG, *etc.* (b) Low-lying HOMO energy level, thus effectively blocking the hole injection from the cathode and reducing the corresponding dark current density. (c) Appropriate molecular ordering and orientation, which can enhance hole mobility, accelerate carrier transport and significantly improve the EQE and responsivity of OPDs.

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FIGURE 4

Donor design for high-performance OPDs. (a-c) D-unit tuning, (d-f) A-unit tuning, (g-i) side chain tuning of donors and the corresponding OPD performance. (b and c) Reproduced with permission from Ref. [86]. Copyright 2020, Wiley. (e and f) Reproduced with permission from Ref. [87]. Copyright 2015, Wiley. (h and i) Reproduced with permission from Ref. [88]. Copyright 2019, American Chemical Society.

(d) Special functional unit, which can induce favorable vertical phase separation, substantially reducing the dark current density. Although, the existing donors for OPDs have the absorption cutoff of ~1600 nm [75], the OPD detectivity can only reach ~10<sup>10</sup> Jones. The low OPD performance may be attributed to low spectral responsivity and high  $J_{dark}$ . We can introduce some special functional unit to enable the appropriate molecular ordering and orientation to enhance the performance of infrared OPDs. Due to the limited research on the donor polymer design in the OPD field, we can draw lessons from the design strategies for OSCs. Li group and Hou group recently summarized the various design strategies of donor polymers for the solar cells with bulk heterojunction, which can provide a reference for the community [96,97].

## Nonfullerene acceptor design

Since Zhan group [98] and Zou group [99] reported the star nonfullerene acceptors, 3,9-bis(2-methylene-(3-(1,1-dicyanomethy lene)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3

-d:2',3'-d']-s-indaceno[1,2-b:5,6-b']dithiophene (ITIC) and 2,2'-(( 2Z,2'Z)-((12,13-bis(2-ethylhexyl)-3,9-diundecyl-12,13-dihydro-[1 ,2,5]thiadiazolo[3,4-e]thieno[2",3":4',5']thieno[2',3':4,5]pyrrolo[ 3,2-g]thieno[2',3':4,5]thieno[3,2-b]indole-2,10-diyl)bis(methany lylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diyli dene))dimalononitrile (Y6), the great optical and electrical properties of nonfullerene acceptors have enabled the power conversion efficiency (PCE) of above 18% for OSCs. It is not surprising that applying nonfullerene acceptors also becomes a research hotspot in the OPD field. Here, we first outline the great advantages of nonfullerene acceptors over the fullerene acceptors for high-performance OPDs. Subsequently, we discuss various design strategies of nonfullerene acceptor in detail and the corresponding OPD performance and the corresponding chemical structures are shown in Fig. 5. Meanwhile, we also provide the design guidelines of nonfullerene acceptors for highperformance OPDs.

Fullerene and its derivatives have been widely used in the OPD field, due to the high electron mobility, high-lying LUMO

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energy level and isotropic molecular ordering and orientation [37,100–103]. Nevertheless, fullerene acceptors have a lot of disadvantages, including low light-absorption coefficient and range, difficult molecular structure tuning and relatively poor stability, *etc.* [49,104,105]. These notorious disadvantages have severely limited the commercialization of OPDs, especially for the applications at infrared bands (PPG, *etc.*). Instead, versatile non-fullerene acceptors with high light-absorption coefficient have tunable absorption range, energy level and molecular packing [36,106–110]. Most strikingly, nonfullerene acceptors generally have significantly better stability in bulk heterojunction over that of fullerene and its derivatives. For instance, Jang et al. [49] recently compared the performance difference between the OPDs with the nonfullerene acceptor, ethylhexyl-rhodanine-ben zothiadiazole-coupled indacenodith-iophene (EH-IDTBR) and widely used fullerene acceptor, [6,6]-phenyl C71 butyric acid methyl ester (PC<sub>71</sub>BM). The working diagrams of the OPDs with the two acceptors are plotted in Fig. 6a. Evidently, the OPD with eh-IDTBR markedly outperformed that with PC<sub>71</sub>BM, due to the significantly lower  $J_{dark}$  (Fig. 6a and b). This can be mainly attributed to the high-lying LUMO energy level of eh-IDTBR acceptor, which can effectively block the electron injection from the



## FIGURE 5

Chemical structures of some representative nonfullerene acceptors, polymer acceptors and fullerene acceptors used in OPDs.

anode (Fig. 6a). Thus, the OPDs with eh-IDTBR acceptor can achieve substantially higher detectivity over that with PC71BM acceptor covering the whole band of 400-700 nm (Fig. 6c). Additionally, Wu et al. [105] recently reported that the OPDs with the widely used ITIC derivatives can achieve significantly higher performance over the OPDs with PCBM acceptors, mainly due to the substantially lower J<sub>dark</sub> (Fig. 6d-f). Nevertheless, the LUMO energy level of PCBM acceptors is slightly shallower than that of the nonfullerene counterparts, which theoretically leads to higher J<sub>dark</sub> for the OPD with nonfullerene acceptors, as discussed above. The opposite results can be ascribed to the sharp drop off in the distribution of bandtail states for nonfullerene acceptors, i.e., the lower disorder (Fig. 6d and e). Thus, nonfullerene acceptors have higher thermal barriers, which can enable much higher shunt resistance and reduce thermal noise. These two reports provide conclusive evidence that tunable nonfullerene acceptors hold great potential for high-performance OPDs over the fullerene counterpart.

OPDs with nonfullerene acceptors have gradually become one of the hotspots in the OPD field. Here, we discuss the performance of OPDs with nonfullerene acceptors via structure modification. For most of the widely used nonfullerene acceptors, the chemical structure mainly includes central unit, end group and side chain, *e.g.*, A-D-A structure (ITIC and its derivatives, *etc.*) and A-D-A-D-A structure *e.g.*, Y6. First of all, the central unit tuning strategy is discussed of nonfullerene acceptors for highperformance OPDs (Fig. 7a). Bristow et al. [91] recently explored the OPD performance with two nonfullerene acceptors via tun-

ing the central unit. O-IDTBR with indacenodithiophene electron-donating core can greatly reduce the bandgap, thus broadening the corresponding absorption spectra. Nevertheless, (5Z,5'Z)-5,5'-((7,7'-(4,4,9,9-tetraoctyl-4,9-dihydro-s-indaceno [1,2-b:5,6-b']dithiophene-2,7-divl)bis(benzo[c][1,2,5]thiadiazole-7,4-divl))bis(methanylylidene))bis(3-ethyl-2-thioxothiazolidin-4 -one) (O-IDTBR) has significantly low-lying LUMO energy level and high-lying HOMO energy level, as compared with O-FBR with fluorene core. Consequently, the OPD with O-IDTBR acceptor exhibited inferior performance with a higher J<sub>dark</sub> and a markedly lower photocurrent, resulting in a significantly lower detectivity (Fig. 7b and c). Except for  $J_{dark}$ , carrier extraction also plays a critical role in OPD performance. Wen et al. [111] recently developed three nonfullerene acceptors with dithiophene core except for the varied central heteroatoms. Despite of the similar energy level, OPDs with the nonfullerene acceptors of carbon central heteroatom can achieve a substantially higher detectivity over that of the other two nonfullerene acceptors. This can be attributed to the distinct carrier extraction caused by different molecular packing of the three nonfullerene acceptors, thus leading to distinct mobility.

The end group tuning is another effective strategy to modify the optical and electrical properties of nonfullerene acceptors via the intramolecular charge transfer (Fig. 7d). For instance, fluorination of end group can markedly broaden absorption spectra and lower energy level, due to the strong electron-withdrawing. Moreover, fluorination also has a profound impact on the molecular ordering and orientation via non-covalent interactions, *e.g.*,



#### FIGURE 6

OPD performance differences with fullerene and nonfullerene acceptors. (a–c) Different OPD performance from (a–c) distinct energy levels and (d–f) bandtail disorder. (a–c) Reproduced with permission from Ref. [49]. Copyright 2020, Wiley. (d–f) Reproduced with permission from Ref. [105]. Copyright 2020, Springer Nature.



#### FIGURE 7

Acceptor design for high-performance OPDs. (a–c) Central unit tuning, (d-f) end group tuning, (g and h) side chain tuning of donors and the corresponding OPD performance. (b and c) Reproduced with permission from Ref. [91]. Copyright 2020, American Chemical Society. (e and f) Reproduced with permission from Ref. [90]. Copyright 2021, The Royal Society of Chemistry. (h) Reproduced with permission from Ref. [112]. Copyright 2019, The Royal Society of Chemistry.

 $F \cdots H$ ,  $F \cdots S$ , and  $F \cdots \pi$ , thus enhancing electron mobility. Recent work by Babics et al. [90] provided direct evidence for the great impact of end group tuning on OPD performance. The authors developed two nonfullerene acceptors with and without the fluorinated end group, i.e., O4TIC and O4TFIC. As clearly demonstrated in Fig. 7e, fluorination of the end group significantly lowers both HOMO and LUMO energy levels, which will increase the J<sub>dark</sub> of the corresponding OPDs theoretically. Nevertheless, the OPDs with the two nonfullerene acceptors performed equally well in the suppression of dark current density (Fig. 7f). This may be attributed to the lower disorder caused by the enhanced rigid and planar structure. More strikingly, the OPD with O4TFIC acceptors can achieve a pronouncedly high responsivity of ~0.5 A/W at 890 nm without applying voltage bias, about three times higher than its counterpart. The main reason is that noncovalent interactions enhance the intermolecular packing and crystallinity, thus improving carrier transport (higher mobility). More broadly, other strong electron-withdrawing end units (chlorine and bromine atom) may also have a similar impact on OPD performance. Nevertheless, nearly no research efforts have been devoted to the promising strategies of end group tuning.

Additionally, side chain also impacts the OPD performance. In brief, side chain tuning can not only engineer the energy level of nonfullerene acceptors, but also can control the molecular packing via intermolecular interaction, *e.g.*, non-covalent confor-

mation lock, etc. (Fig. 7g). For instance, Lv et al. [112] recently designed three nonfullerene acceptors, CIDT-BC with alkyl side chains, CIDT-BOC and IDT-BOC with alkoxyl side chains. These three nonfullerene acceptors have a similar energy level but completely distinct morphology, when paired with P3HT donor (Fig. 7h). The corresponding OPDs with alkoxyl side chains significantly outperformed the counterpart in the critical figure of merits, e.g., responsivity and detectivity. This can be mainly ascribed to the more rigid and planar structure of the nonfullerene acceptors with the  $S \cdots O$  interactions, thus resulting in substantially higher exciton dissociation and electron mobility. Additionally, recent work by Lee et al. [89] provided complementary insight into the mechanism of side chain tuning. The authors designed three isostructural nonfullerene acceptors with different side chains on thiophene spacers. The HOMO energy levels of acceptors have a pronounced shift toward that of the donor, with the increase of the alkoxyl side chains on thiophene spacers, resulting in significantly lower responsivity and detectivity.

A general design rule of nonfullerene acceptors for highperformance OPDs can be established: (a) Broad absorption spectra via various strategies, but still having enough HOMO energy level offset to enable efficient exciton dissociation. (b) High-lying LUMO energy level, thus effectively blocking the electron injection from the anode and reducing the dark current density. (c) Appropriate molecular ordering and orientation, enabling the optimal crystallinity when paired with polymer donors (enhance mobility and accelerate carrier transport). (d) enhanced rigid and planar structure, which can reduce structure disorder and enhance crystallinity, ultimately leading to higher detectivity. Additionally, Zhan et al. [113] Hou et al. [114], Yan et al. [115], Chen et al. [116], Zou et al. [117] recently summarized the various design strategies of nonfullerene acceptors for OSCs. These insights into the nonfullerene acceptor design may help make great progress in the OPD field. Nevertheless, the acceptors only have the absorption cutoff reaching ~900 nm, which may place some restrictions on the detection range of infrared OPDs. Additionally, more efforts should be devoted to the challenge that how to achieve the favorable energy level arrangement and preferred morphology control for high-performance OPDs.

## Polymer acceptor design

To fulfill the potential of organic semiconductor materials in terms of flexibility and stretchability, increasing research efforts have been devoted to all-polymer optoelectronic devices. Encouragingly, all-polymer solar cells have recently achieved an unprecedented PCE of ~16%, indicating an extraordinary milestone for the commercial applications of OSCs [118,119]. As compared to the great progress in OSCs, all-polymer OPDs have been less explored, due to the slow development of polymer acceptors. To date, all-polymer OPDs reported are nearly all based on naphthalene diimide (NDI)-based and perylene diimide (PDI)based polymer acceptors [123–128]. For instance, Sen et al. [121] reported an all-polymer OPD with the classical polymer acceptor, P(NDI2OD-T2), also known as poly[[N,N-bis(2-octyldodecyl)-na phthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-(2,2'-bithi ophene)] (N2200). The developed all-polymer OPD can achieve a responsivity of ~0.247 A/W at 560 nm and a  $J_{dark}$  of ~10<sup>-6</sup> A/cm<sup>2</sup> at a low bias of -0.5 V. Remarkably, the all-polymer OPD exhibited great stretchability with the ability to bear large strains of over 60% without fracture, indicating the unparalleled application potential in wearable monitoring devices. Additionally, Xu et al. [53] employed the roll-to-roll compatible lamination method to develop the all-polymer OPD with a detectivity over 10<sup>11</sup> Jones for the first time. Recently, Xia et al. [56] also reported an all-polymer OPD with the NDI-based polymer acceptors (PNDI-T10), via lamination method. The reported all-polymer OPD can achieve an inferior detectivity up to 10<sup>11</sup> Jones at 400-750 nm and a LDR of ~75 dB. Furthermore, Kim et al. [122] reported an all-polymer planar heterojunction OPD for the first time. Donor polymer was successfully stacked on P (NDI2OD-T2) layer using doping-dedoping method and the developed all-polymer OPD achieved a high detectivity of  $1.12 \times 10^{12}$  Jones and low  $J_{dark}$  of  $3.7 \times 10^{-8}$  A/cm<sup>2</sup> at a reverse bias of 1 V.

As evidenced above, all-polymer OPDs with the existing NDIbased and PDI-based polymer acceptors can only achieve inferior performance with a limited detection range up to ~800 nm, compared to that of the OPDs with fullerene/nonfullerene acceptors. To address this gap, one can tune the molecular structure of polymer acceptors via molecular engineering. For instance, Wang et al. [123] reported the all-polymer OPDs with A–A type conjugated polymer acceptors, based on isoindigo and NDI/PDI units. The results indicated that the OPD with PDI-based polymer

acceptors can achieve a significantly higher detectivity over  $10^{12}$  Jones with a markedly lower  $J_{dark}$  of ~7.5 ×  $10^{-8}$  A/cm<sup>2</sup>, compared to those of OPDs with NDI-based polymer acceptors. Moreover, the PDI-based OPD with 2-ethylhexyl side chain can achieve superior performance over that with 2-octyldodecyl side chain, due to the better morphology when paired with the donor polymer. Furthermore, Hu et al. [124] also reported the all-polymer OPDs based on NDI-based polymer acceptors with different side chains. The results indicated that the OPD with 5-decylpentadecyl side chain can achieve a significantly higher detectivity up to 1013 Jones at 300-800 nm and a much lower  $J_{dark}$  of  $\sim 10^{-10}$  A/cm<sup>2</sup> (-0.1 V bias), compared to those of 2-octyldodecyl and phenoxy side chains. This can also be attributed to the better morphology for the blend with 5-decylpentadecyl side chain, which can markedly enhance the balance of electron/hole mobility and reduce dark current density. Although side chain tuning can effectively modify the blend morphology, the slight energy level change still puts great restrictions on the response range of all-polymer OPDs. To address this issue, we can modify the backbone of polymer acceptors via copolymerization with the small bandgap polymers. For instance, Hu et al. [125] designed a series of random copolymers with NDI and DPP units. The absorption spectra had a significant red shift up to ~1100 nm with the introduction of DPP units. Impressively, the best all-polymer OPD with 10% DPP units can achieve a specific detectivity over 10<sup>12</sup> Jones in a broad spectral region of 340-960 nm (-0.1 V bias).

We proceed to discuss the general design rules of polymer acceptors, which is roughly consistent with that of nonfullerene acceptors for high-performance OPDs. Here, we mainly discuss the appropriate molecular ordering and orientation to achieve optimal crystallinity when paired with polymer donors. Since 2007-2009, some researchers have designed the NDI/PDI-based polymer acceptors with high electron mobility up to  $\sim 10^{-3}$  cm<sup>2</sup>  $V^{-1}$  s<sup>-1</sup> in SCLC devices [126,127]. However, all-polymer OSCs only achieved a low PCE of 1-2%, due to the large phaseseparated domain structure (high crystallinity). Thus, it can be inferred that inappropriate crystallinity is the main reason for the low performance of all-polymer OPDs for the existing NDI/ PDI-based polymer acceptors. Thus, we can introduce the highly miscible groups with the given donor polymers, when designing polymer acceptors. Lee et al. [128] and Wang et al. [129] recently summarized the guide rules of polymer acceptors, which can provide useful insights for the community. Additionally, with the rise of Y-series nonfullerene acceptors, the corresponding polymer acceptors with Y-units have enabled all-polymer OSCs to achieve the record PCE over 17% [118]. Nevertheless, the performance of OPDs with Y-based polymer acceptors has not been explored, which may be the next success for all-polymer OPDs. Nevertheless, the polymer acceptors also have the absorption cutoff of ~900 nm, which should be broadened for infrared OPD applications. Moreover, we provide a summary of the performance of representative OPDs with molecular engineering in Table 2.

As discussed above, there exist a lot of similarities in molecular design for high-performance OSCs and OPDs. For instance, the donors and acceptors for high-performance OPDs generally need appropriate molecular ordering and orientation, enabling the optimal crystallinity. Moreover, the blends for both devices require favorable energy level arrangement to realize fast exciton dissociation, carrier transport and extraction. Contrary to OSCs, OPD performance is significantly dependent on  $J_{dark}$ , while is generally not sensitive to open circuit voltage. Therefore, the design guidelines of donors and acceptors for high-performance OPDs are slightly different from those of OSCs, *e.g.*, the low-lying HOMO energy level of donors and the high-lying LUMO energy level of acceptors. Additionally, infrared OPDs generally require the broad absorption ranges of donors and acceptors, while the absorption cutoff for OSCs only reaches ~1000 nm.

## **Morphology control**

Morphology control has a great impact on the performance of OPDs, mainly including responsivity/EQE, detectivity and dark current density. In this section, we first discuss the morphology control of OPDs with low bias via various strategies and outline the corresponding morphology requirements for the high-performance OPDs. Subsequently, we further discuss the morphology control of OPDs with photomultiplication and the corresponding requirements. Finally, we employ quantitative analysis of Flory-Huggins interaction parameter  $\chi$ to describe the miscibility of the blend for high-performance OPDs and high-light the great benefit of this method for further progress in the OPD field.

## Morphology for low-bias OPDs

In this section, we focus on the morphology control [134,135] of OPDs without or with low bias (generally lower than 2 V), especially for self-powered OPDs, which have attracted considerable attention. More specifically, we mainly discuss the significant impact of additive strategy, annealing strategy and ternary strategy on OPD performance. Furthermore, we proceed to outline the morphology requirements for high-performance OPDs with low bias.

## Additive strategy

Solvent additives play a great role in the morphology control of the blend, and significantly affect the performance of optoelectronic devices [134,135]. For instance, Hou and Li groups [136] reported that the OSCs with P3HT:ICBA system can achieve a PCE of above 7% with the solvent additives of chloronaphthalene (CN) and N-methyl pyrrolidone (NMP), which retained the record PCE for the OSCs with P3HT:fullerene system. The record performance can be mainly attributed to the superior morphology control via solvent additives, which can markedly modulate the aggregated structure of the blends. More specially, solvent additives affect the intermolecular interactions with the blends and enable the longer morphology evolution time during casting and annealing processing, thus having a great impact on the aggregated structure and crystallization behaviors of the blend. As one of the most common additives, 1,8-diiodooctane (DIO) has been widely used in morphology control of the blend for both OSCs and OPDs. Liu et al. [137] reported that fullerenebased OPDs with 3% DIO additive can achieve a significantly higher detectivity of  $\sim 2.9 \times 10^{12}$  Jones as compared to that without DIO additive (~1.1  $\times$  10<sup>12</sup> Jones). The great detectivity improvement can be ascribed to the favorable morphology control with DIO additive, which can greatly improve responsivity/ EQE and reduce the corresponding  $J_{dark}$ , which is consistent with the report by Wang et al. [82]. Furthermore, recent work by Benavides et al. [138] revealed that fullerene-based OPDs with DIO additive can significantly improve the donor–acceptor interfaces and reduce the roughness of the blend, enhancing the electron/hole transport pathways and carrier transport. Thus, the OPDs with additives can reduce a  $J_{dark}$  by one order of magnitude and improve the detectivity from  $1.66 \times 10^{11}$  Jones to  $3.34 \times 10^{12}$  Jones.

With these benefits in mind, we further discuss the performance improvement of OPDs with other promising additives. Ha et al. [52] employed the classical OPD blend, P3HT:PCBM to investigate the impact of additive strategy on OPD performance. For P3HT: PCBM system, P3HT polymers have high crystallization and PCBM acceptors tend to have large fullerene aggregation and over-sized domain, leading to over-sized phase separation. The authors reported the blend with CTAB additive can achieve the markedly smoother surface (reduced over-sized domain) with root mean square (RMS) roughness of ~1.3 nm, compared to that without additive (Fig. 8a and b). Further analysis by GIWAXS indicated that CTAB additive can help the blend form the great interpenetrating network morphology (Fig. 8c and d), which is favorable for exciton dissociation and carrier transport. Moreover, CTAB additive can form a dipole layer between the indium tin oxide (ITO) and the blending film, which can substantially reduce the ITO work function. With these benefits, the OPD with CTAB additive can achieve significantly higher detectivity and lower  $J_{dark}$  (Fig. 8e). Encouragingly, the CTAB-added OPDs can achieve a markedly higher LDR of ~100 dB (Fig. 8f), indicating the great capability of detecting weak light.

As discussed above, solvent additives have a great impact on OPD performance. Nevertheless, there exist limited reports on the impact of solvent additives on OPD performance, especially for nonfullerene-based OPDs. We can also derive some promising additives from the well-developed OSC field, including CN, NMP, 1,6-diiodohexane (DIH), diphenyl ether (DPE) and 1-methylnaphthalene (MN), *etc.* [139,140]. It is worth noting that when designing high-performance OPDs, we should seek out more favorable additives according to the blend with the given donor and acceptor materials.

#### Annealing strategy

The annealing strategy has a great impact on the morphology control of the blend film. Generally, annealing strategies mainly include the thermal annealing (TA) and solvent vapor annealing. It is widely accepted that TA is a widely used strategy that the blend is heated to above glass transition temperature ( $T_g$ ) to provide enough energy for the movement of molecular chains and reduce the free volume of the blend, making the film smooth for higher exciton dissociation and carrier transport [141]. Through fine-tuning the annealing temperature and time, the blend system can achieve the favorable phase separation, close to the thermodynamic equilibrium state, which facilitates the performance improvement of OPDs (responsivity and EQE). More importantly, TA strategy can optimize the contact between the blend and electrode, which can not only enhance carrier

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RESEARCH

## TABLE 1

# Summary of the performance of recent OPD reports in Fig. 2-

Wavelength (nm)	D* (10 <sup>12</sup> Jones)	J <sub>dark</sub> (10 <sup>-6</sup> A/cm <sup>2</sup> )	LDR (dB)	Response time ( $\mu s$ )	Cut-off frequency (kHz)	OPD type	Refs.
350	9.5 × 10 <sup>11</sup>	9 × 10 <sup>-9</sup>	-	-	38	Broadband	[46]
350	(-1) 4.9 × 10 <sup>10</sup>	(-1) 3.29 × 10 <sup>-8</sup>	-	-	-	Narrowband	[47]
450	(-10) $1.8 \times 10^{12}$	(-10) 1.46 × 10 <sup>-5</sup>	128	-	-	Narrowband	[48]
510	(-1) 8 × 10 <sup>11</sup> (-1)	(1) 10 <sup>-9</sup> (1)	80	-	1	Broadband	[10]
540	(-1) 1.61 × 10 <sup>13</sup>	(-1) $10^{-9}$	143	2.72	-	Broadband	[49]
550	(-1) 1.89 × 10 <sup>12</sup>	(-1) 3.8 × 10 <sup>-6</sup>	115	-	-	Narrowband	[48]
550	(-1) 3.0 × 10 <sup>13</sup>	(-1) 5 × 10 <sup>-4</sup>	148	-	91	Broadband	[50]
560	(-1) 6.6 × 10 <sup>10</sup>	(-1) 9.0 × 10 <sup>-5</sup>	132	-	864	Broadband	[51]
600	(-2) 1.1 × 10 <sup>12</sup>	(-2) 7 × 10 <sup>-8</sup>	100	-	4	Broadband	[52]
600	(-1) 2 × 10 <sup>12</sup>	(-1) 10 <sup>-10</sup>	160	-	15	Broadband	[43]
650	(-1.5) 5.8 × 10 <sup>12</sup>	(-1.5) $1.5 \times 10^{-8}$	105	_	-	Broadband	[53]
650	(-3) $1.1 \times 10^{12}$	(-3) 9 × 10 <sup>-9</sup>	170	-	38	Broadband	[46]
650	(-1) 1.3 × 10 <sup>11</sup>	(-1) 9 × 10 <sup>-7</sup>	160	_	-	Narrowband	[54]
660	(-10) 2.19 × 10 <sup>13</sup>	(-10) 3.4 × 10 <sup>-5</sup>	160	_	50	Broadband	[55]
670	(-5) 1.55 × 10 <sup>12</sup>	(-5) 7.63 × 10 <sup>-6</sup>	110	-	-	Narrowband	[48]
700	(-1) $10^{11}$	(-1) 1.48 × 10 <sup>-9</sup>	75	-	350	Broadband	[56]
700	(-5) 3 × 10 <sup>13</sup>	(-5) 9 × 10 <sup>-9</sup>	180	-	250	Broadband	[57]
740	(-0.3) 1.41 × 10 <sup>13</sup>	(-0.3) 5.9 × 10 <sup>-8</sup>	77.9	2.1	118.3	Narrowband	[58]
/40	$2 \times 10^{12}$ (-0.5)	9 × 10 ° (-0.5)	114	-	100	Broadband	[59]
740	$1.4 \times 10^{13}$ (-0.5)	2 × 10 <sup>-9</sup> (-0.5)	232	-	12	Broadband	[60]
750	$3 \times 10^{14}$ (-1)	$9.62 \times 10^{-7}$ (-1)	204	-	-	Broadband	[41]
770	$3 \times 10^{12}$ (-10)	$10^{-8}$ (-10)	120	-	-	Broadband	[17]
800	$4 \times 10^{13}$	$10^{-9}$	65.14	-	20	Broadband	[61]
820	(-0.1) 1.93 × 10 <sup>14</sup>	(-0.1) $10^{-6}$	-	-	-	Broadband	[62]
860	(-0.3) 9.5 × 10 <sup>12</sup>	(-0.3) 6 × 10 <sup>-8</sup>	-	-	_	Narrowband	[63]
900	(-0.1) 5.84 × 10 <sup>12</sup>	(-0.1) $10^{-8}$	-	5.03	_	Broadband	[26]
920	(-1) 2.4 × 10 <sup>13</sup>	(-1) 8 × 10 <sup>-6</sup>	-	_	-	Broadband	[64]
930	(-2) 4.6 × 10 <sup>13</sup>	(-2) 3.5 × 10 <sup>-5</sup>	159	_	4.5	Broadband	[44]
940	(-0.1) 3.31 × 10 <sup>13</sup>	(-0.1) 2 × 10 <sup>-7</sup>	148	-	240	Broadband	[65]
1000	(-2) 6 × 10 <sup>11</sup>	(-2) $10^{-7}$	135	7.1	2000	Broadband	[66]
1050	(-1) $10^{12}$ (-2)	(-1) 9 × 10 <sup>-7</sup> (-2)	145	-	-	Broadband	[67]
1200	0.03 (-0.65)	(-2) 10 (-0.65)	-	_	-	Broadband	[68]

(continued on next page)

#### TABLE 1 (CONTINUED)

Wavelength (nm)	D* (10 <sup>12</sup> Jones)	J <sub>dark</sub> (10 <sup>-6</sup> A/cm <sup>2</sup> )	LDR (dB)	Response time ( $\mu s$ )	Cut-off frequency (kHz)	OPD type	Refs.
1300	0.8 (-1)	10 (-1)	-	-	-	Broadband	[69]
1350	0.023 (-0.5)	0.07 (-0.5)	-	-	-	Broadband	[70]
1360	10 (-2)	$8 imes10^{-4}$ (–2)	-	-	-	Broadband	[71]
1400	0.0011(-0.2)	9	-	1	-	Broadband	[72]
1400	0.01 (-2)	900 (-2)	180	-	1000	Broadband	[73]
1450	3 (-0.1)	0.005 (-0.1)	100	-	-	Broadband	[45]
1500	0.22 (-0.5)	0.001 (-0.5)	-	-	-	Broadband	[74]
1600	0.03 (-0.1)	$1.38 \times 10^{-5}$	-	-	-	Broadband	[75]

Note: Response speed can be charactered with f<sub>-3dB</sub> and response time. f<sub>-3dB</sub> (kHz) is the frequency response with a unit of kHz, while response time can be defined as the rise time from 10% to 90% and decay time from 90% to 10% with a unit of μs.

transport but also prevent the unfavorable phase separation, leading to large  $J_{dark.}$  For instance, Ko et al. [60] recently employed TA strategy to improve the OPD performance with nonfullerene acceptor (ITIC). The GIWAXS results indicated that without TA treatment, the diffraction patterns experienced little change when adding ITIC acceptor. Instead, after thermal annealing treatment, the blend exhibited a significantly improved face-on orientation with the significant increase of the (010) peak intensity, which is favorable for the carrier transport. As a result, the optimized OPD can achieve a high specific detectivity over  $10^{13}$  Jones and an unprecedentedly wide LDR of 232 dB.

Solvent vapor annealing (SVA) strategy with non-volatile and well-soluble solvents is another widely used post-treatment strategy to rearrange molecule order and enhance the morphology for high-performance optoelectronic devices. Especially for the highly crystalline P3HT system, SVA strategy can significantly reduce the over-sized phase separation, thus enhancing OPD performance. Liu et al. [142] improved the performance of the P3HT-based OPDs via the SVA strategy of orthodichlorobenzene (o-DCB). Similar to the morphology control via TA strategy, the blend film can achieve a smoother surface with SVA treatment, indicating the greater OPD performance. As expected, the OPD with SVA treatment can achieve a detectivity over 1013 Jones and a striking EQE of ~80% at 500 nm, two times higher than that without treatment. Furthermore, recent work by Zhang et al. [143] indicated that SVA strategy can also modulate the vertical composition distribution of nonfullerene molecules. The corresponding OPDs with ultrasonic-assisted SVA treatment can achieve a dramatically high detectivity of  $2.17 \times 10^{12}$  Jones at 688 nm, one order of magnitude higher than that of the control counterpart. This can be mainly attributed to the markedly reduced J<sub>dark</sub>, caused by the vertical phase separation in the blend.

Based on the above discussion, annealing strategies have driven unprecedented successes in modulating the molecular stacking and improving the blend morphology. More importantly, annealing strategies are highly compatible with other strategies, *e.g.*, molecular engineering and additive strategies, that is, we can finely tune the blend morphology via a series of successive strategies. Nevertheless, it is worth noting that over-annealing can also produce an unfavorable blend morphology, thus reducing the OPD performance. The over-annealing blend generally have excessive roughness and over-sized domain, due to the aggregation of some molecules [144,145].

#### Ternary strategy

Ternary strategy has been widely explored to improve the performance of organic optoelectronic devices. It is widely accepted that the addition of a third component is generally used to broaden the spectral response range for OSCs and OPDs. More strikingly, the third component can also be used to modulate molecular stacking and control the blend morphology, further enhancing the performance of optoelectronic devices. For the well-developed OSCs, ternary strategy has been discussed in detail to exploit the full potential [146,147]. Here, we mainly discussed the performance improvement of OPDs with the promising ternary strategy.

For the classical P3HT:fullerene OPD system, the small absorption spectra places great restrictions on commercial applications, especially for promising PPGs. Except for molecular engineering, ternary strategy can also be used to address this issue. For instance, An et al. [148] recently employed the wide-absorption PCPDTBT donor (up to ~850 nm) into P3HT:PC<sub>61</sub>BM system to broaden the spectral response range. As expected, the OPDs with ternary strategy can achieve high EQE and detectivity up to ~850 nm. Nevertheless, atomic force microscope (AFM) results revealed that the RMS roughness gradually increased with the rise of PCPDTBT component, mainly due to the interaction between the backbone or side chain of P3HT and PCPDTBT donors. For the highly crystalline P3HT system, further increasing crystallization may place restrictions on the fine-tuning of blend morphology and even compromise the OPD performance with the excessive addition of the third component. Similar results have been reported by Wang et al. [149] with the addition of PffBT4T-2OD donor (up to 800 nm).

On the other hand, the incorporation of nonfullerene acceptors can also broaden the spectral response range for the classical P3HT: fullerene OPD system. Since the nonfullerene acceptor ITIC was reported, nonfullerene acceptors have enabled great progress in the OPD field. Yang et al. [150] employed the small-bandgap ITIC acceptor (up to ~800 nm) into P3HT:PC<sub>71</sub>BM system to broaden absorption spectra and simultaneously enhance OPD performance. As a result, the OPD can achieve a high EQE of ~43.9% and a detectivity of ~2.67 × 10<sup>12</sup> Jones at 710 nm with the ternary ratios (P3HT: PC<sub>71</sub>BM: ITIC) of 1:0.5:0.5. This can be attributed to the smoother morphology of the blend with the addition of ITIC acceptor, which can enhance exciton dissociation and carrier transport, resulting in a striking EQE for the OPD with low bias. Additionally, Liu et al. [62] reported that the addition of nonfullerene acceptor

TA	BLE	2
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Summary of	f the	performance of	f recent	OPDs wit	h molecula	r engineering.

	Device structure	D* (Jones)	J <sub>dark</sub> (A/cm²)	LDR (dB)	Response speed (µs/kHz)	Refs.
Donor design	ITO/PEDOT:PSS/PDDTT:PC <sub>61</sub> BM/BCP/AI	$1.4 \times 10^{12}$ (-0.1 V/800 nm)	$1.1 \times 10^{-9}$	-	_	[130]
	ITO/PEDOT:PSSP/PBT(EDOT):PC <sub>61</sub> BM/PFN/AI	$3.5 \times 10^{13}$	$1.6 \times 10^{-10}$	-	-	[87]
	ITO/PEDOT:PSSP/PDT:PC <sub>61</sub> BM/BCP/AI	(-0.2  V/010 mm) 2.6 × 10 <sup>12</sup> ( 0.1 V/000 pm)	(-0.2  V) $1.4 \times 10^{-10}$	-	-	[75]
	ITO/AZO:PDIN/P2:PC71BM/BCP/AI	$(-0.1 \sqrt{900} \text{ mm})$ 3 × 10 <sup>12</sup>	(-0.1  V) 2 × 10 <sup>-3</sup>	-	-	[71]
	ITO/PEIE/PTTBAI:PC71BM/MoO <sub>3</sub> /Ag	(-0.1  V/70  nm) $10^{12}$	(-2v) 2 × 10 <sup>-7</sup>	170	25 μs/30 μs	[67]
	ITO/PEDOT:PSS/PNTT-H:PC71BM/PNDIT-PF3N-Br/Ca/AI	(-20/1050  mm) 1.39 × 10 <sup>13</sup>	(-2v) 2.1 × 10 <sup>-9</sup>	65.1	20 kHz	[61]
	ITO/ZnO/PCPDTSBT:PCBM/MoOx/Ag	(-0.1  V)/60  hm) 1.54 × 10 <sup>12</sup>	(-0.1  V) 7 × 10 <sup>-9</sup>	128	(-0.1 V)	[88]
	ITO/MoO <sub>3</sub> /H3:PC61BM/BCP/AI	(-0.5  V/840 nm) $10^{10}$	(-0.5  V) 8.8 × 10 <sup>-9</sup>	-	-	[131]
	ITO/ZnO/PBTQ(OD):PC <sub>71</sub> BM/MoOx/Ag	(-3V/530  nm) 3 × 10 <sup>11</sup> (-2V/960  nm)	(-3V) 2 × 10 <sup>-7</sup> (-2V)	180	1000 kHz (–2V)	[73]
Nonfullerene	ITO/ZnO/P3HT:IDT-BOC/MoO <sub>3</sub> /Ag	$2.1 \times 10^{11}$	$6.3 \times 10^{-6}$	-	-	[112]
acceptor design	ITO/ZnO/PTQ10:O-FBR/MoOx/Ag	$(-0.5 \ \sqrt{650} \ \text{mm})$ 9.6 × 10 <sup>12</sup>	(-0.5  V) $1.7 \times 10^{-10}$	72		[91]
	ITO/ZnO/PTB7-Th:W1/MoOx/Ag	(-20/610  hm) 4.28 × 10 <sup>12</sup> (0.1/(820 pm))	(-2 V) -	150	8.5 μs	[111]
	ITO/PEDOT:PSSP/PBDTTT-EFT:eh-IDTBR/AI	(0.07830  hm) 1.61 × 10 <sup>13</sup> ( 1)/(540 pm)	$1.1 \times 10^{-9}$	143	2.72 μs/4.32 μs	[49]
	ITO/PEIE/BDT-Th-3 T:ITIC/MoO <sub>3</sub> /Ag	(-10/340  mm) $1.4 \times 10^{13}$ (-0.5  V/740  pm)	$(-1^{9})$	232	12 kHz	[60]
	ITO/PEDOT:PSSP/P3HT:ETBI-F/AI	$(-0.5 \ \sqrt{740} \ \text{mm})$ 9.5 × 10 <sup>12</sup> ( 20 \\/600 \ \mmmmm)	(-0.5  V) 5 × 10 <sup>-5</sup>	100	-	[132]
	ITO/PEDOT:PSS/PM6:O4TFIC/Phen-NaDPO/Ag	$(-20^{10})^{10}$ 9 × 10 <sup>11</sup> (0 )/(015 pm)	$(-20^{\circ})^{\circ}$ 8.3 × 10 <sup>-5</sup>	-	3.8 μs/4.3 μs	[90]
	ITO/ZnO/PM6:PDTTIC-4F/MoO <sub>3</sub> /Ag	(0  V/913 hm) 2.44 × 10 <sup>13</sup> (0 V/920 nm)	(-2  V) 1.6 × 10 <sup>-9</sup> (0 V)	-	-	[64]
Polymer acceptor	ITO/ZnO/PTB7-Th:PIIG-PDI(EH)/MoO <sub>3</sub> /Ag	$6 \times 10^{11}$	$7.5 \times 10^{-8}$	-	-	[123]
	ITO/PEDOT:PSS/PolyD:PolyAA50/ZnO/AI	$(-0.2 \sqrt{720} \text{ mm})$ 4.7 × 10 <sup>12</sup>	(-0.2  V) 1.2 × 10 <sup>-9</sup>	-	-	[133]
	ITO/PEDOT:PSS/PDTP-DPP:PNDI-DPP10/BCP/AI	(-0.1  V/900 mm) 2.4 × 10 <sup>12</sup>	(-0.1  V) $1.3 \times 10^{-9}$	-	-	[125]
	ITO/ZnO/PBDBT:PNDIT10/P3HT/MoO <sub>3</sub> /AI	$(-0.1 \ \sqrt{900} \ \text{nm})$ 5.8 × 10 <sup>12</sup>	(-0.1  V) 1.5 × 10 <sup>-8</sup>	105	-	[53]
	ITO/PEDOT:PSS/PTB7-T:PNDI5DD/ZnO/AI	(-37/650  nm) 3 × 10 <sup>13</sup>	(-3 v) 1.2 × 10 <sup>-10</sup>	-	-	[124]
	ITO/TIPS pentacene/P3HT:PIDT-2TPD/AI	(-0.1  V/700  nm) $1.1 \times 10^{12}$	(-0.1  V) 6.4 × 10 <sup>-8</sup>	-	1.5 kHz	[120]
	PET/PEDOT:PSSP/ZnO/PEI/TB7Th:PNDI-T10/PEDOT:PSSP/PET	(-5  V/610 nm) 10 <sup>11</sup>	(-5  v) 8.3 × 10 <sup>-9</sup>	75	(-5 V) 450 kHz	[56]
	ITO/ZnO/P(NDI2OD-T2)/P3HT/MoO <sub>3</sub> /Ag	(0 V/700 nm) $1.1 \times 10^{12}$ (-1 V/550 nm)	(0  v) 3.7 × 10 <sup>-8</sup> (-1 V)	181	(–4 v) 2.9 kHz (–1 V)	[122]

Note: Response speed can be charactered with  $f_{.3dB}$  and response time.  $f_{.3dB}$  (kHz) is the frequency response with a unit of kHz, while response time can be defined as the rise time from 10% to 90% and decay time from 90% to 10% with a unit of  $\mu$ s.

can reduce the over-sized domain caused by the aggregation of fullerene acceptors for the fullerene-based OPD (FD Ternary in Fig. 9a). Instead, for the nonfullerene-based OPD (NFD ternary in Fig. 9a), fullerene acceptors can slightly improve the phase separation of the blend, close to the thermodynamic equilibrium state, which significantly improves carrier transport, compared with the FD Ternary (Fig. 9b). Thus, the OPD with NFD Ternary can achieve a markedly higher responsivity over that with FD Ternary (Fig. 9c).

In summary, ternary strategy can not only broaden the spectral response range of OPDs, but also modulate the blend morphology. Nevertheless, it is worth noting that the morphology control by a third component mainly depends on the property difference and interaction between each component, *e.g.*, the **RESEARCH: Review** 



## FIGURE 8

Morphology control of OPD with additives. (a-b) AFM topography images of the blends of P3HT:PC<sub>60</sub>BM with/without the CTAB additive. (c-d) 2D-GIWAXS patterns of the blends with/without the CTAB additive. (e) Dark current density-voltage (J-V) characteristics and (f) LDR of the blends with/without the CTAB additive. (a-f) Reproduced with permission from Ref. [52]. Copyright 2017, American Chemical Society.



## FIGURE 9

Morphology control of OPD with ternary strategy. (a) TEM images of PTB7-Th: IFIC-i-4F, NFD ternary, FD ternary and PTB7-Th: PC<sub>71</sub>BM blends. (b) Schematic of the morphology of NFD ternary and FD ternary blends. (c) OPD responsivity of the above four blends. (a–c) Reproduced with permission from Ref. [62]. Copyright 2019, Elsevier.

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morphology difference with the addition of polymer donor/nonfullerene acceptors. Thus, when employing a ternary strategy, we must carefully seek out the appropriate component in the pursuit of high-performance OPDs.

## Morphology for photomultiplication-type OPDs

Due to the limit of photovoltaic working mechanisms, conventional OPDs generally cannot realize the high EQE over 100%, which places restrictions on some special applications. The trap-assisted photomultiplication mechanism was used in designing high-performance OPDs [35,54,83,151]. Unlike PC-OPD, photomultiplication-type OPD is a sandwich-type diode with asymmetric electrodes, where a Schottky junction is formed under reverse bias between donor and cathode, resulting in a significantly lower dark current density compared to PC-OPDs with Ohmic junctions at both electrode interfaces. Specifically, photomultiplication-type OPDs generally employ the extremely few acceptors/donors (~1%) to trap electrons/holes via discontinuous phase distribution, which can also enhance the opposite charge tunneling injection [80,101]. Taking the widely explored acceptor traps, for example, the traps are mainly distributed near the interface between cathode and donor and can help turn the original diode into pseudo-ohmic junction under illumination (band-bending), which can enhance carrier the transport and extraction. Moreover, photomultiplication-type OPDs commonly work at a much higher bias (generally higher than 2 V) to overcome the inevitable barriers and improve carrier transport [34,39]. The morphology requirement for photomultiplicationtype OPDs is in stark contrast to that for the OPDs with low bias.

Nevertheless, most of the reports on photomultiplicationtype OPDs focus on the performance improvement via appropriate device design and trap molecule screening (e.g., nonfullerene acceptors). Only few reports pay close attention to the morphology control for photomultiplication-type OPDs. For instance, Yoon et al. [132] recently reported a high-performance photomultiplication-type OPD with an unprecedentedly high EQE of 156 000% at -20 bias. They designed the ETBI nonfullerene acceptors with different end groups, thus having different energy levels and surface energy (Fig. 10a and b). Among them, ETBI-F has the most low-lying LUMO energy level and the smallest surface energy difference with P3HT donor, due to the fluorination effect. As a result, the blend with P3HT: ETBI-F can achieve a significantly higher miscibility, indicating the larger D:A interfacial area, which will yield the maximized trap state, resulting in a striking EQE for photomultiplication-type OPDs. Moreover, the OPDs with different ETBI nonfullerene acceptors achieved a similar  $J_{dark}$ , leading to a marked difference in OPD detectivity (Fig. 10c and d).

Here, we summarize the morphology requirement for photomultiplication-type OPDs. Due to the high bias and the trap-assisted band-bending, photomultiplication-type OPDs generally have significantly high carrier transport and extraction, compared with that of the OPDs with low bias. As a result, high-performance OPDs with photomultiplication generally



#### FIGURE 10

Morphology control of the OPD with photomultiplication. (a) The contact angles of P3HT and ETBI acceptor thin films and the corresponding surface energy ( $H_2O$  and diiodomethane (DIM)). (b) Schematic of the energy levels of the photomultiplication-type OPDs. (c) Dark current density *J–V* characteristics and (d) Detectivity of the reported OPDs. (a–d) Reproduced with permission from Ref. [132]. Copyright 2021, Wiley.

need the smoother blend morphology, that is, higher miscibility of the donor: acceptor blend, which can enhance the corresponding D:A interfacial area.

#### Miscibility for high-performance OPDs

As discussed above, different OPDs have significantly distinct morphology requirements and the corresponding miscibility requirement for the donor: acceptor blend. It is substantially essential to control the appropriate blend morphology for high-performance OPDs. Nevertheless, there is still no standard benchmark to quantitatively compare the morphology difference for the OPDs with different biases. Here, we introduce a quantitative analysis method from the well-developed OSC field, *i.e.*, applying Flory-Huggins interaction parameter  $\chi$  to compare the miscibility of the blend for high-performance OPDs. The method has been successfully used to quantitatively discuss the morphology difference for fullerene and nonfullerene-based OSCs [152–156].

According to Flory–Huggins solution theory, when mixing two components together in a solvent,  $\chi$  is the dimensionless binary interaction parameter representing the interaction between the two components [157–159]. Moreover, the interac-

tion parameterzcan be estimated via differential scanning calorimetry (DSC) and contact angle measurements. For DSC measurement,  $\chi$  can be estimated from the theory of melting point depression, which means that the miscibility of the blend system causes the amorphous components to disrupt the arrangement of the crystalline components, leading to the decrease of melting point. For weakly crystalline or amorphous blend systems, contact angle measurement can be used to derive  $\chi$  parameter from the surface energy of each component. After deriving $\chi$  parameter, the mixing behaviors can be illustrated by using the  $\chi - \phi_s$  phase diagram of the amorphous blend, where  $\phi_s$  represents the volume fraction of small acceptors. The binodal curve divides the phase diagram into the phase separated regime (above) and homogeneous regime (below) [160]. For the most efficient blends (polymer donor: acceptor),  $\chi$  parameter is located in the phase separated regime (triangles in Fig. 11a) and lower  $\chi$ indicates a higher miscibility of the blend [161]. More importantly, the state of the blend in  $\chi - \phi_s$  phase diagram may vary with the processing parameters, for instance, SVA time.

According to  $\chi$  parameter, we can divide the  $\chi - \phi_s$  phase diagram into three regions, *i.e.*, low  $\chi$  (region I), ideal  $\chi$  (region II) and high  $\chi$  (region III) (Fig. 11b). For OSCs, low  $\chi$  (region I) rep-



#### FIGURE 11

Miscibility analysis of the blend with Flory-Huggins interaction parameter  $\chi$ . (a) amorphous  $\chi - \phi_s$  phase diagram of two polymer:small molecule blends. (b) Classification of high  $\chi$  and low  $\chi$  regions in the  $\chi - \phi_s$  phase diagram for OSCs. (c) Proposed region classification for high-performance OPDs in  $\chi - \phi_s$  phase diagram. (a) Reproduced with permission from Ref. [161]. Copyright 2020, Wiley. (b) Reproduced with permission from Ref. [160]. Copyright 2020, The Royal Society of Chemistry.

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resents a high miscibility of the blend, indicating a bad performance, due to the low carrier transport and extraction. Instead, high  $\chi$  (region III) represents the over-sized phase separation (too pure domain), reducing the stability of the blend. Ideal  $\gamma$  (region II) is close to the percolation threshold, where the blend can achieve desired charge transport and separation. Additionally, for OPDs with low bias, morphology control can refer to the blend miscibility and the corresponding  $\gamma$  parameter in the for OSCs. above three regions Nevertheless, for photomultiplication-type OPDs, high miscibility is essential to achieve large interfacial areas. In stark contrast to the ideal $\chi$ parameter for high-performance OSCs, the blend with a low $\chi$ parameter can achieve significantly higher performance for photomultiplication-type OPDs (EQE/spectral responsivity and specific detectivity, etc.). Based on the above discussion, we can schematically map out the  $\gamma - \phi_c$  phase diagram for highperformance OPDs as a function of the bias, which can provide a critical reference for the morphology control of the blends (Fig. 11c). Moreover, we here provide a summary of the performance of representative OPDs with morphology control (Table 3).

## Device structure design

After discussing the molecular engineering and morphology control of the blend, we proceed to summarize the research efforts for high-performance OPDs from device structure design. Since there are some systematic and accessible reviews involving OPD device structures [24,32,33], here we only discuss some striking device structure designs for special OPD applications. More specifically, we first outline the device structure designs for color-selective OPDs and elucidate the corresponding mechanism. Subsequently, we mainly discuss the promising tandem structures for multifunctional OPDs, including photomultiplication, dual-wavelength response and dual-mode response.

## Structure for color-selective OPDs

In this section, we focus on color-selective OPDs which is an essential elements of organic image sensor. For commercial silicon photodetectors, it is inevitable to employ optical filters to achieve a spectral selective response. The optical filter strategy may complicate the design of devices and simultaneously lead to the degradation of performance. On the other hand, OPDs can achieve color-selectivity without optical filters since organic semiconductors have color-selective absorbing nature. Therefore, we mainly discuss about Schottky OPDs and narrowband OPDs to achieve color-selectivity.

#### Schottky OPDs

A definite and simple method for achieving a color-selectivity is a Schottky OPD which requires only one semiconductor by using semiconductor/metal Schottky junction instead of PN junction. Thus, it is possible to easily realize various color-selectivities from

#### TABLE 3

	Device structure	D* (Jones)	J <sub>dark</sub> (A/cm²)	LDR (dB)	Response speed (µs/kHz)	Refs.
Additive/annealing strategies	ITO/ZnO/PBDB-T:ITIC/MoO <sub>3</sub> /Ag	$2.17 \times 10^{12}$	$1.2 \times 10^{-7}$	_	_	[143]
	(DIO)	(-0.5 V/688 nm)	(-0.5 V)			
	ITO/P3HT:PCBM/AI	$8.3 \times 10^{12}$	$1.5$ $ imes$ $10^{-9}$	120	-	[142]
	(o-DCB)	(-0.5 V/500 nm)	(-0.5 V)			
	ITO/PEDOT:PSS/P3HT:PC71BM/AI	$4.04 \times 10^{14}$	$6 \times 10^{-7}$	-	-	[82]
	(o-DCB)	(–19 V/610 nm)	(-10 V)			
	ITO/ZnO/PBDTT-8ttTPD:PC71BM/MoO3/Ag (DIO)	$1.13 \times 10^{13}$	$3.7 \times 10^{-9}$	-	-	[162]
		(–2V/610 nm)	(-2V)			
	ITO/P3HT:PC <sub>60</sub> BM/MoO <sub>3</sub> /Ag (CTAB)	$2 \times 10^{12}$	10 <sup>-8</sup>	100	4 kHz	[52]
		(–1V/610 nm)	(-1V)		(—1V)	
	ITO/ZnOx/PCPDTBT:PC <sub>61</sub> BM/MoO <sub>3</sub> /Ag (DIO)	$2.47 \times 10^{12}$	$1.4 \times 10^{-8}$	-	-	[137]
		(-0.5 V/800 nm)	(-0.5 V)			
	ITO/TFB/PDPP3T:PC <sub>70</sub> BM/AI	$3.34 \times 10^{12}$	10 <sup>-8</sup>	-	63.8 kHz	[138]
	(140 °C, DIO)	(-5V/900 nm)	(-5V)		(—5V)	
	ITO/PEIE/BDT-Th-3 T:ITIC/MoO <sub>3</sub> /Ag	$1.4 \times 10^{13}$	$10^{-9}$	232	12 kHz	[60]
	(TA)	(-0.5 V/740 nm)	(-0.5 V)		(-0.5 V)	
Ternary strategy	ITO/ZnO/PEIE/PTB7-Th:COi8DFIC: PC71BM/MoO3/Ag	10 <sup>12</sup>	10 <sup>-5</sup>	135	4000 kHz	[66]
, 5,		(-1V/660 nm)	(-1 V)		(-1 V)	
	ITO/PFN-OX/P3HT:PTB7Th:PC <sub>61</sub> BM/AI	2.8 × 10 <sup>11</sup>	$2 \times 10^{-7}$	180	_	[163]
		(–10 V/750 nm)	(-10 V)			
	ITO/PEDOT:PSS/P3HT:PTB7-Th:IEICO/AI	$7.1 \times 10^{12}$	$6.4 \times 10^{-3}$	118	42000 μs	[164]
		(–25 V/780 nm)	(-25 V)			
	ITO/ZnO/PTB7-Th:IFIC-i-4F:PC <sub>71</sub> BM/MoO3/Ag	$1.93 \times 10^{14}$	$1.2 \times 10^{-11}$	-	360 μs/450 μs	[62]
		(0 V/840 nm)	(0 V)			
	ITO/PEDOT:PSS/P3HT:PC71BM:ITIC/Bphen/Ag	$2.67 \times 10^{12}$	$5 \times 10^{-8}$	-	-	[150]
		(0 V/840 nm)	(0 V)			
	ITO/PEDOT:PSS/P3HT:PTB7:PC61BM/AI	$2.86 \times 10^{12}$	$1.1 \times 10^{-7}$	-	-	[148]
		(–1V/530 nm)	(-1V)			

Note: Response speed can be charactered with f<sub>-3dB</sub> and response time. f<sub>-3dB</sub> (kHz) is the frequency response with a unit of kHz, while response time can be defined as the rise time from 10% to 90% and decay time from 90% to 10% with a unit of μs.



#### FIGURE 12

Device structures and performance enhancement strategies for Schottky OPDs. (a and b) Device structure and detectivity spectrum of the blue-selective OPD using a Schottky junction between donor polymer and ITO/ZnO cathode. (c and d) Device structure and detectivity spectrum the UV-selective OPD using a Schottky junction between donor polymer and AI cathode. (e and f) Sulfur doping method for a low temperature sol–gel-derived ZnO restoration to improve the performances. (g and h) Reactive dedoping method for donor to reduce the acceptor-defect density and enhance the performances. (a and b) Reproduced with permission from ref.[165]. Copyright 2016, Wiley. (c and d) Reproduced with permission from Ref. [167]. Copyright 2018, Wiley. (g and h) Reproduced with permission from Ref. [168]. Copyright 2019, American Chemical Society.

blue to NIR, depending on the use of color-selective materials as a photoactive layer. Exciton dissociation at the Schottky junction occurs by built-in potential in depletion region, which can be effectively generated when the energy difference between the work function values of the semiconductor and metal is large enough: either a combination of donor/low-work function metal (cathode) or acceptor/high-work function metal (anode). In addition, the resulting Schottky junction induces a high Schottky barrier, which is more advantageous in suppressing the dark current density than in the case of bulk heterojunction.

In 2016, Yoon et al. [165] reported a blue selective OPD using the junction between low work function metal of ITO/zinc oxide (ZnO) cathode and donor for the first time. Owing to the nonabsorbing nature of the ITO/ZnO cathode, the corresponding OPD could intactly reflect the absorption spectrum of the donor polymer with an FWHM of 110 nm (Fig. 12a and b). The developed OPD achieved a high detectivity of 1.15  $\times$   $10^{12}$  Jones and a low  $J_{dark}$  of  $1.3 \times 10^{-9}$  A/cm<sup>2</sup> at a reverse bias of -5 V. Afterwards, many reports have adopted the Schottky junction between ITO/ ZnO and donor material to successfully achieve B/G/R/NIR selectivities [88]. For instance, Sung et al. [169] reported a greenselective OPD using a green-selective phenanthrocarbazolebased donor polymer. The corresponding OPD achieved a detectivity of  $1.42 \times 10^{12}$  Jones, an FWHM of 118 nm, and a  $J_{dark}$  of  $2 \times 10^{-9}$  A/cm<sup>2</sup>. Similarly, Yoon et al. [88] reported a NIRselective OPD using PCPDTSBT in conjunction with ITO/ZnO cathode. The developed OPD achieved a detectivity of  $1.54 \times 10^{12}$  Jones and LDR of 128 dB at -1 V. In addition, Azadinia et al. [166] employed a Schottky junction between Al cathode, another low work function metal, and a polyfluorene-based

donor polymer for a UV-selective OPD. The resulting OPD showed a detectivity of  $2 \times 10^9$  Jones at 380 nm and  $J_{dark}$  of  $2.2 \times 10^{-6}$  A/cm<sup>2</sup> under -5 V (Fig. 12c and d).

Furthermore, several studies have been reported on improving the overall performances of Schottky OPDs. Kim et al. [167] reported a sulfur doping method for a low-temperature sol-gelderived ZnO to restore the deep-level defect states. The reduced interface trap states could increase the Schottky barrier height and enlarge not only the effective built-in potential but also the depletion region width. Thus, the developed Schottky OPD achieved a remarkably low  $J_{dark}$  of 2.6  $\times$  10<sup>-10</sup> A/cm<sup>2</sup> and a high detectivity of  $2.4 \times 10^{13}$  Jones at a bias of -3 V (Fig. 12e and f). More specifically, the sulfur-doped ZnO enabled exceptionally robust electrical performances against air exposure more than 20 days. In addition, Kang et al. [168] employed a reactive dedoping strategy to improve the Schottky OPD performances. The donor polymer film dedoped by 1-propylamine solution showed the reduced acceptor-defect density and thus the decreased intrinsic doping level, leading to the expanded depletion region of the Schottky junction. The resulting OPD achieved a high detectivity of  $6 \times 10^{12}$  Jones and a low noise-equivalent power of  $5.05 \times 10^{-14}$  W/Hz<sup>0.5</sup> even under zero bias (Fig. 12g and h).

#### Narrowband OPDs

According to the above discussion, narrow absorption character of organic semiconductors can be used to realize the spectral selective response with a full-width-at-half-maximum (FWHM) of  $\sim$ 200 nm [16,170]. But, the suppression of spectral response outside the chosen range remains an open challenge, which compromises the superiority of the achieved selective response.

As a result, it is exceedingly essential for the community to develop viable strategies to achieve the spectral selective response with significantly narrower FWHM [171].

In 2015, Armin et al. [172] introduced a new concept of charge collection narrowing (CCN) to achieve a spectral selective response. More specifically, CCN strategy uses a thick bulk heterojunction, in which different wavelength photons can reach different positions, e.g., red and near infrared lights can penetrate deeper (Fig. 13a). As a result, the corresponding OPDs can achieve the narrow spectral response with a narrower FWHM below 100 nm via selectively collecting these carriers and can be spectrally fine-tuned over a range of ~100 nm (Fig. 13b). More strikingly, thick bulk heterojunction can markedly reduce the corresponding J<sub>dark</sub> and thus enable the CCN-based OPDs to achieve a high specific detectivity of  $\sim 10^{12}$  Jones. Additionally, the CCN strategy exhibits broad applicability in designing the narrowband OPDs with response in different spectral ranges, e.g., at 680 nm and 950 nm (Fig. 13c). Similarly, Xie et al. [63] recently employed thick heterojunction to achieve the narrow spectral response via manipulating localized Frenkel exciton dissociation. The corresponding OPDs can achieve the spectral selective response with an exceedingly narrow FWHM of  $\sim$ 50 nm. Impressively, the promising strategy results in a peak EQE of  $\sim$ 65% and a specific detectivity over 10<sup>13</sup> Jones, which are comparable to those of commercialized silicon photodetectors.

On the other hand, bulk heterojunction with donors and acceptors can yield intermolecular charge-transfer (CT) states, which can enable additional optical transitions below their bandgaps. This can be used to realize the narrowband OPDs with near infrared response, which has great application prospects [12,14,175,176]. Nevertheless, CT state is too weak to be detected via direct intermolecular absorption. Thus, it is essential to carefully design OPD device structures to achieve a spectral selective response. For instance, Siegmund et al. [173] employed resonant microcavity to enhance the optical field in absorber blend, thus making full use of the broadband weak CT absorption (Fig. 13d–f). More specifically, they employed optical transfermatrix simulations to optimize the thicknesses of the transport and Ag layers for the absorber blend of 50 nm (Fig. 13e). As a



#### FIGURE 13

Device structure for narrowband OPDs. (a–c) Narrowband OPDs and the corresponding performance with CCN strategy. (d–f) Molecular structure, device structure and EQE of the narrowband OPDs with cavity-enhanced CT strategy. (g–i) Device structure and the corresponding OPD performance for two terminal responses. (a–c) Reproduced with permission from Ref. [172]. Copyright 2015, Springer Nature. (d–f) Reproduced with permission from Ref. [173]. Copyright 2017, Springer Nature. (g–i) Reproduced with permission from Ref. [174]. Copyright 2018, Wiley.

result, the OPDs with visible light absorption (Fig. 13f) can realize the narrowband spectral response with a FWHM of ~36 nm at near infrared band, even up to 1600 nm. Impressively, the corresponding OPDs can achieve an enhanced peak EQE of ~20%, which is 40 times higher than that without resonant microcavity. Similarly, Tang et al. [175] also employed resonant microcavity to achieve the narrowband spectral response with an exceedingly low FWHM of ~14 nm, which is favorable for the performance of the spectrophotometer.

Based on the above structure design for narrowband spectral response, we can realize a lot of multifunctional OPDs for special applications. For instance, the work by Wang et al. [174] indicated that the OPDs with thick-film bulk heterojunction can achieve two-terminal response with the simple modification of the cathode (Fig. 13g). As revealed above, thick bulk heterojunction can help OPDs achieve the narrow spectral response at reverse bias. Thus, the OPDs with thick bulk heterojunction can achieve the narrowband response with a FWHM of ~30 nm under bottom illumination (Fig. 13g). On the other hand, the transmissivity of the metal cathode gradually increases with the drop of cathode thickness. As a result, the OPDs can also work under top illumination with a broad spectral response range covering 300-700 nm (Fig. 13i). Moreover, the EQE of the OPD working under bottom illumination gradually improved with the increase of cathode thickness, due to the enhanced light absorption by the metal cathode, while that under top illumination had the opposite result (Fig. 13g-i).

Although CCN and cavity-enhanced CT strategies can enable OPDs to achieve the narrowband response and even twoterminal response, the thickness optimization of photoactive layer and interface layers may compromise some other OPD metrics, e.g., responsivity etc. [15,38,177,178]. As a result, when designing a narrowband OPD, various critical parameters should be carefully balanced to achieve high-performance OPDs. For example, CCN method requires a thick thickness to achieve the narrowband response with high selectivity ratio (the ratio between the highest detectivity peak within a desired range and the highest detectivity peak within an undesired range), but there is the only case where high selectivity ratio was achieved without thickening the photoactive layer. The work by Kang et al. [168] indicated that red/NIR-selectivities could be achieve in thin-film (~500 nm) PN planar heterojunction OPDs by controlling depletion region widths formed as a result of PN junction. By intentionally raising the charge carrier concentration of donor or acceptor layers, depletion region widths were systematically controlled. Thus, the thin-film OPDs exhibited narrowband (FWHMs <70 nm) responses in red/NIR regions with specific detectivity values over 10<sup>12</sup> Jones.

As discussed above, Schottky OPDs and narrowband OPDs are strategies for achieving color-selectivity, but differ in structure, FWHM, and performances. Schottky OPDs can be fabricated with a simple structure and can achieve high stability by using only a donor semiconductor, but it shows relatively low EQE compared to other BHJ-based OPDs. On the other hand, narrowband OPDs can have very narrow FWHM for specific wavelength bands, but it is limited in red/NIR regions and requires complex and sophisticated structural control. These two methods can be appropriately selected depending on the desired conditions such as FWHM, targeted wavelength, or device performance.

### Tandem structure for multifunctional OPDs

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Subsequently, we proceed to discuss the achieved multifunctional OPDs with tandem structure. Due to the relatively narrow absorption range of organic semiconductors, tandem structure has been widely used to broaden the spectral response range for broadband OPDs, especially for the applications at nearinfrared band. For instance, Menke et al. [179] used the three bulk heterojunctions in tandem to broaden the spectral response range from 700 nm up to 1100 nm. Recently, Liu et al. [180] employed two acceptors with complementary absorption (ITIC and FOIC) to develop tandem OPDs and the corresponding response range was broadened from 750 nm to 900 nm. Except for broadband OPDs, tandem structure can also be used to realize the narrowband OPDs with dual-wavelength response. Recently, Wang et al. [181] designed the tandem structure in Fig. 14a to achieve the narrowband spectral response in 790-1180 and 1020–1435 nm bands (Fig. 14b and c). More specifically, the tandem OPD can be divided into two resonant microcavities and varying the thickness of each sub-microcavity can form resonance in different wave ranges as indicated above. As a result, the corresponding OPDs can achieve the narrowband spectral responses with a FWHM of ~35 nm at 790-1180 nm band and a FWHM of ~61 nm at 1020-1435 nm band.

Except for the OPDs with dual-wavelength response, tandem structure can also be used to design the OPDs with dual-mode response. For instance, Lan et al. [17] designed the dual-mode OPD with P3HT and PTB7-Th donors paired with PC70BM acceptors (Fig. 14d). The dual-mode OPD can realize the spectral response covering 600-800 nm (near infrared) at a reverse bias, enabled by the trap-assisted charge injection at the cathode (photomultiplication mechanism with 1% PC70BM acceptor). When working at forward bias, the OPD can achieve the spectral response covering 300-650 nm (visible light), due to the trapassisted charge injection at the anode (Fig. 14e and f). More strikingly, the dual-mode OPD can achieve a high responsivity above 10 A/W and a high specific detectivity of  $\sim 10^{13}$  Jones for both visible-light and near-infrared responses. Except for tandem structure, ternary strategy can also be used to realize dual-mode response. Miao et al. [163] also designed the dual-mode OPD with a ternary blend of P3HT, PTB7-Th and  $PC_{61}BM$  (40:60:1). The corresponding OPD can achieve the broadband spectral response covering 350-800 nm at forward bias and narrowband spectral response with a FWHM of ~40 nm (at 750-850 nm band) at reverse bias. The operating mechanism is similar to the above OPD with tandem structure.

In parallel with the dual-wavelength and dual-mode responses, tandem structure can also be used to design the OPDs with photomultiplication. For single-layer OPDs with photomultiplication, achieving the broadband response covering from the ultraviolet to near-infrared band is of great challenge, due to the trapped electron distribution near the hole injection electrode. Additionally, for ordinary OPDs, over-unit EQE is hard to be achieved even at a large bias according to the working mechanism. Nevertheless, photomultiplication-type OPDs can simultaneously achieve high EQE and broadband spectral response with tandem structure. Zhao et al. [182] developed a photomultiplication-type OPD with two BHJs of PM6:Y6 and P3HT:PC<sub>71</sub>BM (Fig. 14g). The BHJ of PM6:Y6 is used to achieve the broadband spectral response, while the latter is for photomultiplication. As a result, the OPD can achieve a broad response covering 350–950 nm and a high EQE of ~1200% (Fig. 14h). Moreover, the energy band diagrams at a forward bias can be used to explain the working mechanism of the tandem OPD, *i.e.*, trap-assisted photomultiplication mechanism (Fig. 14i). Additionally, we here provide a summary of the performance of representative OPDs with special device design for reference (Table 4).

As discussed above, tandem structure can enable OPDs to realize photomultiplication response, dual-wavelength response and even dual-mode response, the complex device structure and the corresponding increased processing and cost may place great restrictions on their commercial applications. It is worth mentioning that OPDs with a ternary strategy may also achieve the above multifunctional responses [80,163]. Nevertheless, few efforts have been devoted to this interesting exploration.

## **Device stability**

Although OPDs have achieved promising advances in performance and multi-functions, the desirable device stability is still the prerequisite for commercial applications. The degradation of OPDs can be attributed to the comprehensive effects of multi-factors, including light, electric field, heat, water and oxygen, etc. Generally, the attenuation of OPD performance stems from the degradation of organic semiconductor materials due to the above multi-factors. We can control the working environment, including water, oxygen and heat via encapsulation and heat sink, while photodegradation and electrodegradation are almost inevitable during the operation of OPDs. Moreover, heat and electric field can also result in the increase of noise current, which is significantly deleterious to OPD performance. Nevertheless, there only exist few reports on the degradation of OPDs. In this section, we summarize recent advances of OPD stability, mainly including the devices with fullerene and nonfullerene acceptors. More importantly, we highlight the great potential of nonfullerene acceptors in designing highly stable OPDs.



#### FIGURE 14

Tandem structure for multifunctional OPDs. (a–c) Tandem OPDs and the corresponding performance for dual-wavelength response. (d–f) Detectivity and the corresponding mechanism of the tandem OPD for dual-mode response. (g–i) Device structure, EQE and the corresponding mechanism of the tandem OPD for photomultiplication response. (a–c) Reproduced with permission from Ref. [181]. Copyright 2020, Wiley. (d–f) Reproduced with permission from ref.[17]. Copyright 2020, American Association for the Advancement of Science. (g–i) Reproduced with permission from Ref. [182]. Copyright 2020, American Chemical Society.

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## TABLE 4

## Summary of the performance of recent OPDs with special device design.

	Device structure	D* (Jones)	J <sub>dark</sub> (A/cm <sup>2</sup> )	LDR (dB)	Response speed (μs/kHz)	FWHM (nm)	Refs.
Color-selective OPDs	ITO/ZnO/F8T2/MoO <sub>3</sub> /Au	$1.15 \times 10^{12}$ (-5V/450 nm)	$1.3  imes 10^{-9}$ (-5V)	125	10.6 kHz (–3 V)	110	[165]
	ITO/ZnO/PP-Th/MoO <sub>3</sub> /Ag	$1.42 \times 10^{12}$ (-3V/510 nm)	$2 \times 10^{-9}$ (-3V)	84.9	3.1 kHz	118	[169]
	ITO/ZnO/PCPDTSBT/MoO <sub>3</sub> /Ag	1.54 × 10 <sup>12</sup> (–1V/830 nm)	$1.1  imes 10^{-8}$ (-1V)	128	10.1 kHz (—1V)	-	[88]
	ITO/PEDOT:PSS/BFE/AI	2 × 10 <sup>9</sup> (–5V/380 nm)	$2.2  imes 10^{-6}$ (-5V)	-	0.17 kHz	-	[166]
	ITO/ZnO (S-doped)/F8T2/MoO <sub>3</sub> /Au	2.4 $ imes$ 10 <sup>13</sup> ( $-$ 3V/450 nm)	$2.6 \times 10^{-10}$ (-3V)	122	17.6 kHz (–3V)	-	[167]
	ITO/ZnO/P3HT (dedoped)/MoO <sub>3</sub> /Ag	6 × 10 <sup>12</sup> (0 V/520 nm)	5.1 × 10 <sup>-11</sup> (0 V)	201	13 kHz (0 V)	-	[168]
	Glass/Au/PEIE/PBTTT:PCBM/MoO <sub>3</sub> /Ag	10 <sup>13</sup> (0 V/1000 nm)	10 <sup>-9</sup> (0 V)	130	1000 kHz	14	[182]
	ITO/PEDOT:PSS/P3HT:PTB7-Th:PC <sub>71</sub> BM/AI	5.7 × 10 <sup>11</sup> (–10 V/793 nm)	10 <sup>-7</sup> (-10 V)	170	0.018 kHz (–20 V)	30	[174]
	ITO/PFN-OX/P3HT:PTB7Th:PC <sub>61</sub> BM/AI	2.8 $ imes$ 10 <sup>11</sup> (–10 V/750 nm)	$2  imes 10^{-7}$ (-10 V)	180	-	40	[163]
	ITO/PEDOT:PSS/PCDTBT:PC <sub>70</sub> BM/C60/AI	4.8 × 10 <sup>12</sup> (–1V/930 nm)	$5  imes 10^{-10}$ (-1V)	160	100 kHz (-1V)	90	[172]
	ITO/C60F36/BFDPB:C60F36/ZnPc/Bphen/Al	10 <sup>11</sup> (–1V/995 nm)	$5 \times 10^{-6}$ (-1V)	108	0.003 μs/0.151 μs	36	[173]
	ITO/PEDOT:PSS/PolyTPD:SBDTIC/LiF/AI	1.41 × 10 <sup>13</sup> (0 V/7400 nm)	$5.9  imes 10^{-8}$ (0 V)	77.9	3 μs/1.2 μs	141	[58]
Tandem OPDs	Ag/n-Bphen/D6:PC <sub>60</sub> BM/p-MeOTPD/Ag/ n-Bphen/ZnPc:PC <sub>60</sub> BM/p-MeO-TPD/Ag	8.51 × 10 <sup>10</sup> (–0.5 V/990 nm)	$2  imes 10^{-6}$ (-0.5 V)	139	-	35–61	[181]
	ITO/PFN-Br/P3HT:PC70BM/P3HT/ P3HT:PTB7-Th:PC70BM/AI	9.85 × 10 <sup>12</sup> (–45 V/770 nm)	$1.9  imes 10^{-6}$ (10 V)	92	-	-	[17]
	ITO/ZnO/PM6:Y6/PC <sub>71</sub> BM:P3HT/Au	6.8 × 10 <sup>12</sup> (10 V/900 nm)	9.5 $ imes$ 10 <sup>-8</sup> (5 V)	158	-	-	[182]
	ITO/TAPC/AIE:C70/C70/MoO <sub>3</sub> :C70/BCP/AI	2.31 × 10 <sup>12</sup> (-6V/900 nm)	$3.5  imes 10^{-8}$ (-1 V)	100	0.03 kHz (—6V)	-	[102]
	ITO/ZnO/PTB7-Th:ITIC/PTB7-Th:FOIC/MoO <sub>3</sub> /Ag	2.58 × 10 <sup>11</sup> (0 V/830 nm)	$6.5  imes 10^{-8}$ (-0.1 V)	-	0.026 μs	-	[180]

Note: Response speed can be charactered with  $f_{.3dB}$  and response time.  $f_{.3dB}$  (kHz) is the frequency response with a unit of kHz, while response time can be defined as the rise time from 10% to 90% and decay time from 90% to 10% with a unit of  $\mu$ s.

## Stability with fullerene acceptors

Fullerene acceptors have been widely used in designing highperformance OPDs with the merits compared to or even higher than that of inorganic photodetectors [43,45]. To advance the commercial applications of OPDs with fullerene acceptors, it is highly essential to investigate the performance stability, especially for the OPDs with bulk heterojunction. For instance, Kielar et al. [50] employed the PCDTBT:PCBM blend to develop a photomultiplication-type OPD with high detectivity and low  $J_{dark}$ . Moreover, the authors developed a handmade aging setup (Fig. 15a and b), i.e., a Faraday cage with a constant nitrogen flow of 100 mL/min to protect the OPDs from the ambient factors, including oxygen and humidity. For the accelerated measurement, the authors set the light intensity to  $1 \text{ mW/cm}^2$ , enabling on/off current ratio to keep close to 10<sup>6</sup> (Fig. 15c). The OPD responsivity experienced a sharp reduction during the first 500 h, due to the burn-in, which was widely observed during the degradation of OSCs with PCDTBT donors (Fig. 15d). This can be attributed to the photochemical reaction in the active

layer and the reorganization of PCDTBT film. Nevertheless, after the first 500 h, the responsivity achieved a linear degradation, which actually determined OPD lifetime. Thus, they set this degradation as the benchmark to evaluate OPD lifetime to reach 80% of the responsivity after burn-in. The developed OPD can achieve a lifetime of 14,400 h at 1 mW/cm<sup>2</sup>, indicating an excellent stability of fullerene-based OPDs in nitrogen environment.

Nevertheless, it is still worth investigating the stability performance of fullerene-based OPDs in the air for commercial applications. Kielar et al. [183] recently explored the performance stability of the OPDs with the same blend. When the developed OPD was kept in nitrogen environment, the authors also observed a slow drop of responsivity from 0.30 to 0.27 A/W and the light/dark current densities remained almost unchanged during the test period, consistent with the above work (Fig. 15e). Nevertheless, when under air exposure, the OPD experienced rapid degradations of responsivity and dark current density, even within the first 10 min (Fig. 15f), indicating the poor air stability of fullerene-based OPDs. The authors attributed the poor stability

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## FIGURE 15

OPD stability with fullerene acceptors. (a and b) Photographs of the handmade aging setup. (c and d) On/off current ratio and responsivity of the developed OPD as a function of time. (e and f) Fullerene-based OPD performance variation as a function of time in  $N_2$  and air flow, respectively. (a–d) Reproduced with permission from ref.[50]. Copyright 2016, Springer Nature. (e and f) Reproduced with permission from Ref. [183]. Copyright 2018, Wiley.

achieved in the air to the rapid degradation of the active layer, due to the generation of shallow traps (0.2 eV) with a concentration of  $10^{16}$  cm<sup>-3</sup>. The shallow traps markedly reduced the charge carrier mobility, which is not favorable for charge transport and extraction.

## Stability with nonfullerene acceptors

As revealed from the above discussion, OPDs with fullerene acceptors have inferior device stability under air exposure. Recently, nonfullerene acceptors have enabled markedly superior OPD performance over their fullerene counterparts. As a result, it is highly worth exploring the performance stability of nonfullerene-based OPDs for commercial applications. Additionally, it is widely reported that OSCs with nonfullerene acceptors exhibit significantly higher stability, compared to those based on fullerene acceptors. Thus, we discuss in detail the OPD stability with nonfullerene acceptors in this section.

Recently, Jang et al. [49] developed a high-performance OPD with EH-IDTBR acceptors, which can achieve a higher detectivity of ~ $1.61 \times 10^{12}$  Jones and a faster response time of ~ $2.7 \mu$ s, compared to that with fullerene acceptors ((PC<sub>71</sub>BM). The higher OPD performance can be attributed to the significantly lower dark current density and trap density for the EH-IDTBR-based OPD. More strikingly, the OPD with EH-IDTBR acceptors can achieve substantially higher operation stability even under electrical and thermal stress. As indicated in Fig. 16a and b, the EH-IDTBR-based OPD showed almost unchanged current density under reverse bias or thermal stress, while the fullerene counterpart expe-

rienced a significant reduction of current density. The superior device stability with EH-IDTBR acceptors can be explained via morphology and crystallography analyses. AFM results revealed that the RMS roughness of the blend with fullerene acceptors increased from 4.09 nm to 4.28 nm under 100 heating, which indicated an increase in the size of the separated phase, leading to higher charge recombination (Fig. 16c). Instead, the RMS roughness with EH-IDTBR acceptors dropped slightly under thermal stress, which was favorable for exciton dissociation. Similarly, TEM results also provided overwhelming evidence on the higher stability of EH-IDTBR-based OPDs (Fig. 16d).

As discussed above, fullerene-based OPDs exhibit inferior stability under reverse bias or thermal stress, compared with nonfullerene-based OPDs. This can be further explained via the use of Flory-Huggins interaction parameter  $\gamma$ . It is widely accepted that fullerene acceptors tend to have large aggregation and over-sized domains, which are not favorable for the performance and stability of OPDs as revealed in Fig. 11c. This indicated that OPD stability can also be evaluated via quantitative analysis, according to Flory-Huggins theory. Additionally, although there still exists no report on the stability of allpolymer OPDs, it is expected that they can achieve significantly greater stability over the OPDs with polymer: small molecule blend. The main reason can also be explained via interaction parameter. Theoretically, all-polymer OPDs can generally present more favorable morphology, which is beneficial for the improvement of OPD stability.

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#### FIGURE 16

OPD stability with nonfullerene acceptors. (a and b) OPD performance variation with heating and bias, respectively. (c and d) AFM and TEM images of the active layers with and without heating. (a–d) Reproduced with permission from Ref. [49]. Copyright 2020, Wiley.



Summary of the challenges and research directions for OPDs with highperformance and stability.

## Summary and outlook

Through continuous research efforts, OPD performance has approached or even surpassed that of commercial silicon photodetectors in some metrics. In this review, recent advances of critical OPD metrics, including dark current density, specific

detectivity, LDR and response speed are clearly summarized. Subsequently, the promising strategies for high-performance OPDs from molecular engineering and morphology control are further outlined. We highlight the impact of molecular design on OPD performance improvement and outline the corresponding design guideline of donors, nonfullerene acceptors and polymer acceptors. Moreover, the morphology control of the OPDs with low bias and photomultiplication is discussed and a quantitative analysis method is introduced to provide an excellent understanding of OPD morphology control. Afterwards, some striking device structures for multifunctional applications are discussed to elucidate the corresponding mechanism for narrowband response, photomultiplication response, two-terminal response, dual-wavelength response and dual-mode response. Finally, the research efforts of OPD stability for commercial applications are further outlined and the potential for high-stability OPDs with nonfullerene acceptors is highlighted.

It can be expected that the commercial applications of OPDs can be further pushed forward via continuous research efforts.

Here, we further discuss the remaining challenges and the corresponding research directions for the further improvement of OPD performance and stability (Fig. 17).

## Challenges and research directions

## (1) Inferior OPD performance at infrared band

Infrared OPDs have great potential in some promising applications *e.g.*, PPG. Nevertheless, the detectivity of infrared OPDs especially beyond 1000 nm is generally inferior to the visible counterparts. The inferior performance of the existing infrared OPDs may be attributed to low spectral responsivity and high  $J_{dark.}$  Therefore, we can improve the infrared detectivity via molecular design and device design. Previously, most efforts are devoted to develop infrared OPDs via broadening the absorption range of donors, which may lead to inferior carrier transport when paired with acceptors due to the improper band alignment. It's worth noting that nonfullerene acceptors can achieve excellent carrier transport even with extremely low HOMO difference, which can enable the significantly higher OPD detectivity. Additionally, further reduction of  $J_{dark.}$  can also improve the detectivity of infrared OPDs, *e.g.*, developing suitable block layers.

## (2) Low performance of all-polymer OPDs

All-polymer optoelectronic devices have attracted increasing attention due to their high flexibility and stretchability. To date, all-polymer OPDs reported are nearly all based on NDI-based or PDI-based polymer acceptors. As a result, the existing all-polymer OPDs generally have inferior performance in terms of responsivity/EQE, LDR,  $J_{dark}$ , and detectivity. To fulfill the potential of all-polymer OPDs for commercial applications, it is inevitable to design the matched polymer acceptors to achieve further performance improvement. We have discussed the corresponding design strategies of NDI/PDI-based polymer acceptors in the section of polymer acceptor design. Here, we further highlight the promising prospect of Y-series polymer acceptors [116,119] in designing all-polymer OPDs with high performance.

## (3) Low OPD detectivity with photomultiplication

Photomultiplication-type OPDs can achieve substantially higher EQE even over 150000%, which may compromise OPD detectivity. This can be attributed to the significantly higher  $J_{dark}$ over  $10^{-6}$  A/cm<sup>2</sup>, which is about four orders of magnitude higher than that of the ordinary OPDs. It is accepted that photomultiplication-type OPDs generally work at high bias, which can lead to significantly higher  $J_{dark}$ . Therefore, there exists a balance between EQE and J<sub>dark</sub> to achieve the maximum detectivity. Additionally, photomultiplication-type OPDs generally employ minor acceptors/donors as the trap to achieve photomultiplication effect. Nevertheless, the minors may function as the recombination centers, which markedly reduce OPD performance. Therefore, we should pay more attrition to the distribution of minors and the corresponding OPD morphology. As discussed above, there exist limited reports on OPD morphology control, especially for photomultiplication-type OPDs. It is significantly essential to introduce or develop the quantitative miscibility analysis and appropriate control strategies to achieve

more favorable morphology for high-performance OPDs with photomultiplication.

## (4) Slow response speed

Except for response speed, OPDs have the close or even superior performance over their inorganic counterparts. The slow response speed of OPDs mainly stems from the intrinsic properties of organic semiconductor materials including exciton dissociation, carrier transport and extraction. Recent report by Saggar et al. concluded that the slow response speed can be attributed to the inferior carrier transport and extraction of OPDs due to the unbalanced electron and hole mobilities. They developed a fullerene-based OPD with a high response speed of 4.5 MHz f-3dB via tuning the composition ratio of the bulk heterojunction. Nevertheless, they explained the results via a simple analytical model based on the assumptions including uniformly photo-generated charges, low charge carrier density and negligible bimolecular recombination, which seems not to represent the real operation of OPDs. Additionally, the work ignores the impact of exciton dissociation on OPD response speed, which is the main difference from that of the inorganic OPDs. More efforts to OPD exciton dissociation may bring great benefits in address the challenge.

## (5) Low stability

Compared with inorganic photodetectors, the low stability of OPDs remains one of the key challenges for their commercial applications. As discussed above, the dominant fullerene-based OPDs have relatively poor device stability under air exposure, while nonfullerene-based OPDs show significantly higher air stability, even under bias and thermal stress, mainly due to the more favorable morphology of the blend. Nevertheless, it has been accepted that BHJs via the blend casting method have relatively poor stability in term of blend morphology, compared with that via sequential deposition. Recently, Xie et al. reported that sequential deposition can enable narrowband OPDs with a FWHM of ~50 nm and a high detectivity over  $10^{13}$  Jones at 860 nm [63]. Further investigations of the stability of OPD made by sequential deposition are highly desired.

## Outlook

We proceed to provide a critical outlook for high-performance and high-stability OPDs from molecular engineering, morphology control and device design.

## (1) Molecular engineering

In the section of molecular engineering, we have summarized recent advance and guidelines of donor design, nonfullerene acceptor design and polymer acceptor design. Here, we highlight the critical role of the design of nonfullerene acceptors and polymer acceptors on the performance and stability of OPDs. We can draw insights from the design strategies of nonfullerene and polymer acceptors for OSCs, *e.g.*, Y-series acceptors. Nevertheless, the acceptors often have the absorption cutoff of ~900 nm, which may place some restrictions on the detection range of infrared OPDs. Further research efforts should be devoted to

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develop nonfullerene and polymer acceptors with a broad absorption range. Furthermore, low cost [184,185] is an additional need for the scalable applications of OPDs.

## (2) Morphology control

Morphology control also has great impact on the performance and stability of OPDs. We have discussed some control strategies to achieve more favorable morphology for high-performance OPDs. Here, we underline the significance of quantitative analysis of the preferred morphology for different types of OPDs. As noted above, OPDs with low bias generally require a moderate miscibility of the donor:acceptor blend to achieve the favorable phase separation for high performance. Instead, photomultiplication-type OPDs generally need significantly higher miscibility, which can enhance the D:A interfacial area. Therefore, propose the use of a quantitative metric, i.e., Flory-Huggins interaction parameter  $\gamma$  to describe the miscibility of the blend for high-performance OPDs. More detailed analysis on the miscibility of high-performance and high-stability OPDs is urgently needed to provide more guidelines for morphology control.

## (3) Novel device design

Device design plays a great role in developing highperformance and multifunctional OPDs. More specifically, it can help to improve OPD performance via reducing dark current density and enhancing responsivity/EQE. On the other hand, special device design can enable multifunctional OPDs to meet various application requirements, including narrowband response, two-terminal response, dual-wavelength response and dual-mode response, *etc.* Nevertheless, the device designs for some special applications may have to compromise other critical OPD metrics. For instance, the device structure of CCN-based OPDs probably lead to the drop of response speed. Moreover, tandem structures may increase OPD complexity and place restrictions on the improvement of response speed. As a result, when designing OPD devices, we should carefully balance critical metrics to achieve optimized performance.

## **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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