**Organic Solar Cells** 



# Integrated Perovskite/Bulk-Heterojunction Organic Solar Cells

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The recently emerged integrated perovskite/bulk-heterojunction (BHJ) organic solar cells (IPOSCs) without any recombination layers have generated wide attention. This type of device structure can take the advantages of tandem cells using both perovskite solar and near-infrared (NIR) BHJ organic solar materials for wide-range sunlight absorption and the simple fabrication of single junction cells, as the low bandgap BHJ layer can provide additional light harvesting in the NIR region and the high open-circuit voltage can be maintained at the same time. This progress report highlights the recent developments in such IPOSCs and the possible challenges ahead. In addition, the recent development of perovskite solar cells and NIR organic solar cells is also covered to fully underline the importance and potential of IPOSCs.

## 1. Introduction

Solar cells, which directly convert absorbed sun radiation into electricity, have emerged as one of most promising clean and renewable energy strategies to solve serious environmental and energy problems. In principle, the power conversion efficiency (PCE) of solar cells is limited by the thermodynamic principles based Shockley–Queisser (S–Q) limit of ≈33% for single junction devices.<sup>[1]</sup> To circumvent the thermodynamic limits of photovoltaic efficiencies, series-connected tandem solar cells have been developed by stacking two or more sub-cells with complementary absorption range to broad the solar spectral coverage and better using the solar light.<sup>[2,3]</sup> Thus, the higher energy photons are captured by sub-cell with larger bandgap material, and lower energy photons are absorbed by the subcell using the material with smaller bandgap, resulting reduced thermalization loss (Figure 1).<sup>[4]</sup> Series-connected tandem devices with two sub-cells using materials with matched bandgaps (complementary absorption range) would increase the efficiency limit to 42% under AM 1.5G (1 Sun) light illumination.<sup>[5]</sup> Ideally, the  $V_{\rm OC}$  of tandem cell equals to the sum of those of sub-cells, and  $J_{SC}$  is limited by the lowest current of the sub-cells. In order to achieve the maximal PCE, J<sub>SC</sub> of each subcell should be optimized to be equal or similar to prevent the

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accumulation of photogenerated charge carrier. In addition, in a tandem device, the sub-cells are connected monolithically by a recombination layer (or a tunnel junction), which is rather challenging to be optimal because both energy level alignment and light transmittance need to be considered. Clearly, this causes a great challenge for the fabrication of tandem cells to achieve best performance.<sup>[2,3]</sup> Recently, a novel device structure of integrated perovskite/ bulk-heterojunction (BHJ) organic solar cells (IPOSCs) without any recombination layer was developed and high performance has been demonstrated.<sup>[6-9]</sup> In this kind of device, two stacked photovoltaic layers, namely a perovskite bottom layer and an

organic BHJ top layer, are fabricated using orthogonal solvents, thus direct deposit of solution-processed BHJ layer will not damage the perovskite layer, allowing sequential deposition of the two absorption layers. Perovskite layer and near-infrared (NIR) organic BHJ layers have complementary light absorption spectra, which dramatically minimizes spectral losses, as shown in Figure 1c, offering a new strategy to reach high-performance photovoltaic cells.

In this Progress Report, the recent developments of IPOSCs will be highlighted. We will first discuss the unique advantages of metal halide perovskites and NIR organic semiconductor materials for IPOSC applications, highlight current developments of IPOSCs, and then discuss the remaining challenges that remain to be solved to further improve the performance of IPOSCs. With these, a comprehensive understanding of the relationship between material properties with the performance of IPOSCs would be expected.

## 2. Perovskite Solar Cells

Metal halide perovskite solar cells have attracted much attention due to the rapid increase in the PCEs as well as their potential to be solution processed at low cost.<sup>[10]</sup> The metal halide perovskite exhibits excellent material properties for solar cells, such as a suitable bandgap, high absorption coefficient, low exciton binding energy, long charge-carrier diffusion length, and ambipolar charge transporting properties.<sup>[10–12]</sup> Since Miyasaka et al. first introduced perovskite to photovoltaic cells in 2009 and obtained an efficiency of 3.8%, the efficiency has dramatically improved to over 23% very recently.<sup>[13–21]</sup>

The general chemical formula for metal halide perovskite is ABX<sub>3</sub>, which follow the rule of Goldschmidt tolerance factor to maintain its 3D structure, as shown in **Figure 2**a, in which A is monovalent cation (such as  $Cs^+$ ,  $Rb^+$ ,  $CH_3NH_3^+$ , and  $CH(NH_2)_2^+$ ), B is a divalent metal cation (such as  $Pb^{2+}$ ,



Sn<sup>2+</sup>, and Ge<sup>2+</sup>), X is a halide anion (such as I<sup>-</sup>, Br<sup>-</sup>, and Cl<sup>-</sup>).<sup>[22,23]</sup> The typical perovskite shows polycrystalline form in thin film (Figure 2b) and exhibits long charge carrier life time (Figure 2c),<sup>[24,25]</sup> leading to carrier diffusion length over 1 µm, which is much longer than that of organic semiconductor materials.<sup>[26]</sup> Recently, the 2D or quasi-2D perovskites were also developed and showed great promise to improve the performance of perovskite solar cells, while its bandgap is typically larger than that of 3D perovskite, thus limiting its photocurrent.<sup>[27-32]</sup> So far, the major development of highperformance perovskite solar cells have been achieved mainly through the development of new materials and devices optimization methods, such as cation engineering and interface engineering.<sup>[33-35]</sup> However, typical 3D perovskites, such as MAPbI3 or FAPbI3, show an onset light absorption between 800 and 850 nm, which hinders NIR light harvesting and thus impedes the further improvement of photovoltaic efficiency.<sup>[36]</sup> Thus, one important strategy to further enhance the photovoltaic performance of perovskite solar cells lies in improving the solar spectra coverage by extending light absorption to the NIR region. As shown in Figure 2d-f, the bandgaps were easily tuned by alloying Sn/Pb into perovskite and low bandgap NIR materials can be achieved.<sup>[37]</sup> However, although the onset photocurrent response of Sn-based or alloving Sn/Pb-based perovskites extends to NIR region, for example, 1060 nm for MASn<sub>0.5</sub>Pb<sub>0.5</sub>I<sub>3</sub>, the efficiency was compromised by the poor Sn(II) stability and the dramatically reduced  $V_{\rm OC}$ .<sup>[38–40]</sup> Although the efficiency of Sn-Pb based perovskite was further improved through interface engineering or cations engineering, the efficiency and stability is still much lower than that of Pb-based perovskite devices.<sup>[41-44]</sup> Thus, another efficient strategy to further improve the performance of perovskite devices is to broaden the light absorption to the NIR spectral region by integrating perovskite solar cells with other low bandgap materials based solar cells, such as NIR organic BHJ cells.

## 3. NIR Organic Solar Cells

The state-of-the-art BHJ structure by blending organic donor and acceptor materials has shown great promise for low-cost and lightweight organic solar cells.<sup>[45-50]</sup> In the past decade, tremendous progress has been made and the PCEs have reached to over 14% for single-junction device and over 17% for tandem device via designing novel low bandgap NIR photoactive materials.<sup>[51-57]</sup> Comparing with wide bandgap organic photovoltaic materials, low bandgap donor and nonfullerene acceptor materials with wide sun light cover range extended to NIR region, typically exhibit more closely overlapped electronic orbitals, easier delocalized  $\pi$  electrons, larger dielectric constant, stronger dipole moment, and lower exciton binding energy.<sup>[58,59]</sup> These properties make low bandgap photovoltaic materials playing important roles in high-performance organic solar cells including sing-junction devices and tandem devices.<sup>[60]</sup> The most critical challenges in developing ideal low bandgap materials for NIR organic solar cells are to design and synthesize polymers or molecules with high charge carrier mobility and suitable highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) energy



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levels, and energy alignments must also be considered when blending with donor or acceptor materials forming the BHJ layer.<sup>[61]</sup> One main strategy in designing low bandgap organic semiconductor materials, including polymers and small molecules, is using D–A structure, which involves push–pull chromophores or alternative conjugated electron-rich donor unit and electron-deficient acceptor unit.<sup>[61,62]</sup> The simplified model for hybridization of frontier orbitals for low bandgap materials is shown in **Figure 3**a. The HOMOs and LUMOs of the donor and acceptor will interact with each other after connecting with chemical bonding. After the redistribution of the electrons, two new HOMOs and two new LUMOs of the compound will be produced, resulting in a smaller optical bandgap.<sup>[61,63]</sup>

The representative low bandgap donor polymers, PBDTT-DPP and PDTP-DFBT, shown in Figure 3b, are alternative D–A structure with light absorption extended to NIR region.<sup>[52,64]</sup> The single-junction devices exhibit a PCE of 6.5% and an fill factor (FF) of 65.1% for PBDTT-DPP based cell and a PCE of 7.9% and an FF of 65% for PDTP-DFBT based cell, respectively.<sup>[52,64]</sup> Due to the good light absorption with





**Figure 1.** a) Schematic illustration of light absorption in single and multi-junction solar cells. Modified with permission.<sup>[4]</sup> Copyright 2017, American Chemical Society. b) Solar irradiance spectrum (AM 1.5G) from UV-vis to NIR. c) Absorption spectra of perovskite and NIR organic material films.

photoresponse extended to 900 nm as well as a notable FF, the PDTP-DFBT based BHJ cell has been used in IPOSCs and shows high photovoltaic performance as discussed below.<sup>[7]</sup> Low-bandgap nonfullerene acceptors are another type of molecules with D–A structure, which exhibits excellent light absorption ability in NIR region due to the stronger electron-donating unit and electron-withdrawing unit used in the conjugated backbone. Note that one efficient strategy for high performance small-molecule photovoltaic materials, including donor materials and nonfullerene acceptor materials, is using A–D–A structure.<sup>[46,47,65]</sup> As shown in Figure 3c, A–D–A nonfullerene acceptor, IEICO-4F, developed by Hou and co-workers exhibits an ultranarrow bandgap of 1.24 eV due to an enhanced intramolecular charge transfer effect.<sup>[66]</sup>

short-circuit current density of 25.3 mA cm<sup>-2</sup>, which is ascribed to the enhanced photoresponse in NIR region. Recently, Ding and co-workers reported an interesting A–D–A nonfullerene acceptor CO<sub>1</sub>8DFIC with a dramatically reduced bandgap of 1.26 eV by introducing a new carbonoxygen-bridged unit into the conjugated backbone.<sup>[67]</sup> This molecule based device exhibits a very high photocurrent response in NIR region from 780 to 1000 nm, leading to a super high  $J_{SC}$  of 26 mA cm<sup>-2</sup>. After being used as back subcell in tandem photovoltaic devices, a record efficiency of over 17% have been achieved,<sup>[60]</sup> indicating the potential application of this material in IPOSCs. NIR organic conjugated materials play an important role in IPOSCs and should be designed carefully to meet the property requirements, such as matched energy levels, high charge carrier mobility and good

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**Figure 2.** a) Crystal structure of the perovskite with ABX<sub>3</sub> form. Reproduced with permission.<sup>[22]</sup> Copyright 2013, Nature Publishing Group. b) Scanning electron microscope (SEM) image of a typical polycrystalline perovskite thin film. Reproduced with permission.<sup>[24]</sup> Copyright 2018, American Chemical Society. c) Transient absorption spectra of  $CH_3NH_3PbI_{3-x}CI_x$  with and without contacting the interface layer. Reproduced with permission.<sup>[25]</sup> Copyright 2013, American Association for the Advancement of Science. d) Crystal structure of the  $CH_3NH_3Sn_{1-x}Pb_xI_3$  perovskite. e) Monochromatic incident photon-to-electron conversion efficiency (IPCE) spectra and f) *J*–V curves of the devices based on  $CH_3NH_3Sn_{1-x}Pb_xI_3$  (*x* = 0, 0.25, 0.5, 0.75, and 1) perovskites. d–f) Reproduced with permission.<sup>[37]</sup> Copyright 2014, American Chemical Society.

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**Figure 3.** a) Orbital interactions of electron donor and electron acceptor units in D–A type polymers and small molecules resulting in a smaller bandgap. Modified with permission.<sup>[61]</sup> Copyright 2009, American Chemical Society. b) Representative low bandgap donor materials. c) Representative low bandgap nonfullerene acceptor materials.

photocurrent response in NIR region. For a more complete summary of the recent developments in NIR BHJ organic solar cells, see recent review articles.<sup>[68–70]</sup>

## 4. IPOSCs

IPOSCs were developed recently to fully utilizing the sun light, which has two monolithically stacked absorption layers, similar to a tandem device but without a recombination layer (or a tunnel junction) for a much easier fabrication, as shown in **Figure 4**.<sup>[6–9]</sup> In the IPOSCs, the perovskite with a wide bandgap absorbs high energy photons but permits lower energy photons to pass through and be absorbed by low bandgap organic BHJ layer, enabling a more efficient use of photon energy, thus



reducing the thermalization losses due to the complementary light absorption. One important finding for the IPOSCs is that the maintained high  $V_{OC}$  is dominated by the perovskite cells, not the organic photovoltaic cells.<sup>[7]</sup> That means the IPOSCs will have increased photocurrent without sacrificing the  $V_{OC}$  of the perovskite device at the same time. Thus, through capturing more solar light extended from UV-vis to NIR region, the IPOSCs have the potential to approach or even break the S–Q limit by combing the advantages of perovskite solar cells and NIR organic solar cells with the similar and simple fabrication as a single-junction cell.

So far, the IPOSCs have attracted significant attention and some encouraging results have been reported with greatly improved performance.<sup>[8]</sup> The planar device structures of IPOSCs can be divided into the following two categories, regular (N-I-P) and inverted (P-I-N) structures, as shown in Figure 4a,b, respectively. In the IPOSCs, the photogenerated hole and electron carriers from both perovskite and BHJ films can transport through each film and be collected by corresponding electrodes due to the ambipolar charge carrier transport properties of perovskite and BHJ photoactive layers.<sup>[6,9]</sup> Here, we take the N-I-P structure device as an example, as illustrated in Figure 4c. The detailed charge generation and transport process can be summarized as follows. 1) The perovskites are direct bandgap materials and the photogenerated excitons (electron-hole pairs) can be easily separated due to its weak exciton binding energy (≈0.03 eV).<sup>[71]</sup> However, the photogenerated excitons in BHJ film can only be separated into free electrons and holes in the donor-acceptor interface due to the large exciton binding energy of the organic semiconductors.<sup>[72]</sup> 2) The perovskites possess ambipolar charge transport properties with high hole and electron

mobility as well as low recombination loss in the film. Importantly, the donor/acceptor blended BHJ films, which follow the band alignment rules of organic solar cells,<sup>[73]</sup> can also transport both holes and electrons independently due to their nanoscale phase separation with bicontinuous interpenetrating network. 3) The donor materials used in BHJ film can be a useful hole transport channel, thus holes generated in the perovskite film can transport through the donor materials based channels and be collected by anode. Likewise, holes generated from the separated excitons at the donor/acceptor interface in the BHJ film can transport through the donor materials based network and be collected by anode. Note that the HOMO level of donor should be higher than the valance band of perovskite, so the holes can transport from perovskite to donor materials smoothly.<sup>[74]</sup> 4) The electrons generated in the BHJ film can transport





**Figure 4.** a) IPOSC with regular (N–I–P) structure. b) IPOSC with inverted (P–I–N) structure. c) Charge generation and transport mode in IPOSCs.

through electron acceptor materials based network to the perovskite, and then further transport through perovskite film and be collected by cathode due to the high electron mobility and low recombination rate of perovskite materials. Similarly, the electrons generated in the perovskite can transport through perovskite film and be collected by cathode.

Due to the large light absorption coefficient of perovskite, the top BHI layer, even it can fully cover the bottom perovskite layer of light absorption spectra, can mainly absorbed the light that not be absorbed by perovskite film in NIR region. To make the charge transport more efficient in IPOSCs, the BHJ films should have high and balance charge carrier mobility due to the high hole and electron mobility of perovskite. We speculate that it will exhibit high performance for IPOSCs when the hole and electron mobility of BHJ films close to that of perovskites. Note that the charge carrier may recombine in the interface of perovskite film and BHJ organic film. It has been reported that the recombination is not increased for IPOSC in comparison with that of perovskite solar cells by using light intensity dependence of *I*–V measurements,<sup>[7,8]</sup> indicating that the recombination in IPOSCs is not dominated by the interface recombination of perovskite film and BHJ organic film.

#### 4.1. Regular N-I-P Structure Devices

In 2014, Yang and co-workers reported the concept of IPOSCs to extend the absorption range with an N–I–P

device structure of indium tin oxide (ITO)/ TiO<sub>2</sub>/perovskite/BHJ/MoO<sub>3</sub>/Ag, as illustrated in Figure 5.<sup>[6]</sup> IPOSCs were made by coating an organic BHJ layer onto CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3-x</sub>Cl<sub>x</sub> perovskite layer directly, which used orthogonal solvents, allowing sequential deposition of the two photoactive layers. Here, both the perovskite layer and BHJ layer play the role of photoactive layers and charge transporting layers. Typically, the perovskite device with N-I-P structure using amorphous spiro-OMeTAD or PTAA as p-type hole transporting materials, which suffer from low mobility and conductivity of the pristine film and chemical doping are needed to increase its charge transport properties.[75-77] To fabricate IPOSCs, the replacement of the amorphous and wide bandgap hole transporting materials (HTMs) with efficient and high mobility dopant-free conjugated organic molecules HTMs are highly necessary, as the HTMs will play the role of photoactive donor materals in BHJ layer for IPOSC. That means, for an efficient IPOSC, the donor material in the BHJ layer must be an efficient dopant-free HTM. Recently, dopant-free HTMs have been developed and shown great potential for high-performance perovskite solar cells, thus pave the way for IPOSCs.<sup>[74,78-81]</sup> A charge generation and

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transport mechanism of IPOSCs was proposed by Yang and co-workers, as shown in Figure 5b. First, the perovskites are direct bandgap materials with ambipolar transporting properties and the exciton can be easily separated due to its weak exciton binding energy.<sup>[82]</sup> Second, the donor materials used in BHJ film can be a useful hole transport channel, thus holes generated in the perovskite film can transport through the donor materials based network and be collected by anode. Third, the electron that is generated from the separated exciton at the donor/acceptor interface in the BHJ film can transport through electron acceptor materials based network to the perovskite and be collected by cathode due to the high electron mobility of perovskite film.

The IPOSC using wide bandgap small molecule DOR3T-TBDT as donor in the BHJ layer exhibits a high efficiency of 14.3%. The photoresponse was extended to 900 nm when low bandgap polymer PBDTT-SeDPP was used as donor in the BHJ layer and an efficiency of 12.0% was achieved, combined with an improvement in  $J_{SC}$  from 19.3 to 21.2 mA cm<sup>-2</sup> (Figure 5d) in comparison with that of perovskite/PBDTT-SeDPP based device, where PBDTT-SeDPP was used as HTM. As shown in Figure 5e, the external quantum efficiency (EQE) data further confirmed that the improved photocurrent come from the IPOSC with low bandgap polymer PBDTT-SeDPP as donor in the BHJ layer, which deliver an onset photoresponse to ≈900 nm. However, the EQE data of perovskite device using low bandgap PBDTT-SeDPP as HTM shown no photocurrent response larger than 800 nm. The results indicate that the







**Figure 5.** a) Schematic structure of the IPOSC. b) Charge generation and transport mechanism of the IPOSC. c) *J*–V curves of perovskite/HTM photovoltaic device and perovskite/BHJ based IPOSC. d) EQE curves of the corresponding photovoltaic device and absorption spectra of perovskite/HTM and perovskite/BHJ films. e,f) Photoresponse of Perovskite/HTM and perovskite/BHJ based devices at e) 620 nm and f) 850 nm light pulse illumination. All panels reproduced with permission.<sup>[6]</sup> Copyright 2014, American Chemical Society.

IPOSCs with low bandgap BHJ layer can effectively broaden the photoresponse to NIR region, thereby increasing the  $J_{SC}$ and PCE of the devices. Another important finding in this work is that the HTMs, which have good light absorption ability in the N–I–P structure perovskite solar cells, did not contribute photocurrent to the photovoltaic device.<sup>[6]</sup> This finding was further confirmed by photoresponse measurements using a mono color light pulse at either 620 or 850 nm (Figure 5e,f).

A similar work with extended photocurrent response up to 900 nm was further reported in 2016 by Sun and co-workers, who integrated perovskite with a low bandgap small molecule based BHJ layer using a device structure of fluorine-doped tin (FTO)/c-TiO<sub>2</sub>/m-TiO<sub>2</sub>/(FAPbI<sub>3</sub>)<sub>0.85</sub>(MAPbBr<sub>3</sub>)<sub>0.15</sub>/BHJ/ oxide V2O5/Au, yielding improved photocurrent and efficiency.[83] PCEs of 14.8% and 12.3% were obtained for small molecule donor materials M3 and M4 as dopant-free HTMs, respectively. Sun et al. also found that the HTMs they developed show competitive absorption, but do not contribute to photocurrent, leading to low  $I_{sc}$  and efficiency. By adding PC<sub>71</sub>BM in HTMs forming the BHJ layer and careful interface optimization, the IPOSCs showed improved efficiencies of 16.2% and 15.0%, respectively. To evaluate the stability of IPOSCs, the aging tests for unsealed devices performed in ambient conditions (relative humidity (RH) ≈30%) showed that the IPOSCs exhibit poorer stability comparing with that of perovskite/HTM based devices, which was ascribed to the aggregation of PC71BM in BHJ laver.<sup>[84,85]</sup>

Efficient low bandgap organic semiconductor materials with matched energy levels and suitable mobility for BHJ layer are expected to maximize the light harvesting capacity and further

improve the device performance. As shown in Figure 6, Gao et al. made IPOSCs by using a low bandgap porphyrin-based small molecule as donor materials in BHJ layer and achieved a record PCE of 19.02%.[8] The IPOSC exhibits an extra light response in the NIR region from 800 to 875 nm with a  $\approx 40\%$ intensity, resulting in an increased JSC. Gao et al. found that the hole mobility of the BHJ is significantly enhanced from  $3.2 \times 10^{-5}$  to  $9.8 \times 10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> by adding [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PC<sub>61</sub>BM) to DPPZnP-TSEH (10:1) and further increased to  $1.6 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> when the PC<sub>61</sub>BM ratio increased to 4:1. Eventually, an optimized mobility of 2.6  $\times$  10^{-4}  $\rm cm^2~V^{-1}~s^{-1}$  was achieved with donor/acceptor ratio of 1:1. The increased hole mobility was ascribed to better morphology including increased porphyrin crystals and multilength scale morphology,<sup>[86]</sup> leading to higher FF and  $J_{SC}$  in the IPOSCs. Transient absorption spectroscopy (Figure 7f) shows that both BHJ and perovskite are simultaneously excited below the wavelength of 800 nm, indicating that the contribution of photocurrent from BHJ layer located in the entire absorption range and it make the BHJ layer photoconductive during operation, resulting in efficient and ultrafast charge transfer.

By integrating a BHJ layer based on low bandgap nonfullerene acceptor IEICO and wide bandgap polymer donor PBDTTT-E-T on a perovskite layer, Tan and co-workers reported a CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/PBDTTT-E-T:IEICO based IPOSC to harvest the long wavelength solar light.<sup>[87]</sup> The maximum wavelength for light harvesting of the IPOSC was extended to 930 nm, which is significantly wider than that of traditional MAPbI<sub>3</sub> based device (800 nm), thus sharply increasing the utilization of near infrared radiation. The IPOSC exhibits a PCE of



**Figure 6.** a) Chemical structure of **DPPZnP-TSEH**. b) Device structure of the organic photovoltaic (OPV)/perovskite hybrid solar cell. c) Energy level diagram of the related materials in the hybrid solar cell. d) *J*–V curves of the optimized hybrid solar cells with 110 nm thick BHJ film and the optimized perovskite solar cells (PSC) with Spiro-OMeTAD as HTM. e) EQE of the PSC using Spiro-OMeTAD as the HTM and EQE of the hybrid solar cell. f) Photoinduced absorption spectra of films at the pump-probe delay of 2 ps. Signal of BHJ were multiplied by five for visibility. All panels reproduced with permission.<sup>[8]</sup> Copyright 2017, WILEY-VCH.



**Figure 7.** a) Structures of PDPP3T and  $PC_{61}BM$ . b) structures for BHJ cell, perovskite cell, and IPOSC. c,d) *J*–V curves a) and EQE spectra b) for the BHJ solar cell, the perovskite solar cell and the IPOSC. All panels reproduced with permission.<sup>[9]</sup> Copyright 2015, Royal Society of Chemistry.



14.57%, coupled with an increased  $J_{SC}$  over 24 mA cm<sup>-2</sup>. One interesting finding by Tan et al. is that both donor polymer PBDTTT-E-T and nonfullerene acceptor IEICO can play the role of HTM in the BHJ layer, but the polymer PBDTTT-E-T functions much better than the IEICO. The EQE of the IPOSC shows photoresponse intensity exceeding 50% in the near infrared range, indicating a large contribution of photocurrent from NIR region.

#### 4.2. Inverted P-I-N Structure Devices

In 2014, Zuo and Ding first reported a P-I-N perovskite solar cells with expanded photocurrent response up to 970 nm by integrating a CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite layer and a low bandgap polymer PDPP3T ( $E_g = 1.33$  eV) based BHJ layer, as shown in Figure 7.<sup>[9]</sup> IPOSCs were prepared by coating a BHJ layer onto CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite layer. The optimized CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/PC<sub>61</sub>BM based control device exhibits a  $J_{SC}$  of 13.09 mA cm<sup>-2</sup>, a  $V_{\rm OC}$  of 0.90 V, an FF of 80.33%, and a PCE of 9.46%. The IPOSC with a PDPP3T: PC61BM ratio of 1:2 in BHJ film gave an inferior PCE of 6.63%, coupled with a  $I_{SC}$  of 12.67 mA cm<sup>-2</sup>, a  $V_{\rm OC}$  of 0.86 V, and an FF of 60.84% (Figure 7c). The PCE was further improved to 8.8% when PDPP3T:PC61BM ratio was 1: 4. As shown in Figure 7d, both perovskite and PDPP3T/PC61BM BHJ layer contribute to the photocurrent of the IPOSC. To deep understand the charge transport behavior and mechanism in the MAPbI<sub>3</sub>/ PDPP3T:PC61BM based IPOSCs, Zhang et al. reported a simple and effective way by using voltage biased EQE measurement and monochromatic light irradiating J-V measurement.<sup>[88]</sup> The photovoltaic cells exhibit a PCE of 5.15% for PDPP3T:PCBM based

BHJ device, 9.25% for the MAPbI<sub>3</sub> based perovskite device, and 8.92% for the MAPbI<sub>3</sub>/PDPP3T:PCBM based IPOSC. It is obvious that the IPOSC shows a broad photoresponse from 300 to 950 nm, which is ascribed to the combination of the two component cells. Comparing with BHJ device, Zhang et al. found that these IPOSCs offer a higher  $V_{\rm OC}$ , which is attributed to the reduction of thermalization loss.<sup>[88]</sup>

Recently, Kim et al. reported an IPOSC with P–I–N structure by optimizing the BHJ films with a ternary blended BHJ system comprising an NIR donor polymer, a fullerene derivative (PC<sub>71</sub>BM), and an n-type semiconducting polymer (N2200) (**Figure 8**).<sup>[89]</sup> The N2200 was used as an electron transport enhancer and diphenyl ether was used as a solvent processing additive, resulting in well-distributed bicontinuous networks and a high electron mobility of  $10^{-2}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. By introducing the BHJ film into the



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**Figure 8.** a) Device architecture of the P–I–N type IPOSC and chemical structures of the organic donor and acceptor materials: DT-PDPP2T-TT,  $PC_{71}BM$ , and N2200. b) EQE spectrum of a flexible IPOSC with a PET/ITO substrate. A photograph of the device is shown in the inset. All panels reproduced with permission.<sup>[89]</sup> Copyright 2016, WILEY-VCH.

IPOSC, the efficiency of the controlled perovskite solar cells was improved from 14.70% to 16.36% due to the increased  $J_{\rm SC}$  from 17.61 to 20.04 mA cm<sup>-2</sup>. Comparing with the control perovskite device, the IPOSC exhibit additional light harvesting in the NIR region from 800 to 920 nm, suggesting the integration of PSCs with NIR absorbing BHJs is an effective strategy for extending the light absorption bandwidth of the perovskites, thereby further improving the efficiency of photovoltaic devices. Interestingly, the IPOSCs exhibit almost identical Voc values (1.06 V) to the reference perovskite solar cells despite the BHJ based organic solar cells exhibiting a low  $V_{\rm OC}$  of  $\approx 0.67$  V. In this work, flexible IPOSCs (Figure 8b) using polyethylene terephthalate (PET)/ITO substrates were also fabricated and an optimized PCE of 12.98% was achieved, which is among the highest achieved efficiency for flexible photovoltaics.







**Figure 9.** a) Energy levels of the IPOSC. b) Cross-section SEM for the IPOSC without metal electrode. c) *J*–*V* curves of organic photovoltaic device, regular perovskite device, and IPOSC. d) EQE of the corresponding devices. e) The quasi-Fermi level splitting in perovskite layer and BHJ layer in the IPOSC at open circuit condition (top) and detailed band diagrams of electrons and holes of the IPOSC (bottom). All panels reproduced with permission.<sup>[7]</sup> Copyright 2017, American Chemical Society.

Hou and co-workers reported the enhancement of NIR photoresponse of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3-x</sub>Cl<sub>x</sub>-based perovskite solar cells by the integration of low bandgap BHJ absorbers.<sup>[90]</sup> The integration of a commercially available polymer PDPP3T and PCBM-based BHJ boosts the peak EQE by up to 46% in the NIR region (800-1000 nm). This substantial improvement in the EQE over the NIR region offers an additional current density of  $\approx 5 \text{ mA cm}^{-2}$  for the control perovskite solar cell, and a PCE of 12.2% was achieved for the IPOSC, combined with a  $I_{SC}$ of 22.9 mA cm<sup>-2</sup>,  $V_{\rm OC}$  of 0.93 V, and FF of 57.1%. The control perovskite device exhibits a relative low  $I_{SC}$  of 18.2 mA cm<sup>-2</sup>, a  $V_{\rm OC}$  of 0.89 V, and an FF of 63.6%, and thus a PCE of 10.3% was achieved. The enhanced  $J_{SC}$  for IPOSCs indicates that the photocurrent response in NIR region and the device performance of IPOSCs could be manipulated by screening low bandgap polymers in BHJ layers.

In 2017, Yang and co-workers demonstrated highperformance IPOSCs with P-I-N architecture by integrating NIR polymer PDTP-DFBT based BHJ layer on MAPbI<sub>3-x</sub>Cl<sub>x</sub>, leading to increased onset light absorption up to 900 nm (Figure 9).<sup>[7]</sup> The MAPbI<sub>3-x</sub>Cl<sub>x</sub> based reference perovskite device exhibits a PCE of 14.2%, which was further enhanced to 15.8% by integrating with the low bandgap BHJ layer due to the increased photocurrent by harvesting NIR light. One important finding of this work is that perovskite devices, not the organic photovoltaic devices, dominate the V<sub>OC</sub> of the IPOSCs. A quasi-Fermi level pinning model was proposed by Yang et al. to understand the working mechanism and the origin of the  $V_{\rm OC}$  of the IPOSCs (Figure 9e). By analyzing the energy alignment between perovskite and BHJ layer in the IPOSC, as shown in Figure 9e, Yang et al. found that the BHJ structure has an "effective quasi-Fermi levels" very similar to that of the perovskite's quasi-Fermi levels. The "quasi-Fermi level pinning" could only happen when the perovskite layer provides sufficient photogenerated charges to "pin" the quasi-Fermi levels in

the IPOSC structure. Because the  $V_{\rm OC}$  output is closely related to the quasi-Fermi level splitting in a solar cell, therefore, the pinning of the quasi-Fermi level of the IPOSC indeed allows this high  $V_{\rm OC}$  of the perovskite to be preserved. This finding indicated that the IPOSCs could harvest NIR light and further improve the photocurrent without sacrificing  $V_{\rm OC}$ , thus much higher efficiency that close even excess S–Q limit is possible.

## 5. Summary and Perspectives

In summary, IPOSCs face both great challenges and opportunities in photovoltaic performance for future commercialization. This kind of device has great potential to further improve the performance by combining the advantages of perovskite solar cells and NIR BHJ organic solar cells, as the low bandgap BHJ layer can provide additional light harvesting in the NIR region, resulting in enhanced photocurrent. Combining with the reserved high V<sub>OC</sub>, efficiencies that close even exceeding S-Q limit of single junction cell are expected by fully optimizing the perovskite layers and NIR BHJ layers through device engineering and the innovation of materials. So far, the lack of suitable NIR BHJ materials currently limits the development of IPOSCs. The low bandgap NIR donor or acceptor materials with high mobility and suitable energy levels for IPOSCs remain unexplored, and there is much room for performance enhancement in the IPOSCs. In addition, the BHJ layer with hydrophobicity could hinder the perovskite from the moisture interfusion and thus protect the perovskite film from decomposition, but the device stability study is still very limited and need to be addressed before commercialization in future. Finally, in principle, other active materials than the perovskite materials, as long as they could exhibits high ambipolar charge mobility, should be able to be used for the similar integrated devices. This might offer even a greater opportunity.

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## **Conflict of Interest**

The authors declare no conflict of interest.

## **Keywords**

charge transport, integrated solar cells, near-infrared solar cells, organic solar cells, perovskite solar cells

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