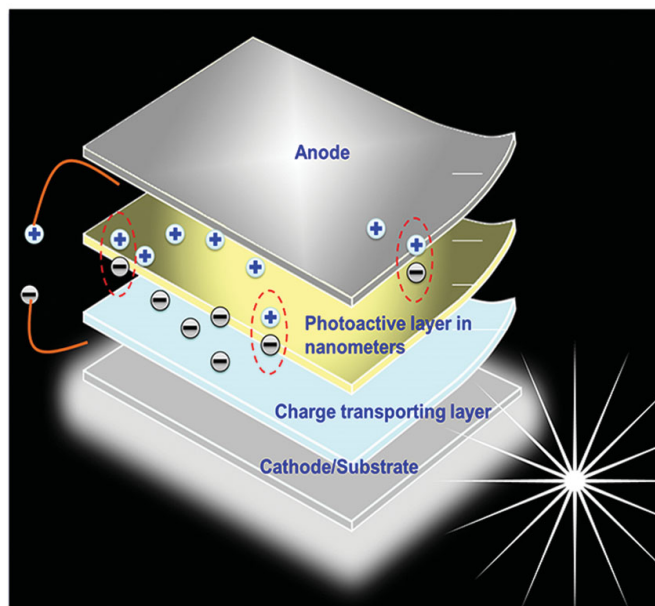


Recent Advances in Organic Photovoltaics: Device Structure and Optical Engineering Optimization on the Nanoscale

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Organic photovoltaic (OPV) devices, which can directly convert absorbed sunlight to electricity, are stacked thin films of tens to hundreds of nanometers. They have emerged as a promising candidate for affordable, clean, and renewable energy. In the past few years, a rapid increase has been seen in the power conversion efficiency of OPV devices toward 10% and above, through comprehensive optimizations via novel photoactive donor and acceptor materials, control of thin-film morphology on the nanoscale, device structure developments, and interfacial and optical engineering. The intrinsic problems of short exciton diffusion length and low carrier mobility in organic semiconductors creates a challenge for OPV designs for achieving optically thick and electrically thin device structures to achieve sufficient light absorption and efficient electron/hole extraction. Recent advances in the field of OPV devices are reviewed, with a focus on the progress in device architecture and optical engineering approaches that lead to improved electrical and optical characteristics in OPV devices. Successful strategies are highlighted for light wave distribution, modulation, and absorption promotion inside the active layer of OPV devices by incorporating periodic nanopatterns/nanostructures or incorporating metallic nanomaterials and nanostructures.

1. Introduction

Solar energy is the most abundant renewable energy source on earth and is ready for use in either direct form (solar radiation) or indirect form (biomass, wind, etc). The sun emits energy at a rate of 3.8×10^{26} W, while the Earth receives 1.74×10^{17} W (174 000 terawatts) of incoming solar radiation at the upper atmosphere, of which about 1.08×10^{17} W reaches the surface of the Earth and the rest is reflected back into space or absorbed by the atmosphere. Therefore, the solar energy received by the surface of the Earth in 90 min is more than the world's total annual primary energy consumption in 2012 ($\approx 5.6 \times 10^{20}$ J).^[1] In other words, the total annual solar radiation falling on the Earth ($\approx 3.4 \times 10^{24}$ J) is about 6000 times more than the total energy used worldwide. Among all kinds of approaches for solar energy utilization, photovoltaic technologies stand as one of the most attractive methods since they can directly convert sunlight into electricity through the photoelectric effect.^[2] The growth of photovoltaics has undergone a rapid development in the past two decades and is becoming a promising mainstream electricity source. As a result, global annual installations reached 40 GW in 2014 and the cumulative photovoltaic capacity reached 178 GW by the end of the year, approaching 1% of the world's current total electricity consumption of 18 400 TWh.^[3] As forecast by the International Energy Agency (IEA), the global PV capacity will reach ≈ 1 TW in 2040, equivalent to 15% of the total energy used worldwide at that time.^[4]

Nowadays, the best power conversion efficiency (PCE) of first-generation solar cells based on crystalline silicon (Si) and gallium arsenide (GaAs) have surpassed 25% and 29%,^[5] respectively, which are approaching the Shockley–Queisser limit of 30%.^[6] However, the very high cost of manufacture of the devices has been the limiting factor for the further manufacturing capacity scale-up and their wide adoption. On the other side, thin-film photovoltaics (PVs) are a much cheaper technology than the conventional crystalline PVs and are among one of the fastest-growing catalogs. It is worth noting that the efficiency for thin-film solar cells based on cadmium telluride (CdTe) or copper indium gallium selenide (CIGS) are now surpassing 20% and becoming the mainstream in current PV systems. However, CdTe or CIGS devices rely on the use of toxic/rare materials, which will also limit their mass production and practical application. Therefore, the development of low-cost, sustainable technology urgently needed in the PV industry.

In recent years, organic photovoltaic (OPV) devices have emerged as a promising alternative for producing clean and renewable energy, mainly owing to their abundant material resources, unique manufacturing advantages by solution processing techniques, and the compatibility with lightweight, flexible substrates and roll-to-roll manufacturing.^[7–15]

OPV devices rely on polymeric semiconductors for light harvesting, whose bandgap is determined by the energy difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels. As compared with inorganic semiconductors, polymeric semiconductors have much lower charge mobility and lower dielectric constants, but usually higher absorption

coefficients.^[16,17] These features enable OPV devices to absorb most of the incident photons by using a photoactive layer of tens to hundreds of nanometers, which in turn can effectively avoid several types of charge recombination. The polymeric semiconductors possess a π -conjugated backbone, which consists of repeated unsaturated units that can provide extended π orbitals (delocalized π electron systems) along the polymer chains. Upon photoexcitation, bound electron–hole pairs and the subsequent charge carriers can be generated and transported along the polymer chains.

Research into OPV devices has gone on a long journey. The fundamental physical processes occurring in OPV devices can be summarized as five essential steps: 1) Photon absorption. 2) Exciton generation. 3) Exciton diffusion and dissociation into free charges. 4) Charge carrier transport to the electrodes. 5) Charge carrier extraction and collection at the respective electrode. The optimization of each single step should lead to an overall enhancement in device performance. As early as 1986, Tang reported a bilayer OPV device with a PCE reaching 1%.^[18] Later, in 1992, Sariciftci et al. reported the discovery of ultrafast photoinduced electron transfer (within 100 fs) from conjugated polymer to a fullerene (C_{60}), which lay a foundation for the invention of bulk heterojunction (BHJ) structure OPV devices.^[19] Afterwards, the use of the BHJ configuration^[20] by blending conjugated polymer with fullerene or its derivative or nonfullerene acceptors^[21] has become the most popular material system for OPV devices, since the phase-separated nanoscale morphologies have often proven very beneficial for exciton dissociation and charge carrier transport.

The PCE of OPV devices is given by the following device parameters: open circuit voltage (V_{OC}), short-circuit current density (J_{SC}), and fill factor (FF). The PCE is equal to the product of these three parameters divided by the power intensity of incident light. Right now, the origin of V_{OC} of OPV devices is under debate,^[22,23] while empirically, the V_{OC} was found to be directly correlated with the difference between the LUMO of the acceptor and the HOMO of the donor.^[24] Consequently, it seems that one of the most promising strategies to enhance the V_{OC} is to deepen the HOMO of the donor by pushing it away from the vacuum level,^[22–27] or to shift the LUMO of the acceptor closer to the vacuum level,^[28–32] or a combination of both.^[33,34] Recently, we reported highly efficient single-junction OPV devices with

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PCEs exceeding 10%, which was achieved by using a newly synthesized narrow-bandgap semiconducting polymer with a deepened HOMO level^[35] in conjunction with control of the tail state density below the conduction band of the electron acceptor. As a result, the fundamental losses in the V_{OC} of OPV devices can be effectively alleviated and can be tuned over a wide range of 100 mV.^[36]

In principle, the maximal value of J_{SC} can be achieved by using low band gap polymers as light absorbers, increasing active layer thickness, and through the incorporation of metal nanoparticles, etc. However, too thick an active layer will result in a long transit time for charge transport and serve charge carrier accumulation, leading to limited charge collection efficiency in the devices and reduction in FF and consequent low PCE in thick devices.^[37] Alternatively, developing novel low-band gap donor materials, which can shift the absorption spectrum to longer wavelengths, have been demonstrated as one of the most common and successful strategies to enhance J_{SC} in the past few years.^[28,38–43] However, a gain in overall efficiency can be achieved only if an obvious decrease in V_{OC} is avoided.^[44]

In addition to attempt to maximize V_{OC} and J_{SC} in OPV devices, enhancement of the FF is also crucial for overall device performance. Compared with other two device parameters, FF is more sensitive and its reduction can be attributed to the poor electrical properties of solar cells such as low conductivity electrode materials, high series resistance,^[45] and non-ohmic contact at the interface between the photoactive layer and electrodes. On the other hand, increasing recombination losses that are associated with a combination of effects in the photoactive layer, such as low charge carrier mobility,^[46] unbalanced charge transport,^[47] and the presence of bulk and surface traps states^[48] are thought to be responsible for the reduction of FF.

In the past few years, as a result of increased knowledge for understanding the working principle of OPV devices,^[49–51] the development of a great variety of novel materials,^[10,14] the control over the nanoscale morphology of the photoactive layer,^[52–55] the optimization in device architectures and processing techniques,^[56–58] the PCE of the single junction devices has reached the 10% milestone^[59–62] while that of the tandem and triple-junction devices can be as high as 11–12%.^[63,64]

Given the rapid development in efficiency, OPV devices have become increasingly feasible for mass production and practical applications. Below we will review recent advances in the field of OPV, with special attention focused on the progress in novel device architectures and optical engineering approaches that lead to improved electrical and optical characteristics in OPV devices.

2. Toward Highly Efficient OPV Devices through Novel Device Architectures

In the journey of OPV research seeking for more efficient devices, apart from the efforts in developing new materials, intense attention has been also focused on the innovation of device structures to maximize the photovoltaic performance

of the resulting devices. In this section, we summarize the major research progress in the aspect of device structure design, which have primarily been obtained through the incorporation of a functional layer in a few to tens of nanometers.

2.1. Donor–Acceptor Bilayer Planar Heterojunctions

Early OPV devices consist of a donor–acceptor bilayer planar heterojunction that is responsible for charge separation and are usually fabricated in a sandwich geometry, between a transparent electrode and a back contact electrode. However, this device structure has been shown to be limited by the localized nature of photo-induced excitons, their much shorter diffusion length (10–20 nm) and the small contacting area between the donor–acceptor (D/A) interfaces. As a result, the device performances of OPV devices based on bilayer planar heterojunction is usually not comparable with that of the BHJ devices. On the other hand, the D/A interfacial area in bilayer OPV devices can be effectively enlarged by thermal annealing, resulting in a more inter-winding nanostructure.^[65] Recently, Zhao et al. reported that after thermal annealing, the PCE of a bilayer OPV cell based on PTB7/PC₇₁BM reached 3.26%, while the non-annealed devices only showed a PCE of 1.81%.^[66] Moreover, a correlation between the interfacial area and PCE was established, where the interfacial area was obtained by using the p/n junction model while the junction capacitance of the D/A interface was measured by AC perturbation.

Similarly, Yang et al. reported thermally annealed bilayer heterojunction OPV devices with superior device performance than that of the blend-solution-processed BHJ devices.^[67] The best device based on P3HT/PC₆₁BM bilayer structure showed an external quantum efficiency approaching 82%, a high FF of 74%, and a PCE of 5.1%, while the BHJ structure showed a PCE of 4.6%. The enhanced performance was attributed to the formation of a richer PC₆₁BM domain close to the cathode upon thermal annealing, thus a significantly reduced bimolecular recombination loss was clearly observed.

Aiming at addressing the problem of inefficient inter-diffusion of acceptor molecules into donor phase and the thin donor layer could not fully absorb the incident photons, Park et al. developed a new approach for bilayer film deposition, which was realized through an evaporation of solvent through surface encapsulation and induced alignment of polymer chains by applied pressure (ESSENCIAL) process.^[68] The resulted film formed well-organized nanodomains and showed improved crystallinity, leading to much better charge carrier transport properties, and consequently a lower recombination coefficient and high internal quantum efficiency approaching 100% in a certain spectral range. Consequently, the devices based on this new bilayer-like heterojunction nanostructure show a high PCE of 4.71% (with a J_{SC} of 13.83 mA cm⁻², a V_{OC} of 0.51 V, and a FF of 66.98%, respectively), while the thermally annealed BHJ device showed a PCE of 3.27% (with a J_{SC} of 9.38 mA cm⁻², a V_{OC} of 0.59 V, a FF of 58.96%, respectively).

Besides the above mentioned approaches, a highly efficient bilayer polymer/fullerene OPV device can be fabricated by delicately controlling the processing conditions. Seok et al. recently reported efficient bilayer solar cells by utilizing nanoscale heterojunction in a PCDTBT/PC₇₁BM bilayer configuration, in which the interfacial area was maximized through the formation of non-planar heterojunction.^[69] The construction of the sequentially deposited bilayer (SD-bilayer) was achieved by adding an ordering agent (OA), for example, 1 vol% of 1,8-Diiodooctane (DIO), to the polymer solution. The incorporation of OA was found to be able to improve the ordering of the PCDTBT chains and prevent the deposited PCDTBT film from dissolving by the subsequently spin casting PC₆₁BM solution. The formation of a nanoscale non-planar heterojunction was achieved by adding a heterojunction agent (HA), for example, diiodomethane (DIM), to the PC₇₁BM solution. The HA enabled the conformal deposition of the PC₇₁BM layer atop of the PCDTBT layer, forming a non-planar heterojunction with large area for efficient exciton dissociation. It is important to note that the approach resulted in a PCE of 7.12%, with an internal quantum efficiency (IQE) of over 90%, which is comparable to that of a BHJ device.

2.2. Ternary OPV Devices

Over the years, significant research efforts have been devoted to the development of low-band gap polymers that can extend absorption range and harvest more solar photons. However, as mentioned above, the V_{OC} of the resulting OPV devices usually decrease as well, which means the enhanced light harvest in low-band gap polymer-based OPV devices is inevitably accompanied by a reduction in V_{OC} . To address this problem, a smart strategy has been proposed to extend the spectral responsivity of wide band gap polymers to the near infrared (IR) region by incorporating multiple or complementary absorber donors. Generally, this type of OPV device comprises either two or more polymer donors and a fullerene acceptor, or one polymer donor and two or more fullerene acceptors, known as ternary OPV devices.

Khlyabich et al. demonstrated ternary OPV devices that containing two P3HT analogues, namely high-band-gap poly(3-hexylthiophene-co-3-(2-ethylhexyl)thiophene) (P3HT₇₅-co-EHT₂₅) and low-band gap poly(3-hexylthiophene-thiophene-diketopyrrolopyrrole) (P3HTT-DPP-10%) as donor polymers, while phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) was used as electron acceptor.^[70] When the ratio of the three components was varied, the V_{OC} increased as the amount of P3HT₇₅-co-EHT₂₅ increased. The dependence of V_{OC} on the polymer composition for the ternary blend regime was found to be linear when the overall polymer:fullerene ratio was optimized for each polymer:polymer ratio (Figure 1). Meanwhile, the J_{SC} of the devices based on ternary blend was superior than those of the binary blends based devices because of the complementary polymer absorption, as verified by the external quantum efficiency measurements. When the composition ratio between P3HTT-DPP-10%:P3HT₇₅-co-EHT₂₅:PC₆₁BM s was fixed at 0.9:0.1:1.1, the obtained

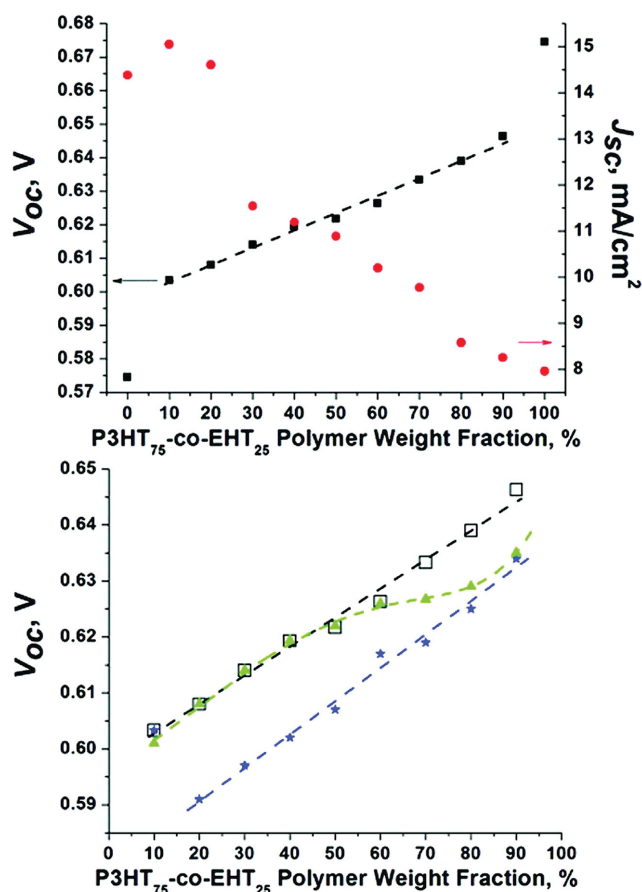


Figure 1. a) V_{OC} (black ■, left axis) and J_{SC} (red ●, right axis) for individually optimized ternary blend BHJ OPV devices containing different fractions of P3HT₇₅-co-EHT₂₅. b) V_{OC} for individually optimized ternary blend OPV devices (□) and cells with fixed overall polymer:PC₆₁BM ratios of 1:1.1 (blue ★) and 1:1.0 (green ▲). Reproduced with permission.^[70] Copyright 2009, American Chemistry of Society.

ternary solar cells showed a PCE of up to 5.51%, mainly due to the intermediate V_{OC} , increased J_{SC} and high FF, exceeding those of the corresponding binary blends (3.16% and 5.07%, respectively).

In 2012, Yang et al. reported a kind of parallel-like BHJ OPV device that incorporating two donor polymers with different band gaps as the donors and PC₆₁BM as the acceptor. In this ternary-blend system, donor-polymer-linked channels and fullerene-enriched domains were responsible for charge transport.^[71] Owing to the parallel-like junction in these BHJ OPV devices, most of the photo-generated charge carriers inside the device were successfully collected by the electrodes. As a result, the ternary devices fabricated at all compositions showed higher J_{SC} values when compared to the binary devices. For example, the highest J_{SC} of ternary-blend devices is 14.1 mA cm⁻², which is about 16% and 10% higher than those of binary devices. Moreover, the authors found that the reported parallel-like BHJ OPV devices worked very well at any composition of the two donor polymers, regardless of their various HOMO levels. Meanwhile, the V_{OC} of the ternary devices is approximately equal to the average of the individual voltages of the sub cells, while the FF remained nearly as high as that of the binary devices, implying that the proposed

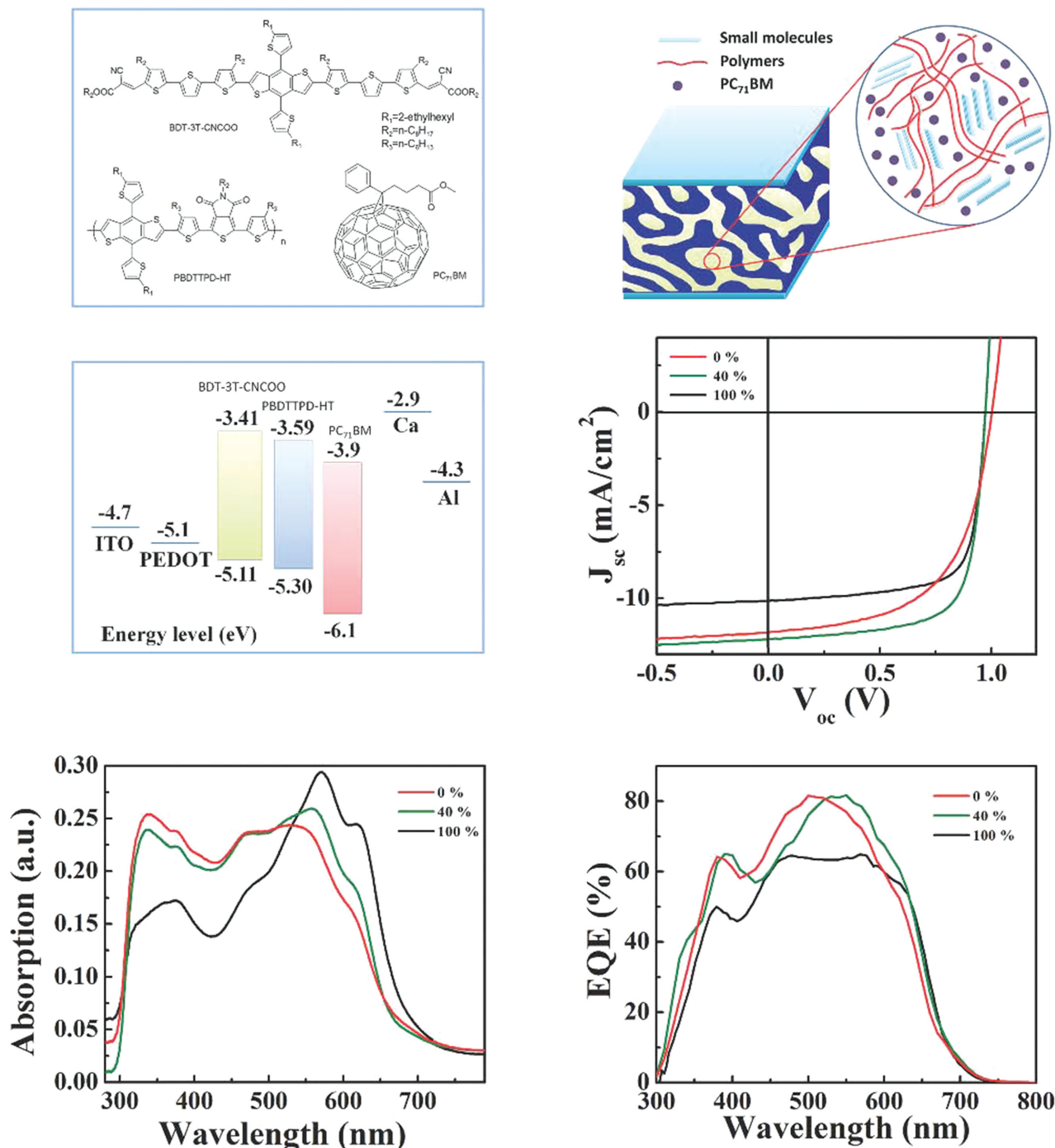


Figure 2. a) Chemical structures of BDT-3T-CNCOO and PBDTTPD-HT, PC₇₁BM. b) Illustration of the active layer of ternary OPV devices, in which the addition of small molecules increased the crystallinity of the donor phase. c) Energy levels of electrodes and active layer materials used in ternary blend OPV devices. d) *J*-*V* curves of the ternary OPV devices with BDT-3T-CNCOO ratio of 40%, small molecule-based binary OPV devices (labeled as 100%) and polymer-based binary OPV devices (labeled as 0%). e) UV-vis absorption spectra of the active layer corresponding to the same composition as in (d). f) EQE curves of the OPV devices corresponding to the devices in (d). Reproduced with permission.^[72] Copyright 2014, WILEY-VCH.

device can be a successful method to obtain high performance OPV devices. When a binary weight ratio of 1:1 between the large band gap polymer and small band gap polymer was used, the optimized device showed a highest PCE of 7.02% (with a $J_{SC} = 13.7 \text{ mA cm}^{-2}$, $V_{OC} = 0.87 \text{ V}$ and FF = 58.9%).

Highly efficient ternary OPV devices can be also fabricated by using polymer and small molecule donor as the

key components. Recently Zhang et al. reported a new type of ternary OPV devices which contain a high performance polymer PBDTTPD-HT (Figure 2a), and a newly designed small molecule (Figure 2a) with high crystallinity.^[72] The most notable effect in this ternary OPV device system is that the small molecules can increase the crystallinity of the donor phase and the fraction of the small molecules in the blend

can play an important role in tuning the domain size of the resulted films (Figure 2b). As a result of extending absorption coverage and the formation of favorable nanostructures for charge generation and collection, the obtained optimal ternary OPV exhibits a very high efficiency of 8.40% (with a V_{OC} of 0.969 V, a J_{SC} of 12.17 mA cm⁻², and a FF of 71.23%), which is much higher than that of binary systems based on small molecules (7.48%) or polymers (6.85%). As polymers and small molecules is complementary to each other in nature, a rational design and selection of donor materials should further improve the efficiency of OPV devices of this type.

More recently, Yang et al. studied the structural, electronic and photovoltaic characteristics of several ternary BHJ OPV systems and proposed the design rule for this kind of device.^[73] Aiming at covering a broader section of the solar spectrum, each of the multi-polymer/fullerene blend systems contained a high-band gap polymer and a low-band gap polymer with sufficient structural compatibility (with similar crystallinity and molecular orientation). As evidenced by the photoluminescence spectra data, the authors excluded the exciton energy transfer process as the major working mechanism for the ternary BHJ OPV devices and concluded that the devices work like two parallel connected devices. As expected, ternary BHJ devices show superior device performance, with a maximal PCE of 8.7% in a ternary (PTB7:PBDTT-SeDPP=1:1):PC₇₁BM device, which is significantly higher than those made from its individual donor materials. Furthermore, a four-donor BHJ solar cell with a reasonable performance of 7.8% (V_{OC} = 0.70 V, J_{SC} = 17.3 mA cm⁻² and FF = 64.6%) was demonstrated, indicating mixing two or more donor materials with structural compatibility into one BHJ OPV can be a successful strategy to obtain high performance OPV devices with wide photoreponse range.

Besides acting as photosensitive donor material, the incorporation of a third component, especially polymers with high charge mobility can also be very beneficial to device characteristics. For example, recently Liu et al. reported a novel method to enhance the efficiency of OPV devices by introducing a small amount of high-mobility conjugated polymer as an additive in a polymer donor/fullerene acceptor blend.^[74] The authors showed that upon the addition of 0.5 wt% poly[2,5-bis(alkyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione-*alt*-5,5'-di(thiophene-2-yl)-2,2'-(*E*)-2-(2-(thiophen-2-yl)vinyl)thiophene] (PDVT-10), whose hole mobility is on the order of 10 cm² V⁻¹ s⁻¹, the PCE of the resulted OPV devices based on increased from 8.75% to 10.08%. The observed enhancement was ascribed to the improved charge transport properties and longer carrier lifetime in the devices. In addition to the high charge mobility of the added polymer, the authors also verified that its similar HOMO level to that of the donor material is critical to the enhancement.

Emerging ternary OPV devices thereby represent a very promising approach to broaden the absorption spectrum of the existing OPV devices, where the light harvesting properties of the photoactive layer, as well as the device performance, are effectively enhanced. In this regard, optically complementary materials, including low band gap

polymers, small molecules, dyes or nanoparticles can be promising candidates as the third component for BHJ polymer: fullerene solar cells. Besides being complementary in optical absorption, the third component is desired to have sufficient structural compatibility (with similar crystallinity and molecular orientation), thus the resultant film can form an ideal phase-separated nanoscale morphology for efficient exciton dissociation and charge carriers transport or can be optimized readily with the presence of additive or annealing. Moreover, the third component should form a cascade band structure in the OPV devices to avoid the trapping of carriers in the blend. Meanwhile, incorporation of high mobility components has proven to be very beneficial for charge transport in BHJ polymer:fullerene solar cells. Therefore, in the ideal case, simultaneously enhanced J_{sc} , and FF can be achieved and a net increase in PCE is reached in these ternary systems.

To date, the most efficient ternary OPVs exhibited a PCE of over 10%, while appropriate selection of the third component should further enhance the performance of the resultant devices toward even higher efficiency. On the other side, it deserves more research efforts in order to gain a more comprehensive understanding into the working mechanisms and develop more and more suitable materials with better compatibility for this type of device.

2.3. Electrode Interface Engineering and Novel Inverted-Type OPV Devices

In general, OPV devices are fabricated on a glass/ITO substrate, which is used as an anode and coated with thin film of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS) for hole transporting. To manipulate the energy level alignment between the photoactive layer and electrode to ensure an ohmic contact for electron transport and collection, a low work function metals such as Ca or Al was usually used as the back contact metal electrode. In order to facilitate charge transport and collection, a great variety of functional materials have been developed and incorporated between the photoactive layer and electrode as the interfacial layer (with a thickness between a few to tens of nanometers). OPV devices therefore present a stacked thin film architecture, with a basic device structure in which photo-generated holes are collected by the bottom electrode, while electrons are extracted by the metal electrode. On the other hand, the electrical polarity of electrodes in OPV devices can be reversed by various surface modification approaches. On this basis of the revised electrode devices, many inverted type OPV devices have been developed and we have witnessed a rapid progress of this type of OPV device. It is important to note that such an inverted type device architecture is superior to the conventional structure in many aspects. For example, the inverted type device can offer a much better ambient stability by avoiding the use of either a corrosive or hygroscopic PEDOT:PSS layer or reactive metals which are extremely sensitive to oxygen and moisture. In addition, the use of inverted device structure can take advantage of the spontaneous inherent vertical phase separation in the

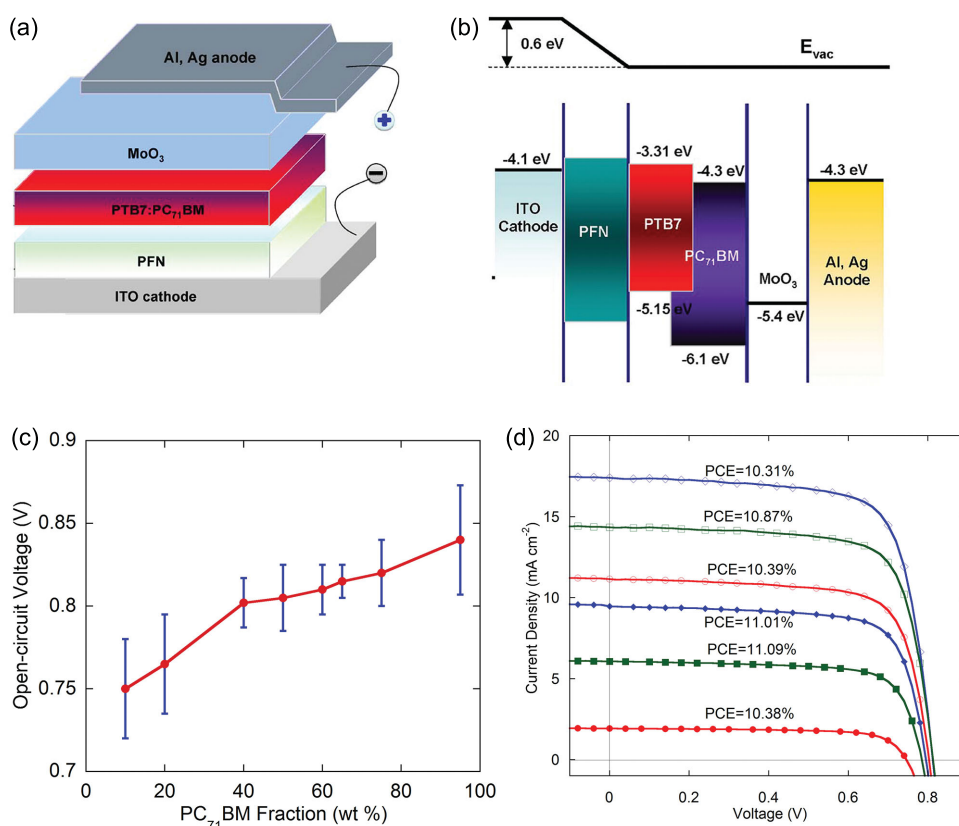


Figure 3. a) Illustration of the inverted type OPV device, in which the photoactive layer is sandwiched between PFN-modified ITO cathode and Al, Ag based top anode. b) Schematic energy level of the inverted device at flat band condition (under open-circuit voltage). Reproduced with permission.^[83] Copyright 2012, Macmillan Publishers Limited. c) Device parameter V_{OC} deduced from $J-V$ measurement. Experimental error bars represent one standard deviation from a set of ten experimental measurements for each type of device. d) $J-V$ characteristic of device with 65wt% PC₇₁BM in the active layer tested under different illumination conditions, as obtained from standard AM 1.5G (1000 W m⁻²) illumination using a set of neutral optical filters. Reproduced with permission.^[36] Copyright 2015, Macmillan Publishers Limited.

active layer, resulting in a better energy level alignment with numerous photoactive materials.

In order to fulfill inverted structure OPV devices, early reports focused on the use of a thin layer of metal oxide or alkali metal salt, such as titanium oxide (TiO_x),^[75] zinc oxide (ZnO)^[76] and cesium carbonate (Cs₂CO₃)^[77] as the electron transporting layer for efficient electron collection. However, the deposition of these thin layers from metal oxides or alkali metal salts involved annealing at high temperature, which is not compatible with roll-to-roll manufacturing techniques. Besides, various solution-processed materials, including self-assembled crosslinkable fullerene,^[78,79] polar molecules,^[80] and conjugated polymers or conjugated polyelectrolytes^[81–83] were also employed as ITO surface modification interlayers for inverted type OPV devices. Owing to their unique processing properties from water or alcohol solution and their orthogonal solubility in commonly used organic solvents, the use of these interlayers may open a new avenue toward the realization of all-solution-processed OPV devices.

In 2010, Na et al. reported the development of inverted OPV devices through engineering an ITO surface with a thin layer (a few nanometers) of an alcohol-soluble conjugated polyfluorene polyelectrolyte by solution spin coating.^[82] As indicated by Kelvin probe studies, the work function of the ITO substrate decreased from 4.66 eV to 4.22 eV upon the

incorporation of the thin layer, ascribed to the formation of a favorable interfacial dipole.

In 2012, our group demonstrated a simple but effective device configuration for inverted type OPV devices (Figure 3a), in which a thin layer of water/alcohol-soluble poly [(9,9-bis(3-(N,N-dimethylamino) propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN) was used as a modification layer atop the ITO surface.^[83] Furthermore, we found that this type of inverted structure can promote device characteristics optimization in both the optical and electrical aspects. In addition to providing ohmic contact for electron collection by lowering the work function of ITO from 4.7 eV to 4.1 eV (Figure 3b), the inverted solar cell can also enhance incident light absorption in the photoactive layer when compared to the normal device. The enhanced light absorption is also supported by the calculation results from the optical modeling based on one-dimensional transfer matrix formalism (TMF) and the experimental reflectance spectra. The resulting device showed a certified PCE of 9.214% and very good device stability. It should be noted that this strategy to enhance efficiency is also applicable to many other typical donor materials. Very recently, we applied this strategy to based devices from a newly synthesized low bandgap polymer, poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b'] dithiophene-co-3-fluorothieno[3,4-b]thiophene-2-carboxylate] (PTB7-Th) and

demonstrated highly efficient single-junction OPV devices with a PCE exceeding 10%.^[36] Our devices showed an even higher efficiency ($\approx 11\%$) when illuminated under relatively lower light intensity conditions (0.3–0.5 sun illumination). In addition, we found that the fundamental losses in the V_{OC} of the devices can be effectively alleviated and modulated over a wide range of 100 mV if tail states density below the conduction band of PC₇₁BM and the disorder degree of the blend were reduced.

In addition to the widely used water/alcohol soluble conjugated polymers for inverted devices, Liu et al. reported the synthesis of a series of metallopolymer with pendent amino groups at the side chain and their applications for high-performance inverted PSCs.^[84] From a practical point of view, this new interlayer has some unique advantages over many other traditional water/alcohol soluble conjugated polymer catalogs, such as higher electrical conductivity and improved electron transport properties. Therefore, the fabricated inverted OPV devices can tolerate a thicker interlayer and work very well even when the thickness varies in a wider range. The best inverted OPV exhibited PCE of 9.11% with an optimized thickness (≈ 11 nm), while the efficiency was still maintained at 8.64% if a thicker interlayer of 19 nm was used.

Besides the applications of the above mentioned materials as electrode interlayers for OPV devices, recently the material catalog has expanded to other newly emerging materials. In 2014, Li et al. reported the use of a new conductive fulleropyrrolidinium iodide (Bis-OMe FPI) as electron transporting layers in highly efficient inverted OPV devices.^[85] These ETLs exhibit high conductivity, orthogonal solvent processability, and good ability in tuning the work function of device substrate. The resulted inverted device showed a very high PCE of $\approx 9.6\%$. More interestingly, unlike many other efficient inverted that can use ultrathin interlayers due to their low conductivities, the performance of the devices can work very well even with thickness of the electron transporting layer up to 50 nm, which suggests the related thin layer can find practical applications in the fabrication of large-area devices.

The potential of other electrode interfacial materials, such as small molecules, have been extensively investigated for OPV devices in all kinds of device configurations. Zhang et al. demonstrated highly efficient inverted OPV devices in which two alcohol-soluble organic small molecules (FBF-N and FTBTF-N) was employed as the interlayer.^[86] Upon the introduction of thin layer of BF-N and FTBTF-N, the work function of ITO substrate decreased by ≈ 0.3 eV, reaching 4.10 eV and 4.06 eV, respectively, as measured by ultraviolet photoelectron spectroscopy (UPS) for coated ITO substrates. The results indicated that both FBF-N and FTBTF-N can be promising cathode interfacial modification layer for efficient devices. With FBF-N as the cathode interlayer, the inverted PSCs exhibited an average PCE of 7.85% ($V_{OC} = 0.75$ V, $J_{SC} = 15.67$ mA cm⁻², and FF = 66.62%), while an average PCE of 8.93% ($V_{OC} = 0.74$ V, $J_{SC} = 17.30$ mA cm⁻², and FF = 69.85%) was reached for FTBTF-N based devices.

Unlike some other inorganic materials, nanocrystals of metal oxides such as TiO_x and ZnO, can be processed via solution based technology and the corresponding thin films

can be deposited through a sol-gel process at low temperature, which is very beneficial for low-cost, large area size fabrication. Liao et al. reported a simple and novel method for modification of ZnO nano-film as the cathode interlayer for inverted OPV devices through dual doping with the novel fullerene derivative (BisNPC60-OH) and indium (InCl₃) simultaneously.^[87] In this novel InZnO-BisC60-based cathode interlayer, dual gradient concentration profiles exist for two dopants, but in opposite distributions. The doping in the ZnO nano-film not only resulted in an improved surface conductivity (by a factor of 270), but also an enhanced electron mobility (by a factor of 132). Furthermore, the authors demonstrated a record high efficiency of 10.31% in single junction OPV devices.

Similarly, novel electron transport layer can be obtained from n-doped, cross-linkable fullerene derivatives. Chang et al. reported the doping of conductive fullerene by using solution-processable tetrabutylammonium iodide (TBAI) as an effective n-type dopant.^[88] The TBAI-doped fullerene film showed reasonable electrical conductivity (2.8×10^{-3} S cm⁻¹), relative weak thickness-dependent performance property, and moderate cross-linking temperature (≈ 140 °C), which can be classified as an ideal electron transport layer for OPV devices. As expected, with the introduction of the ETL, the fabricated OPV devices delivered an improved PCE of 8.8% for single junction devices and 10.1% for double-junction tandem devices, respectively. Equally important is that the cross-linking process is handled at moderate temperature (≈ 140 °C), thus making the ETL compatible with the fabrication of PSCs on flexible substrates. Therefore, the authors further demonstrated the fabrication of flexible PSCs, with a record high PCE of 9.2%.

In short, in the past few years many novel inverted types of OPV devices have been established, in which the thin layers from novel interfacial materials play an important role. With this successful device structure, all-solution-processed, efficient OPV devices have become increasingly feasible in large area sizes and/or on many types of flexible substrates. The chemical structures of the representative materials for ternary blend OPV devices and electrode interfacial materials for inverted type OPV devices are summarized in **Figure 4**.

2.4. OPV Devices with Thick Active Layers of Hundreds of Nanometers

Usually, the optimized active layer thickness in OPV devices was determined on the basis of empirical results. As a result, typical OPV devices were fabricated with an active layer thickness of around 100 nm, at which it is adequate to absorb most of the incident photons because of their very high absorption coefficients. On the other side, recent detailed studies on the influence of active layer thickness on the short-circuit current density and efficiency revealed that thicker OPV devices ($\approx$ hundreds nanometers) can result in a very high short-circuit current density and can simultaneously meet the requirements for low-cost, high-throughput

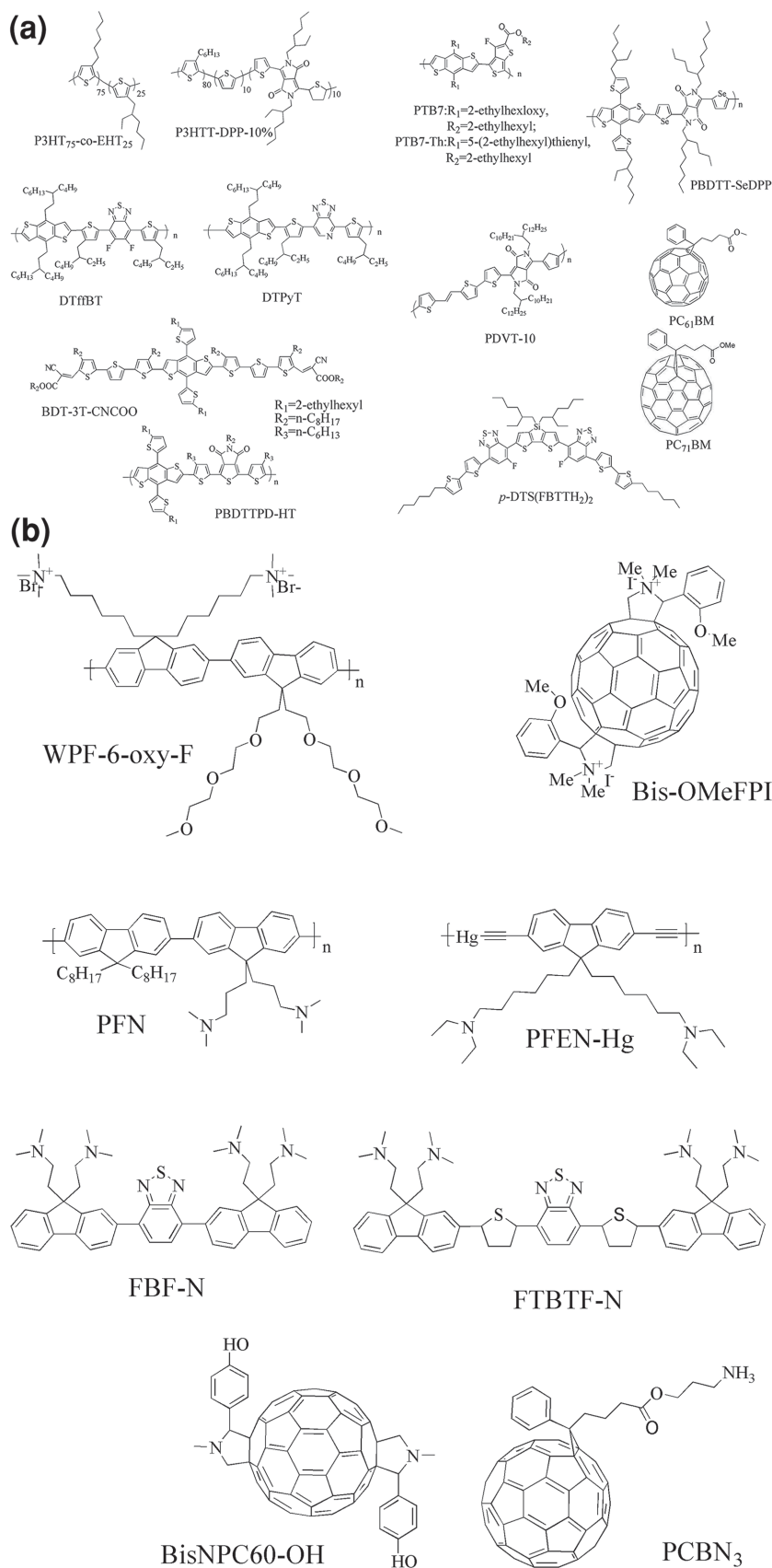


Figure 4. The chemical structures of a) representative materials for ternary blend OPV devices and b) electrode interfacial materials for inverted type OPV devices.

production techniques, i.e., roll-to-roll printing methods with high reproducibility,^[89] in which large thickness variations (up to hundreds of nanometers) in the active layer should be tolerated. However, increasing the thickness of the active layer may also lead to a rapid reduction in fill factor and the overall efficiency as a result of increasing charge recombination loss. To overcome this difficulty, it is crucial to develop various novel polymers with high charge mobility. In this section, we summarize recent progress on the development of OPV devices based on a thick active layer.

In 2011, You's group reported the design and synthesis of two new polymers incorporating benzodithiophene (BnDT) as the donor and either benzotriazole (HTAZ) or its fluorinated analog (FTAZ) as the acceptor.^[89] The obtained polymers possess high hole mobility and low-lying HOMO energy levels, with a medium band gap of 2.0 eV. The hole mobility for the PBnDT-FTAZ: PC₆₁BM blend was found to be around $1 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is at the same order of magnitude for P3HT:PC₆₁BM blends. With a thick layer thickness of 250 nm, the devices showed a remarkable PCE of 7.1% (with a V_{OC} of 0.79 V, a J_{SC} of 12.45 mA cm^{-2} , and a FF of 72.2%, respectively). Moreover, even with an unprecedented active layer thickness of 1 μm , the device can also deliver a high PCE of 6%, which was mainly attributed to the increased hole mobility in the fluorinated polymer.

More recently, Janssen's group reported the synthesis of a new diketopyrrolopyrrole-based semiconducting polymer and its application as a promising electron donor for thick active layer devices.^[90] The resulting OPV devices show a high fill factor up to 0.74 and PCEs above 6% for active layers between 100 and 300 nm, while the highest PCE of 6.9% was reached when a 220 nm thick film was used. The observed performance is consistent with the measured hole and electron mobilities of DT-PDPP2T-TT (0.8 and $1.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively), indicating a balanced charge transport in the DT-PDPP2T-TT:PC₆₁BM blends. Besides the high charge mobilities, nano-scale morphology consisting of tightly interconnecting and crossing crystalline fibrous structures with lengths of hundreds can be clearly observed, which are very beneficial for providing sufficient charge transporting pathways.

In order to further enhance the hole mobility in benzothiadiazoles-based polymer, Chen et al. proposed a new strategy to develop a low band gap D-A conjugated polymer FBT-Th₄(1,4), in which 5,6-difluorobenzothiadiazole (FBT) and quarterthiophene (Th₄) was incorporated as the A-unit, and D-unit, respectively.^[91] Owing to the strong interchain aggregation behavior of chains, FBT-Th₄(1,4) show very high FET hole mobilities up to $1.92 \text{ cm}^2 (\text{V s})^{-1}$, which is among the highest values for fluorinated BT-based conjugated polymers reported to date. As expected, the devices based on showed a high PCE of 6.5% and a weak dependence on active layer thickness in wide range (from 100 to 440 nm), while the highest PCE of 7.64% was achieved when a 230-nm thick active layer was used. The results clearly demonstrated that these types of high mobility donor polymer can be a promising candidate for large-area OPV devices fabricated via solution printing technology.

Proper aggregation and morphology control in the above-mentioned type donor polymers have been shown to be crucial for achieving even higher efficiency. Liu et al. report the realization of record high efficiency (up to 10.8%, with fill factors of $\approx 77\%$) OPV devices by manipulating the temperature-dependent aggregation behavior of the donor polymers during the film-forming process.^[59] Moreover, owing to the high molecular ordering and the high hole mobility ($\approx 1.5\text{--}3.0 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), the devices with thicker film ($\approx 300 \text{ nm}$) can also exhibited high performance, while the state-of-the-art PTB7-based materials systems only perform well when the active layer was around $\approx 100 \text{ nm}$.

We also note that recently Woo et al. also demonstrated a clear molecular design strategy toward semi-crystalline polymers with high, balanced hole and electron mobilities, highly ordered organization and favorable film morphology.^[92] With the presence of processing additive and methanol, the devices based on the resulted polymer showed a PCE up to 9.39% in a 300 nm thick conventional device structure.

Small molecular donor-based OPV devices with relative thicker active layer thickness are also very attractive. Recently Sun et al. reported the synthesis of a newly designed benzodithiophene terthiophene rhodanine (BTR) and its application as a molecular electron donor material for highly efficient OPV devices with PCEs > 9%.^[93] The incorporation of the side chains endowed the molecule liquid crystalline (LC)-like property, which results in strong intermolecular interactions in the film and concomitant high hole mobilities up to 0.1 and $1.6 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, as measured by organic field-effect transistor (OFET) and space-charge-limited current (SCLC) methods, respectively. Thus, the devices showed a maximal PCE of 9.3%, with a very high FF of 77%. It is also worthy to note that the devices with thick active layers (300–400 nm) could still afford high efficiency over 8%, which makes the reported small molecules particularly promising for practical applications.

2.5. Organic Tandem Solar Cells and Multiple-Junction Devices

In the past few years, organic tandem solar cells have been demonstrated as the most effective approach to obtain high efficiency, in which two or more sub-cells based on different band gap semiconductors are stacked together by interconnection layers to harvest complementary portions of the solar spectrum. To ensure efficient exciton dissociation, the active layer of each sub-cell should be sufficiently thin while the overall device thickness needs to be thick enough to achieve complete absorption. Furthermore, in order to achieve high PCE, a balanced consideration on light harvest (for high J_{sc}), matched electronic structure (for high V_{oc}), and charge transporting properties (for high FF) should be implemented. In an ideal case in which the front cell and back cell were fabricated from semiconductor with a band gap of $\approx 1.6 \text{ eV}$ and $\approx 1.0 \text{ eV}$, respectively, the obtained tandem cell can deliver an efficiency above 15%. Furthermore, an efficiency of up to 22.3% is achievable for a triple-junction solar cells in case of FF = 0.6 and EQE = 65%.^[94] Therefore, tandem photovoltaic

devices represent a promising route to realize the most efficient OPV devices.

In general, tandem photovoltaic devices rely on using semiconductors with complementary absorption ranges as photoactive materials in each sub-cells. In recent years, there have also been some attempts to fabricate so-called homogenous tandem solar cells, in which an identical photoactive layer was used in each sub-cell. This type of tandem solar cell is expected to improve the net absorption and thus enhance the PCE. However, the early study of homogenous tandem solar cells did not show superior device performance, mainly due to the lack of an appropriate low band-gap polymer donor-material system and non-ideal interconnecting layers which joined the sub-cells together.

In 2013, the Yang group employed a promising low band gap (< 1.4 eV) PDTP-DFBT as an electron donor for tandem solar cells, in which two identical sub-cells were electrically connected by a graded interconnecting layer ($\text{MoO}_3/\text{modified-PEDOT:PSS}$ (M-PEDOT:PSS)/ ZnO).^[95] As compared with that of the single junction devices, the maximum absorption in visible region of the tandem cells increases from 70% to 90%, resulting in a significantly improved PCE (from 8.1% in single junction to 10.2% in tandem cells), demonstrating tandem cells based on identical photoactive layers can be an effective approach to obtain high efficiency as in traditional tandem solar cells.^[63] The authors also found that internal quantum efficiency and the filling factor of the tandem cells are much higher than those of the single junction devices with the same thicknesses of the active layer, suggesting that the tandem devices with identical sub-cells are indeed an effective way to increase the absorption while maintaining the charge transfer and collection abilities.

Aiming at simplifying the device structure, Kang et al. report the introduction of a self-organized recombination layer for homogenous-tandem solar cells, as obtained through a one-step nano-composite solution process from an organic nanocomposite consisting of photoactive PTB7-Th:PC₇₁BM blends and a non-conjugated polyethyleneimine (PEI).^[96] The devices were in a simplified four-layer tandem structure, where a single PEDOT:PSS thin film (≈ 20 nm) plays the role of recombination interlayer. Moreover, the device structure takes advantage of the spontaneous vertical phase separation in the active layer which occurred when the nano-composites were spin cast atop a bare ITO substrate. It was found that a self-organized PEDOT:PSS/PEI recombination layer and ITO/PEI cathode were formed during this one-step nano-composite solution process (**Figure 5**). As a result of the thicker photoactive layers in the tandem cells (200 nm vs. 80 nm for a single junction cell), minimal optical loss owing to high transmittance in the UV-Visible spectra range and the efficient processes for charge separation and collection, the tandem cells showed a very high PCE of 10.8%.

In addition to incorporating PEDOT:PSS as the recombination layer for tandem cells, a thin layer of conjugated polyelectrolyte, in combination with a metal oxide, such as ZnO or TiO_x, were also been applied to achieve highly efficient devices. In 2015, Zhou et al. realized homogenous-tandem solar cells with remarkable efficiency of 11.3% by using pH-neutral conjugated polyelectrolytes as the p-type

hole transporting layer and ZnO as the n-type electron transporting layer, and PTB7-Th as the donor material, respectively.^[97] The estimated internal quantum efficiency in both types of device were found to be very close to each other, indicating that the charge extraction efficiency in the tandem cells remains as high as that of the single-junction cells. On the other side, compared with that of the single-junction solar cells, the tandem cells exhibited a 25% enhancement in efficiency which mainly arises from their more efficient light harvest.

Recently, Choy et al. reported a new metal-oxide based recombination layer structure of all-solution processed metal oxide/dipole layer/metal oxide for efficient tandem solar cells are demonstrated. The dipole layer modifies workfunction (WF) of molybdenum oxide (MoO_x) to eliminate pre-existed counter diode between MoO_x and TiO_2 .^[98] Three different amino functionalized water/alcohol soluble conjugated polymers (WSCP)s have been studied to show that the WF tuning of MoO_x is controllable. Their results show that thermionic emission within the dipole layer plays a critical role for helping recombination of electrons and holes, while the quantum tunneling effect is weak for efficient electron and hole recombination. This is based on the recombination layer structure and poly(4,8-bis(5-(2-ethylhexyl)-thiophene-2-yl)-benzo[1,2-b:5,6-b']dithiophene-alt alkylcarbonylthieno[3,4-b]thiophene) (PBDDTTT-C-T) based homo-tandem OPV devices. The obtained homogenous-tandem solar cells showed a high Voc of 1.54 V with a high PCE of 8.11%, which is a 15.53% enhancement as compared to its single cell. The results indicate that this metal oxide/dipole layer/metal oxide interconnecting layer (ICL) provide a new strategy to develop other qualified ICLs with different hole transporting layer and electron transporting layer in tandem OPV devices.

3. Achieving Efficient OPV Devices through Optical Engineering on the Nanoscale

As an optical system with an architecture consisting of stacked thin films of tens to hundreds of nanometers, the performance of OPV devices is critically dependent on the optical properties of each thin layer. In the past decade, more and more research has been directed towards light management (in-coupling and propagation) in these devices through many optical engineering approaches. In this section, we highlight the recent advances of OPV devices from optical optimization aspects, and special attention will be paid to successful strategies, which modulate the light wave distribution inside the active layer at the nanoscale.

3.1. Optical Spacer Layer for OPV Devices

For common OPV devices, the total thickness of all of the active layers is around several hundred nanometers, which is shorter than or comparable to the wavelength of incident light photons. Therefore, the propagation of incident light in the OPV devices is dramatically dependent on the optical

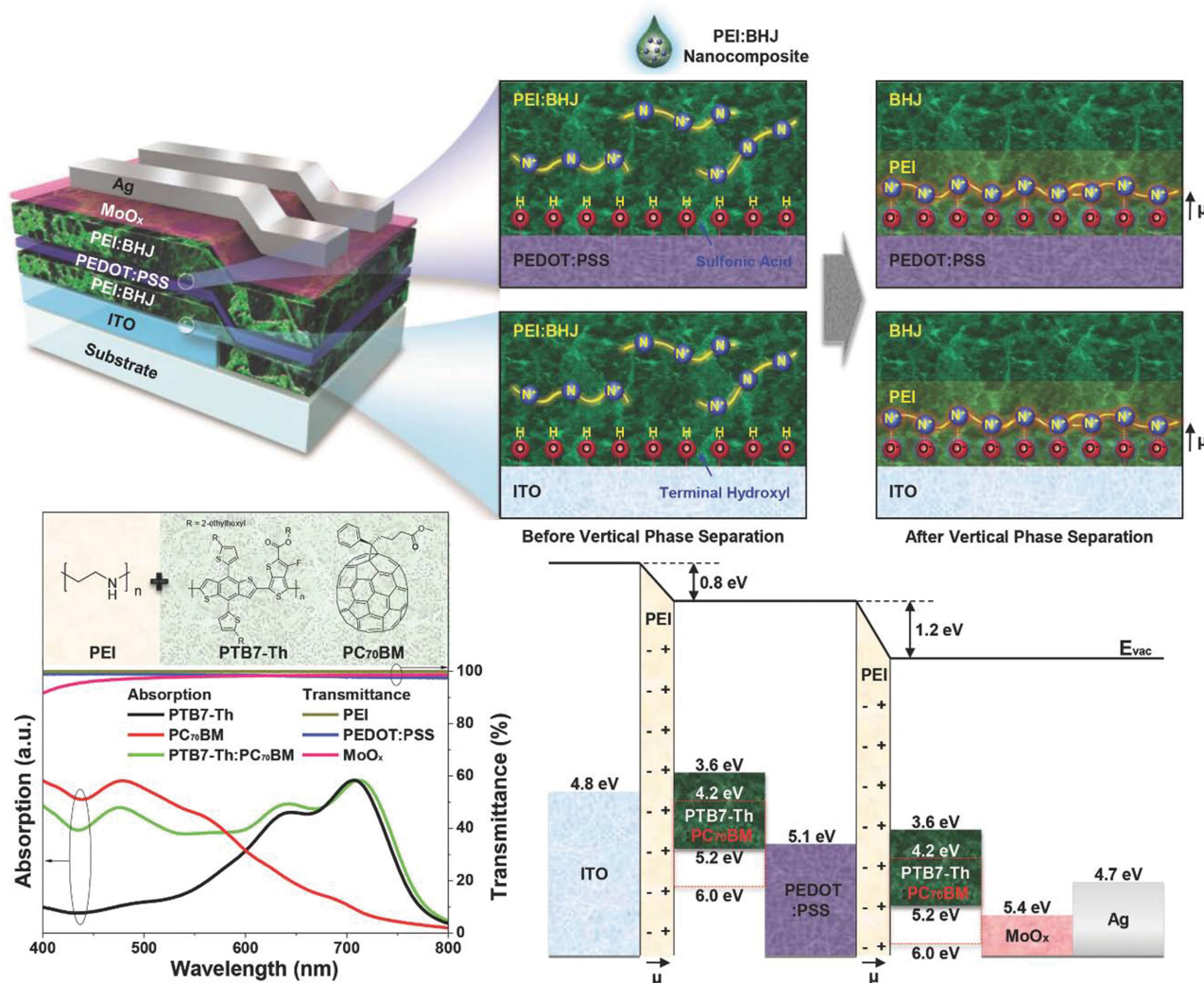


Figure 5. a) Tandem structure containing only four component layers (left) and conceptual diagrams for the PEI:BHJ nanocomposite self-organization on the PEDOT:PSS and ITO surfaces (right). b) Chemical structures and optical properties of the component materials. c) Energy-level diagram of the tandem solar cell. Reproduced with permission.^[96] Copyright 2014 WILEY-VCH.

properties and the thickness of each layer,^[99–102] as well as the device structures.^[83,103]

So far, indium tin oxide (ITO) is the most widely used transparent electrode for OPV devices as a result of its high optical transparency (>85% in the visible spectrum) and low sheet resistance (10–20 Ω/sq for 100–200 nm thick film). However, ITO films are brittle, which may limit their application as electrodes for flexible substrates. Furthermore, the deposition of ITO films is usually costly, which may further prohibit their use in mass production.

In recent years, tremendous efforts have been focused on developing alternative materials for transparent electrode, including conducting polymers,^[104,105] carbon nanosheets or graphene,^[106,107] new types of transparent conducting oxides,^[108] metal nanowires,^[109] metal grids,^[110] and ultra-thin metal films.^[111,112] Amongst all of these, the ultra-thin metal films represent the most promising candidate due to their outstanding properties in terms of low sheet resistance, and robust mechanical flexibility. However, the optical transparency of typical thin metal films in the UV–visible range is too

low for transparent electrode applications. To surmount this obstacle, an anti-reflective coating can be applied to enhance the far-field transparency of thin metal films through a triple-layer (in a sandwich architecture of capping layer/metal film/interfacial layer) electrode structure, in which the capping layer can be a metal oxide,^[113] sulfide,^[114] small-molecule^[115] or even polymer.^[116] Moreover, the whole set of these films can be readily deposited on a great variety of substrates with excellent mechanical flexibility.^[117] Given these competitive advantages over ITO, ultra-thin metal films can be tailored by capping layer and be used as promising alternatives to replace ITO as transparent electrodes for the mass production of OPV devices. Especially, Ag and Cu are usually the metal of choice where transparency, conductivity, abundance of material resources and production cost are the driving considerations.

Aiming at achieving broadband absorption enhancement, Sergeant et al. demonstrated the use of a tri-layer electrode with a structure of MoO₃/Ag(5–20 nm)/MoO₃ for OPV devices.^[118] The MoO₃/Ag/MoO₃ transparent electrode

can create a resonant optical cavity in the photoactive layer, whose optical width is tuned by adjusting the film thickness and can thus coherently trap light for more efficient light harvest. As a result, the Ag thin film (≈ 6 nm)-based electrode can deliver a PCE of 4.4%, as high as that in ITO based OPV devices.

In addition to Ag, a thin layer of Cu is also a promising candidate for the aforementioned tri-layer electrode. However, the far-field transparency of Cu thin film in the UV–visible spectrum is not high enough, which limits its application as a transparent electrode for organic photonic devices. Recently, Hutter et al. reported a new type transparent electrode based on a bilayer structure consisting of Cu (8 nm) and tungsten oxide (WO_3 , 20 nm) films for OPV devices.^[119] The absolute transmittance of the resultant electrode between 550 and 900 nm was found to be improved by 22%. Moreover, the sheet resistance of the electrode was only 10–20 Ω/sq for 100–200 nm thick films, which may be attributed to the low resistance of the ultra-thin Cu film (8 nm) itself, the use of (3-aminopropyl)-trimethoxysilane (APTMS) and (3-mercaptopropyl)trimethoxysilane (MPTMS) as a mixed molecular adhesive layer, and the doping of the WO_3 during layer caused by the diffusion of Cu. With this novel electrode, the authors further demonstrated that the resulting device performed as well as the devices employing an ITO electrode, resulting in a PCE of 6% in an inverted structure.

Besides the above mentioned multilayer electrode structure, resonant optical cavities for enhanced light absorption can be formed by coupling highly reflective, transparent metal thin film, i.e., an ultrathin Ag film, with anti-reflecting, top-capping spacer layer. Using this strategy, Chen et al. fabricated an optical microcavity by using a top-illuminated configuration in which an opaque Ag film and a semitransparent, ultrathin Ag film were employed as a bottom layer and top-capping light in-coupling layer, respectively.^[120] On the basis of results from optical simulations, the authors further proposed the use of tellurium oxide (TeO_2) thin layer as the top-capping optical spacer because of its relatively high refractive index ($n = 2.2$). The calculation showed that when a configuration of active layer (65 nm)/Ag (14 nm)/ TeO_2 (35 nm) is used, an optimal value of J_{SC} ($\approx 16 \text{ mA cm}^{-2}$) can be obtained, which is obviously higher than that of the device based on the ITO electrode ($\approx 13 \text{ mA cm}^{-2}$). Consistent with the optical calculation, the fabricated devices with this ITO-free microcavity structure on glass and flexible plastic substrates showed high PCE of 8.50% and 7.07%, respectively.

When compared to the above mentioned planar geometry structure, implementing a nano-structured pattern on inorganic dielectric materials in a dielectric/metal/dielectric (DMD) multilayer electrode system can more efficiently harvest incident photons from all directions.^[121,122] Ham et al. reported a novel design of polymer/metal/dielectric (PMD) multilayer transparent electrode for OPV devices, in which a hybrid polymer with low refractive index ($n = 1.45$), known as Ormoclear, was used as the bottom layer.^[123] Having a similar refractive index to a glass substrate ($n = 1.52$), the incorporation of the polymer provided the PDM structure with a high optical transmittance ($>88\%$). Moreover, the transmittance is almost independent of the polymer layer in a wide thickness

range (from 0 to 1000 nm, even up to 80 micrometers). Besides the excellent optical properties, the obtained electrode exhibits low sheet resistance (4.8 ohm sq^{-1}), makes it a good candidate for high performance polymer solar cells. Indeed, the devices based on the Ormoclear/Ag/ WO_3 electrode showed a PCE of 7.63%, mainly because of an enhancement in J_{SC} by 10%.

In the meantime, the introduction of suitable interfacial layers as optical spacers between the active layer and electrodes can provide a straightforward method to effectively modulate the distribution of the optical field in the device, which can potentially improve the device performance of OPV devices. For instance, Tan et al. reported high performance PSCs by using solution-processed rhenium oxide (s-ReOx) as the anode buffer layer from methyltrioxorhenium (VII) isopropanol solution.^[124] As compared with the devices with PEDOT:PSS layer, the PSCs with s-ReOx anode buffer layer showed improved efficiency, which mainly arises from additional absorption within the photoactive layer, especially in the wavelength range of 400–550 nm. The optical simulation results from the transfer matrix method confirmed that the incorporation of the s-ReOx layer resulted in a redistribution of the electric field of the incident light in the active layer and a concomitant increase in light absorption. Moreover, the simulations results are in good agreement with the spectral response and the measured J_{SC} of the devices.

3.2. Optical Management in Organic Tandem Cells

The stacked structure of two or more sub-cells with complementary absorption in series or parallel has proven to be an effective approach to achieve high efficiency photovoltaic devices. Apart from the selection of suitable donor materials, acceptor molecules, and interconnection layers, the optical properties and the thicknesses of each sub-cell and the interconnection layer are also very important for determining the overall device performance. In this regard, the active layers and the interconnection layers must be carefully designed in order to ensure optimized performance. Prior to the fabrication of organic tandem cells with complicated methods, it is necessary to apply a transfer matrix method, or a rigorous coupled wave analysis (RCWA) method to simulate the optical absorption in the device to can fully exploit the optimal efficiency potential for a given set of sub-cells combinations.

For example, the Janssen group reported a high performance triple junction solar cell with efficiency up to 9.64%, in which a wide band-gap polymer PCDTBT with PC_{71}BM blend and a newly designed small band-gap copolymer PMDPP3T with PC_{61}BM were used as the active layer for the front cell, and for the middle and back cells, respectively.^[125] The high complementarities of the absorption spectra of the active layers are expected to achieve high photovoltaic performance in tandem and triple configurations. Starting with tandem cells which consist of PCDTBT: PC_{71}BM and PMDPP3T: PC_{61}BM sub-cells, optimization in the sub-cell thicknesses resulted in a high PCE of 8.9%. To further improve the efficiency of OPV devices, multiple junctions

device structure may be very useful by adding more photoactive layers, creating a triple-junction cell with a 1+2 configuration, and so on. However, this motivation toward multiple junction devices is limited by the minimum of the J_{SC} through each sub-cell, especially which of the front cells are from a wide band-gap material. To circumvent this problem, the authors proposed to split the sub-cell based on a small band-gap material into two separate cells, namely a middle and back cell. In practice, to ensure the two separate cells absorb an equal number of photons, and thus produce a balanced photocurrent between the sub-cells, the authors performed electrical-optical simulations prior to the device fabrication. On the basis of the simulation results, an increased efficiency in such 1+2 triple-junction cells is predicted. Moreover, the optimal thicknesses for each sub-cell (125, 95, and 215 nm for the front, middle, and back cells, respectively) is given and used for device fabrication. Indeed, the resultant devices based on the 1+2 triple-junction architecture showed a PCE of 9.6% by exploiting the excess photons through the introduction of the additional sub cell.

From a theoretical point of view, organic multiple junction devices can further deliver even higher PCE if photoactive layers from an optimal combination of band gaps with broad differences are used. Recently, the Yang group reported the design for a highly efficient triple-junction solar cell, in which three materials with different energy band gaps were employed as electron donors.^[64] To obtain a balanced photocurrent in each sub cell, the authors selected donor materials with band gaps on the order 1.9, 1.58, and 1.4 eV for front cell, middle cell and back cell, respectively. With this optimal combination of band gaps and optimized thicknesses (160, 110, 85 nm), based on the calculated results from modeling simulations, a highly efficient triple-junction solar cell with a PCE of 11.55% was achieved, while the combination of sub cells with non-optimized thickness (200, 100, 100 nm) only produced a PCE of 8.74%.

More recently, Yusoff et al. reported fully solution-processed inverted double-junction and triple-junction OPV device by making full use of band gap engineering.^[126] In the tandem architecture, the front cell close to the transparent conducting electrode ITO consists of the wide band gap absorbing donor, in conjunction with a medium band gap absorbing donor, thieno[3,4-b]thiophene/benzodithiophene (PTB7) (**Figure 6**). The inverted tandem cells cover the solar spectrum with wavelengths λ from 300 to 800 nm, with a high PCE of $10.39 \pm 0.03\%$. Furthermore, a third cell based on more narrowband gap material was added, thus forming a triple-junction OPV device with a 1 + 1 + 1 configuration. The best triple-junction cell showed a PCE of $11.83 \pm 0.02\%$, with a V_{OC} of $2.24 \text{ V} \pm 0.01 \text{ V}$, a FF of $67.52 \pm 0.03\%$, and a J_{SC} of $7.83 \pm 0.03 \text{ mA cm}^{-2}$, suggesting huge potential for multi-junction OPV device research.

In summary, optical management plays an important role in organic tandem cells. To ensure optimized performance of the tandem devices, each of the serially connected sub-cells should deliver nearly identical photocurrent. Therefore, in principle all sub-cells should absorb the same amount of incident photons. This can be realized through the careful selection of suitable donor materials, acceptor molecules

and interconnection layers. To fulfill this goal, one of the most commonly used and effective approaches is the application of optical simulation. Through proper optical simulations, the absorption and propagation of incident light in each functional layer can be described quite precisely. By varying the layer thicknesses for a given set of materials, the optimum layer thicknesses can be determined, while at the same time the matched photocurrents in both sub-cells can be maintained.

3.3. Light Trapping and Plasmonic Design for Highly Efficient OPV Devices

The intrinsic problems of short exciton diffusion length and low carrier mobility in organic semiconductors creates a challenge for OPV devices designs for achieving both optically thick and electrically thin device structures to achieve sufficient light absorption and efficient electron/hole extraction. For instance, in common device structure, the active layer region of OPV devices is very thin, which is typically a few hundred nanometers,^[127] thus limiting the incident light absorption efficiency. It is desirable to find ways to enhance the light absorption in active layers while maintaining thin device structures.

Among various techniques for absorption promotion, light trapping designs are adopted in OPV to enhance the light harvesting without physically increasing the thickness of the OPV active layer. The light-trapping scheme can be classified as geometric design and plasmonic design. The geometric designs exploit various periodic patterns and structures other than plasmonic effects such as anti-reflection structures,^[128,129] periodic textures,^[130,131] and random structures (e.g., random microspheres,^[132] random wrinkles.^[133] In plasmonic design, the plasmonic effects are induced by incorporating metallic nanomaterials and nanostructures into different layers of the OPV devices and the performance is enhanced as a result. In this section, the plasmonic-enhanced light harvesting will be discussed and recent advances in plasmonic optical effects in carrier transport layer, active layer, electrodes and dual plasmonic structure will be reviewed.

Plasmon is a collective oscillation of free electrons when the sample with the metal structure is irradiated by the incident electromagnetic waves such as light, which can be used to confine the electromagnetic waves that are of the same order of magnitude as, or even smaller than, sub-wavelength. The strong interaction between electromagnetic wave and surface plasmons of either metallic nanomaterials (i.e., Ag and Au nanoparticles, nanorods, and nanoprisms, etc.) or nanostructures (i.e., nanogratings, and nanoarrays) can cause either enhanced absorption or scattering of light.^[134,135] There are two classes of plasmonics effect—surface plasmon polaritons (SPPs) and localized surface plasmon polaritons (LSPPs). The SPPs are electromagnetic waves propagating along the metal-dielectric or metal-air interface, which are confined at the interface with an exponentially decayed intensity away from the interface.^[135] On the other hand, the LSPPs are the oscillation of non-propagating conduction electron in nanometer-sized curved metallic structure under

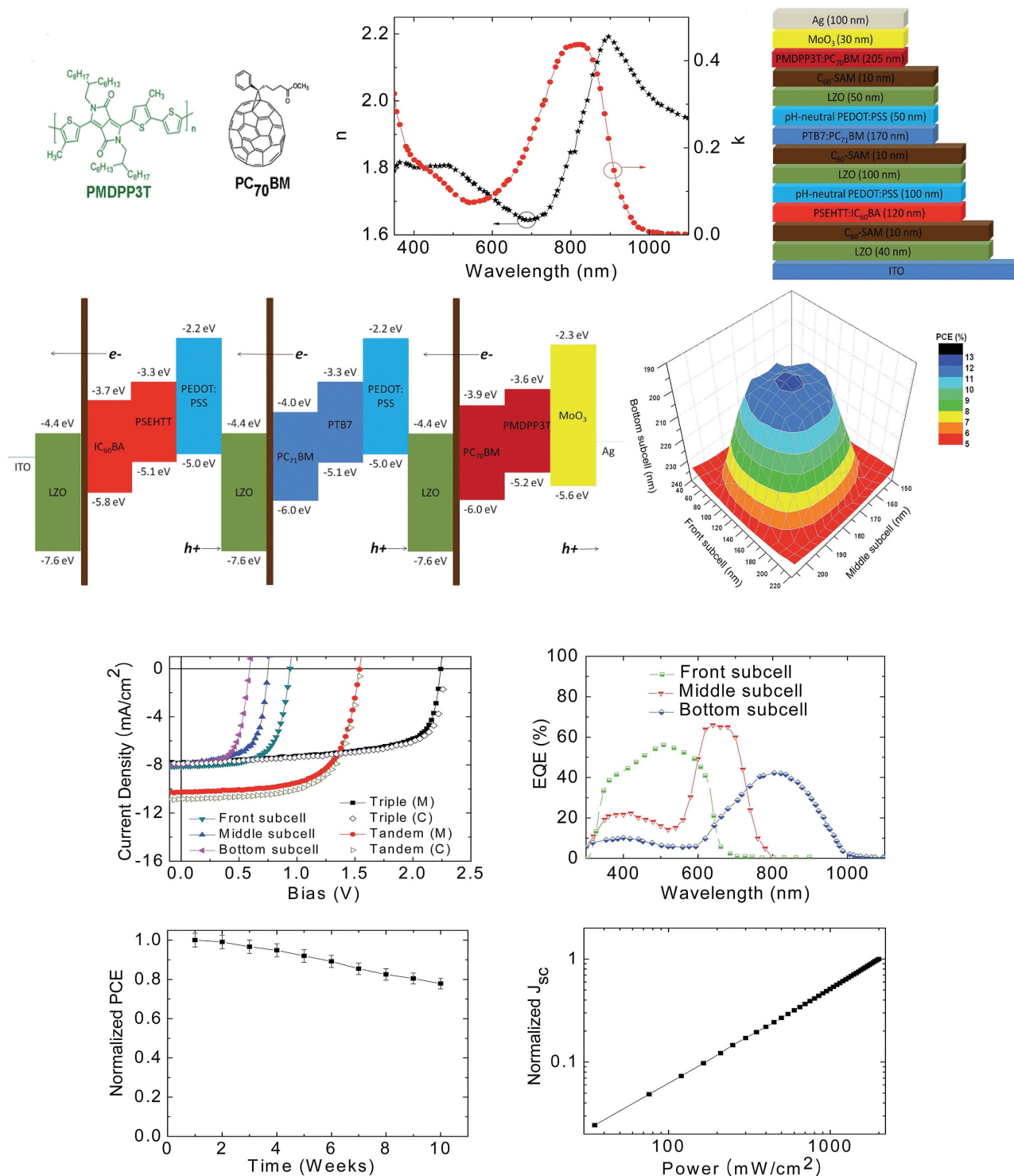


Figure 6. a) Molecular structures of the near infrared absorbing copolymer PMDPP3T, and PC₇₀BM fullerenes. b) Optical parameters n and k for PMDPP3T:PC₇₀BM. c) Inverted triple-junction solar cells: ITO/LZO/C₆₀-SAM/PSEHTT:IC₆₀BA/pH-neutral PEDOT:PSS/LZO/C₆₀-SAM/PTB7:PC₇₁BM/pH-neutral/LZO/C₆₀-SAM/PMDPP3T:PC₇₀BM/MoO₃/Ag. d) Energy band diagram of inverted triple-junction solar cells. e) Predicted efficiency of inverted triple-junction solar cells as functions of the thicknesses of the PSEHTT:IC₆₀BA front subcell, the PTB7:PC₇₁BM middle subcell, and the PMDPP3T:PC₇₀BM bottom subcell. f) J - V curves of front, middle, bottom, tandem and triple-junction cells under air mass (AM) 1.5G illumination (25 °C, 100 mW cm⁻²). g) EQE measured under relevant bias illumination conditions. h) Stability of the inverted triple-junction cells over 10 weeks. i) Normalized (to the value obtained at 2000 mW cm⁻²) J_{sc} of inverted triple-junction cells as a function of illumination intensity. Inverted triple-junction cells show a linear dependence on the illumination intensity up to 2000 mW cm⁻². Reproduced with permission.^[125] Copyright 2014, Royal Society of Chemistry.

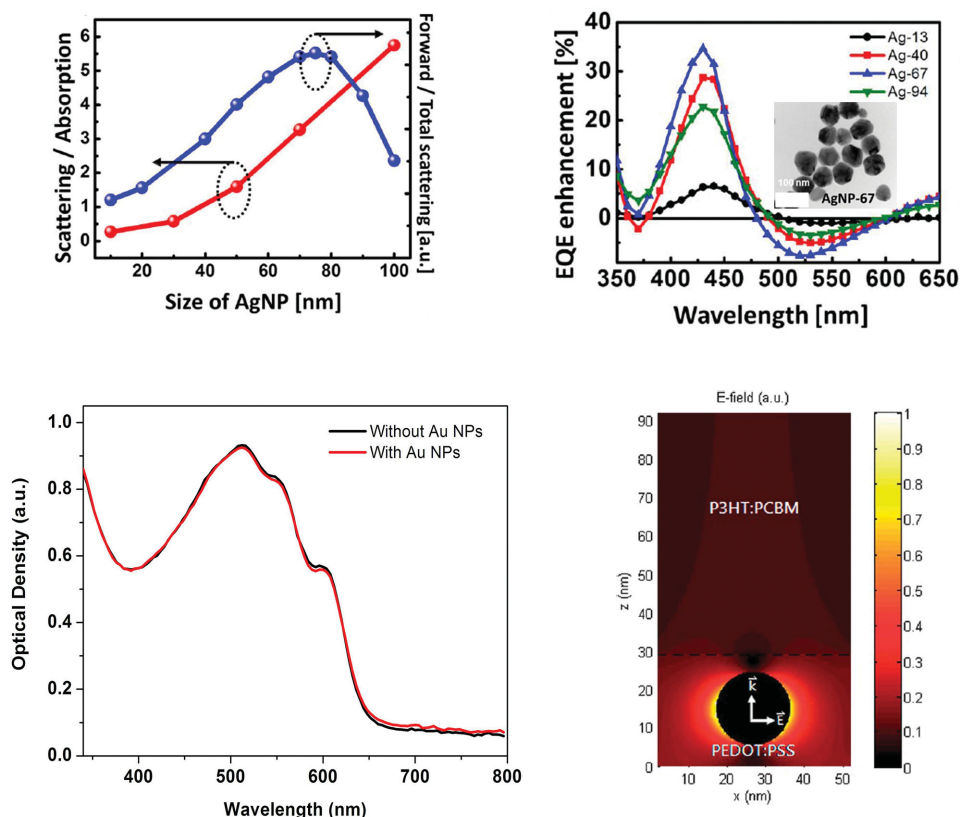


Figure 7. a) Theoretically-obtained ratio of total scattering power to total absorption power value for various sizes of Ag NPs (red) and ratio of forward scattering to total scattering of a spherical Ag NP in PEDOT:PSS (blue). b) The EQE enhancement of devices with various sizes of the incorporated Ag NPs. The inset shows TEM images of Ag NPs with a size of 67 nm. Reproduced with permission.^[150] Copyright 2013, Nature Publishing Group. c) Optical density of PEDOT:PSS/P3HT: PC₆₁BM film with or without Au NPs incorporation (0.32 wt%), d) theoretical electric field profile in the PEDOT:PSS:Au NPs/P3HT: PC₆₁BM device. Reproduced with permission.^[136] Copyright 2011, The Royal Society of Chemistry.

electromagnetic wave illumination. The effective restoring force of the conduction electrons generated by curved surface of the metal nanoparticles enables the resonance to appear at a specific wavelength which is independent from the electromagnetic wave vector.^[135] The device performance was enhanced through incorporating various metal nanomaterials (such as nanoparticles (NPs), nanorods, nanowires, nanocubes, nanoplates, nanodisks and nanoprisms) into different layers of OPV devices and engineering electrodes into metal nanostructures (for instance, 2D and 3D metal nanogratings). The plasmonic optical effects induced by nanomaterials and nanostructures will be discussed.

3.3.1. Metal Nanomaterials in Carrier Transport Layers

PCE improvements are reported by incorporating various metallic nanomaterials (i.e., Au and Ag NPs, nanosphere, nanodisk, and nanomesh) into interface layers of OPV devices such as PEDOT:PSS^[136–145] and MoO_x^[146] for hole-transport layers and TiO₂^[147,148] and ZnO^[149] for electron transport layers. However, whether the dominant contributions to improved performance can be attributed to direct optical effects of the nanomaterials or other effects such as electrical or interfacial influence is still under debate.

Wu et al. blended Au NPs into the PEDOT:PSS hole transport layer for P3HT:PC₆₁BM-based OPV devices and achieved PCE enhancement from 3.57% to 4.24%.^[138] The group attributed the improved photocurrent to higher light absorption in active layers induced by local field enhancement of localized surface plasmon resonance (LSPR) effects from the Au NPs, which is indicated by the improved J_{SC} , IPCE and significantly enhanced maximum exciton generation rate (G_{max}) (G_{max} represents a measure of the maximum number of photons absorbed).^[138] Moreover, Baek et al. doped Ag NPs with the optimized size of 67 nm (the size of Ag NPs are optimized from 10 nm to 100 nm as shown in **Figure 7a**) in a PEDOT:PSS layer, and achieved PCE improvement from 6.4% to 7.6% and from 7.9% to 8.6% for PCDTBT:PC₇₁BM and PTB7:PC₇₁BM based OPV devices, respectively.^[150] The report attributes the enhancement of the PCE mainly to plasmonic scattering by the Ag NPs as the PCE enhancement was dominantly determined by the increased J_{SC} value, meanwhile the EQE and absorption were enhanced at wavelength ranges precisely coinciding with the location of LSPR of the Ag NPs.^[150] The group also investigated the size dependent plasmonic forward scattering effect of Ag NPs by near-field scanning and analytical optical simulations that device performance can be influenced

by tuning the size of the Ag NPs.^[150] Additionally, Yang et al. incorporated Au NPs into the interconnecting layer of PEDOT:PSS for an inverted polymer tandem solar cell which can potentially boost both top and bottom sub-cells simultaneously and achieved an overall PCE enhancement from 5.22% to 6.24%.^[137] The report stated that the improvement was attained from higher active layer absorptions by merit of near-field enhancement by the Au NPs due to high order modes of large metal NPs, which is further supported by near-field simulations and experimental Raman scattering investigations.^[137]

Different to the studies mentioned above, Fung et al. blended Au NPs with PEDOT:PSS layer and demonstrated a $\approx 13\%$ increase in PCE. Through both theoretical and experimental investigations, direct optical effects of the Au NPs are found to provide only a minor contribution to the PCE improvement as the existence of the plasmonic resonance does not contribute to the enhancement of light absorption in the active layer (Figure 7c) due to the lateral distribution characteristics of the strong near-field from LSPRs of the metal NPs (i.e., plasmonic resonance does exist but does not contribute to the enhancement of light absorption in the active layer) (Figure 7d).^[136] Instead, the PCE enhancements are primarily due to the improved electrical effects and morphology modification such as resistivity reduction of the PEDOT:PSS layer and increase in interfacial roughness between the active layer and hole transport layer after the incorporation of Au NPs.^[136] In addition, Li et al. demonstrated PCE improvement from 2.28% to 2.65% for P3HT:PC₆₁BM OPV devices by introducing large Ag NPs (80 nm) into the PEDOT:PSS (55 nm) hole transport layer.^[151] By analyzing the absorption spectrum of PEDOT:PSS (with or without Ag NPs)/P3HT:PC₆₁BM films, it was found that Ag NPs has no obvious effect on the transmission spectrum of the hole transport layer and absorption spectrum of active layer. Instead, the performance enhancement originates mainly from improved conductivity of the PEDOT:PSS layer and decreased hole travel path by introducing Au NPs. Recently, Z. Lu et al. obtained a PCE increase from 2.62% to 3.67% in an inverted P3HT:PC₆₁BM OPV device by inserting an ultrathin Au/LiF interlayer between the ITO and ZnO (20 nm) electron transport layer.^[152] The report concluded that the enhanced performance results primarily from the reduced contact barrier and improved conductivity of the Au/LiF modified ZnO electron transport layer. The plasmonic effect induced by Au agglomerations was confirmed by enhancement in absorption and PL spectra of P3HT:PC₆₁BM active layer. However, the absorption loss and back scattering effect of the Au islands offset the enhanced absorption in active layer as compared with the device with only LiF modified ZnO, which leads to insignificant influence of the plasmonic effects induced by Au islands on the device performance.^[152]

3.3.2. Metal Nanomaterials in Active Layers

Direct light absorption enhancement in active layer and PCE improvement of OPV devices can be achieved by incorporating metal nanomaterials and nanostructures

into active layers. The approach takes advantage of two plasmonically-enhanced optical effects induced by embedding metal nanomaterials into the active layer. The first one is the strong near field of LSPRs induced by metal nanoparticles which acts as a sub-wavelength antenna that concentrate energy in a localized surface plasmonic mode and thus increases the light absorption in surrounding organic material.^[153–155] The second one is the prolonged optical path length resulting from plasmonic scattering, particularly for large nanoparticles that have diameters higher than 40 nm.^[156–158] With both such effects, the metal nanomaterials can couple and trap light into the active layer.^[153,159,160]

When small Au NPs with average diameter of 18 nm were embedded into active layer of poly[2,7-(9,9-dioctylfluorene)-*alt*-2-((4-(diphenylamino)phenyl)-thiophen-2-yl)malononitrile] PFSDCN:PC₆₁BM based OPV devices, strong near-field of LSPs is observed in active layer and the increased active layer absorption was confirmed by both theoretical modeling and experimental results.^[161] By increasing the size of metal nanomaterials such as 70 nm-sized Au NPs^[157] and Ag clusters^[158] composed of 40 nm-sized Ag NPs, strong light scattering effects are observed which lead to increased active layer absorption and PCE enhancement for OPV devices. With optimized blend ratio of 5 wt% of Au NPs, the PCE increased from 3.54% to 4.36% for P3HT/PC₇₁BM device, and the PCE increased from 5.77% to 6.45% for a PCDTBT:PC₇₁BM device, and the PCE increased from 3.92% to 4.54% for a poly[[4,4'-bis(2-ethylhexyl)dithieno(3,2-*b*:2',3'-*d*)silole]-2,6-diyl-*alt*-[4,7-bis(2-thienyl)-2,1,3-benzothiadiazole]-5,5'-diyl] (Si-PCDTBT):PC₇₁BM device.^[156] With 1 wt% of Ag clusters composed of 40 nm-sized Ag NPs, the PCE increased from 6.3% to 7.1% for PCDTBT:PC₇₁BM based OPV devices.^[158] The authors state that larger metal NPs can scatter incident light more efficiently to increase the optical path length, leading to enhanced active layer absorption (Figure 8a).^[158] Besides the enhancement of active layer absorption, metal NPs can improve charge carrier transport and increase the current density, providing additional boosts to the PCE.^[158,161] Meanwhile, Spyropoulos et al. embedded surfactant-free Au NPs with various diameters (1.5–20 nm with an average of ≈ 10 nm sized NPs and meantime with a small fraction of >40 nm-sized NPs) into the P3HT:PC₆₁BM active layer of OPV devices.^[156] Due to the strong near field of LSPRs by small metal NPs and scattering effect by larger NPs simultaneously, PCE enhancement from 2.64% to 3.71% was achieved.

Moreover, other metal nanomaterials such as Al NPs,^[162,163] Cu NPs^[164] and Au/Ag alloy NPs^[165] have also been incorporated into active layer. The enhanced active layer absorption of OPV devices and thereby current density are reported. Chen et al. blended Au/Ag alloy NPs into the active layer of P3HT:PC₆₁BM-based OPV devices and achieved PCE up to 4.73% with 31% improvement by optimally blending the active layer with 1% Au₁₁Ag₈₉ alloy NPs.^[164] The increased optical path length from scattering effects and enhanced charge-carrier transport in the active layer mainly contribute to the enhanced performance.^[165] Meanwhile, Cu and Al nanomaterials are of high interest due to their abundant and low cost advantages compared to other noble metals. Although Al NPs generally have weaker

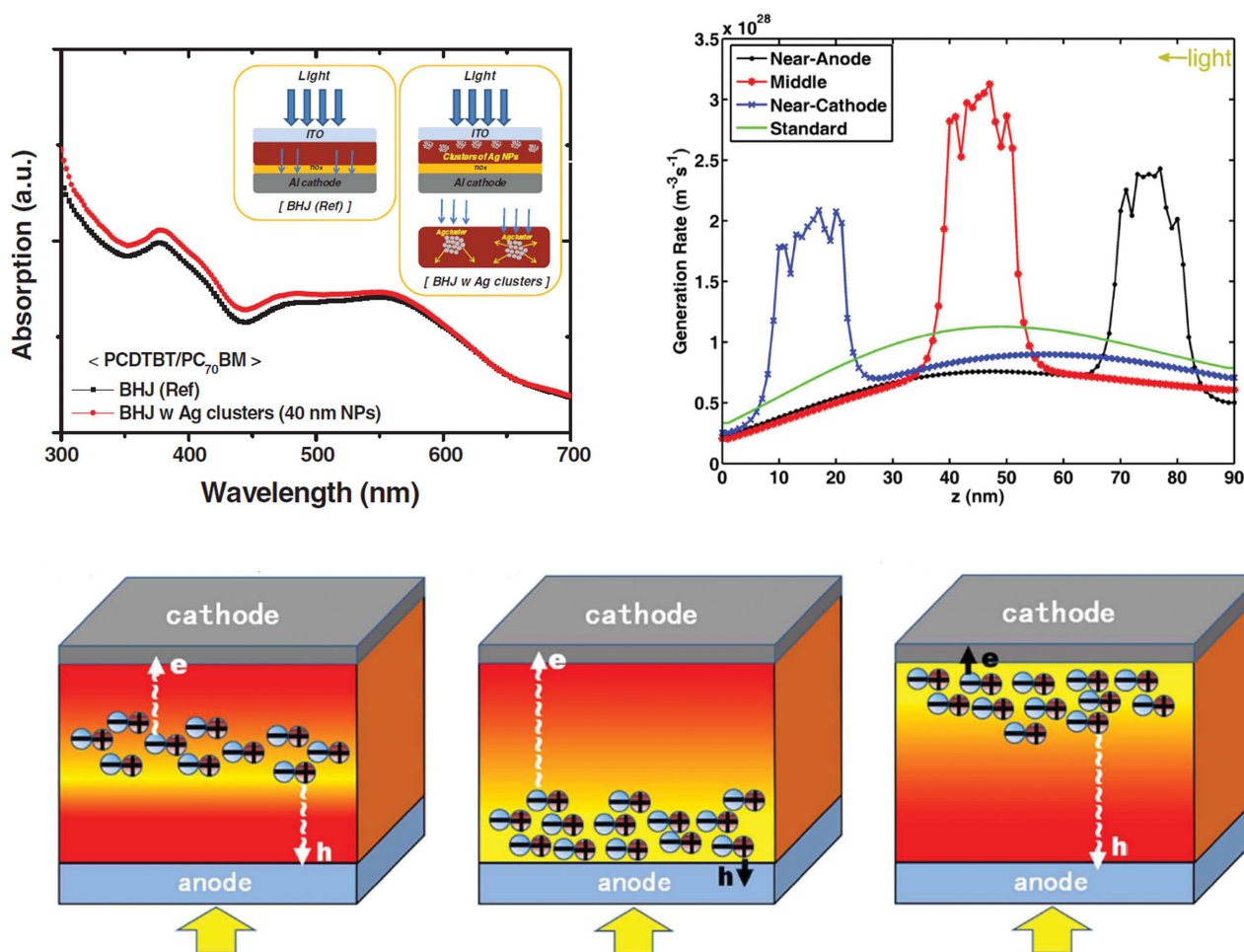


Figure 8. a) The plain PCDTBT/PC₇₁BM BHJ film and the BHJ film with 40 nm-sized NP-based Ag clusters (1 wt%). The inset schematic figures show the light trapping and optical reflection by the scattering and excitation of localized surface plasmons. Reproduced with permission.^[158] Copyright 2011, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. b) Laterally-averaged exciton generation at the active layer of a small-molecule BHJ solar cell. Ag NPs with a size of 10 nm and a spacing distance of 10 nm are embedded into different locations of the active layer. c) Schematic of solar cell devices with Ag NPs embedded (i) at the middle of active layer, (ii) near the anode, and (iii) near the cathode. Reproduced with permission.^[175] Copyright 2013, Nature Publishing Group.

plasmonic resonance strength compared with Au or Ag NPs, strong and long-lived LSP excitations can be supported by Al nanodisks and the total optical cross-sections are comparable to Au and Ag nanostructures of same geometry.^[166] Kochergin et al. suggested that Al NPs have the potential to yield significant absorption enhancement when embedded in the active layer of OPV devices due to high plasmon resonance frequencies of Al NPs, which facilitate an ideal alignment with the absorption band of the active layer.^[162] For instance, Kakavelakis et al. demonstrated the performance and stability of P3HT:PC₆₁BM based OPV devices were enhanced through incorporating various sized Al NPs in active layer.^[167] The PCE increased by 30% and is mainly due to strong scattering effect and improved surface morphology by the large diameter Al NPs.^[167] Although the Al and Cu nanomaterials possess low cost advantages as compared to Au and Ag NPs, further studies are needed to ensure well-controlled size and shape synthesis and to overcome oxidation concerns.

Besides spherical metal NPs, other nanomaterials such as Ag nanoplates,^[168] Ag nanoprisms,^[169–171] Ag nanowires^[172] and Au nanodisks^[173] have also been introduced into the active layer of OPV devices to enhance the device performance. For instance, Wang et al. incorporated Ag nanoplates with controlled shapes into the active layer of P3HT:PC₇₁BM and PCDTBT:PC₇₁BM based OPV devices and achieved PCE enhancement from 3.2% to 4.4% and from 5.9% to 6.6%, respectively.^[168] Moreover, Kim et al. mixed Ag nanowires into the active layer of P3HT:PC₆₁BM and achieved PCE enhancement from 3.31% to 3.91%.^[172] The reports stated that metal nanowires and nanoplates compared to small metal NPs can lead to better overall device performance due to the larger scattering cross-sectional areas^[172] and improved carrier transport.^[168] Meanwhile, triangular Ag nanoprisms exhibit attractive properties such as large electromagnetic field enhancement at the corners of the nanoprisms, broad tenability of plasmonic resonances across the visible spectrum, and non-aggregated self-assembly.^[170,171] The reports

showed that the Raman intensity of the active layer would be significantly boosted when the plasmonic peak of the metal nanomaterials embedded in the active layer aligns with the laser wavelength of the Raman instrument.^[170,174]

Besides optical enhancement, metal nanomaterials introduced into the active layer of OPV devices also provide enhanced electrical properties through plasmonic–electrical effects. Very recently, Sha et al. proposed a general design rule for OPV devices to optimize the photocarrier transport path, and hence the device electrical properties, by utilizing the plasmonic-electrical effect of metal NPs embedded in the active layer.^[175] The incorporated metal NPs have the ability to spatially redistribute light absorption and manipulate photocarrier generation in the active layer. By spatially and spectrally controlling the location of NPs in the active layer and the near-field of LSPs distributed around the metal NPs, dense and inhomogeneous excitons will be generated such that the transport time of electrons and holes will be equalized and as a result the bulk recombination is reduced, which not only lead to increased J_{SC} but also improved V_{OC} and FF. For instance, better PCE can be achieved by depositing metallic NPs closer to the anode for devices with low-mobility holes, as the transport path of low-mobility photocarrier is shortened and electrical properties (i.e., V_{OC} and FF) are enhanced as a result. The theoretical model of small-molecule CuPc:C₆₀-based OPV devices revealed that rather than J_{SC} , the V_{OC} and FF, which are strongly dependent on bulk recombination, have a dominant contribution in overall plasmonic OPV devices and is confirmed by experimental validation.

3.3.3. Nanostructures in Electrode or Active Layers

In addition to incorporating metal nanomaterials into the carrier transport layer and active layer of OPV devices, electrodes with metal nanopatterns have been applied to achieve OPV devices performance enhancement. Recently, studies for imprinting 2-D grating^[176–179] and 3-D grating^[180,181] on the back electrode or active layer^[59] is gaining popularity as it provides light trapping while avoiding optical losses that are expected in front electrodes.^[182,183]

Directly patterned active layer and 2D grating Ag nanostructures have been introduced as back anode reflectors^[178,179] and the achieved PCE enhancement is from 3.09% to 3.68% for P3HT:PC₆₁BM and from 7.20% to 7.73% for PTB7:PC₇₁BM-based inverted OPV devices. The origins of the performance enhancement are improved absorption by SPPs and the scattering effect of the Ag grating.^[177] Different to metal NPs, the metal periodic grating nanostructures exploit an optical enhancement mechanism called plasmonic band edge resonance, due to the formation of a plasmonic band edge and band-gap by the interference of surface plasmonic waves. The plasmonic band edge is formed due to constructive interference between forward and backward SPP waves, while the band-gap is formed due to destructive interference of the traveling waves.^[179] The surface plasmonic waves at the plasmonic band edges exhibit more significant near-field enhancement compared with photonic band edge and have dominant effects in improving the optical

absorption of the OPV devices. The surface plasmonic waves show weak near-field enhancement at the plasmonic band gap, but can achieve a high reflectance for increasing the optical path length.^[179] In addition, the improved absorption in devices by introducing the grating nanostructures as back electrodes have also been demonstrated by several other groups.^[184,185]

However, the polarization dependence of 2D metal nanostructures could potentially lead to weak absorption for polarized incident light. In order to obtain polarization independent optical enhancement, 3D gratings^[180,181] and various random nanostructures^[178,186] have been introduced into OPV devices. Devices with P3HT:PC₆₁BM as the active layer and with 3D gratings of a similar periodicity to the 2D gratings reviewed above exhibit superior performance. This is evident because the PCE of 3D patterned devices can be further improved to 3.85%, which exhibits a 24.6% PCE enhancement compared to a control device with a planar electrode,^[179] while the 2D patterned device can only offer 17.5% PCE enhancement (**Figure 9**).^[181] The further enhancement originates from the polarization independence, greater interfacial area and reduced resistance introduced by 3-D grating.^[181]

Recently, Tang et al. reported a general method for the optical manipulation of light by integrating deterministic periodic nanostructures (DANs) into the active layer through soft nanoimprint lithography (**Figure 10**).^[59] The DAN-based light trapping scheme can effectively enhance broadband light harvesting and provide optimum charge extraction simultaneously, leading to a substantial increase in power conversion efficiency and an overall efficiency exceeding 10% in single-junction OPV devices composed of PTB7-Th:PC₇₁BM blends. Experimental studies and theoretical simulations reveal that the performance enhancement can mainly be ascribed to the self-enhanced absorption resulting from collective effects, including the pattern-induced anti-reflection, and surface plasmonic resonance. Moreover, the method may be applied to other organic optoelectronic devices, such as organic light-emitting diodes (OLEDs), leading to a drastic boost in light out-coupling efficiency and external quantum efficiency.

3.3.4. Dual Plasmonic Structures

Besides incorporating one type of metal nanomaterial and nanostructure in the carrier transport layer, active layer or electrodes of OPV devices for device performance enhancement, the simultaneous incorporation of multiple metal nanomaterials and nanostructures has also been introduced in different layers and regions of OPV devices to further improve the light trapping, electrical properties, and device performance.^[154,155,171,187–191] The incorporated metal NPs typically exhibit a single resonant peak which limits the performance enhancement of OPV devices in a narrow spectral range. Thus obtaining broadband plasmonic absorption in OPV devices is highly desirable. The strategies to induce multiple plasmonic resonances with a variety of metal nanostructures have been investigated for broadband enhancement and are described below.

Introducing various sizes of metal NPs into multiple layers of OPV devices can further improve the

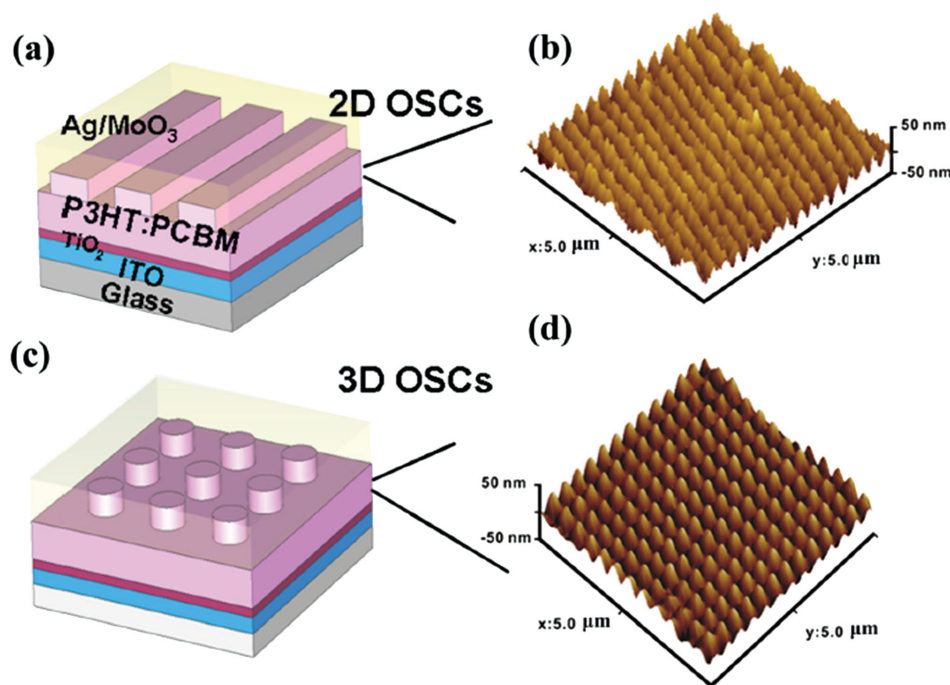


Figure 9. The schematics of a) 2D OSCs and c) 3D OSCs, the AFM images of active layer with b) 2D nanograting and d) 3D nanopattern. Reproduced with permission.^[181] Copyright 2013, AIP Publishing LLC.

device performance. Xie et al. doped 18 nm and 35 nm-sized Au NPs in both a PEDOT:PSS hole transport layer and a P3HT:PC₆₁BM active layer, achieving PCE enhancement from 3.16% to 3.85% as the Au NPs embedded in PEDOT:PSS improved the hole collection and electrical properties. The Au NPs in P3HT:PC₆₁BM promoted light absorption and electrical properties through enhancement of the charge carrier mobility balance (**Figure 11a**).^[154] In addition, Heo et al. incorporated 30 nm and 80 nm sized Au

NPs in PEDOT:PSS and P3HT:PC₆₁BM simultaneously and obtained PCE enhancing from 1.7% to 3.7%.^[189] Moreover, Yang et al. blended 50 nm-sized Au NPs and 70 nm-sized Au NPs into the rear electron transport layer (PEDOT:PSS) and front hole transport layer (C₇₀-bis) respectively. A dual SPR effect is achieved which increased the OPV's PCE from 6.65% to 7.50%.^[190]

Besides this, different sized and shaped nanogeometries of metal nanomaterials are exploited to enhance the optical

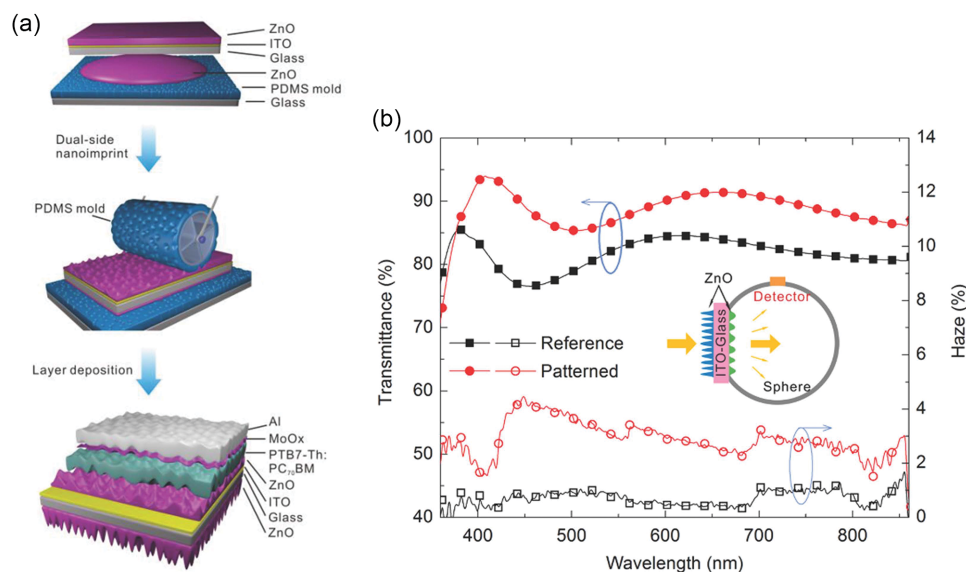


Figure 10. a) Schematic illustration of the fabrication process flow for an OPV containing the dual-sided nanoimprinted DANs. b) Total transmittance and haze values of ITO glass substrates without and with DAN patterns, which were recorded with the incident light from the glass side. Inset depicts the optical measurement configuration using an integrating sphere. Reproduced with permission.^[59] Copyright 2015, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

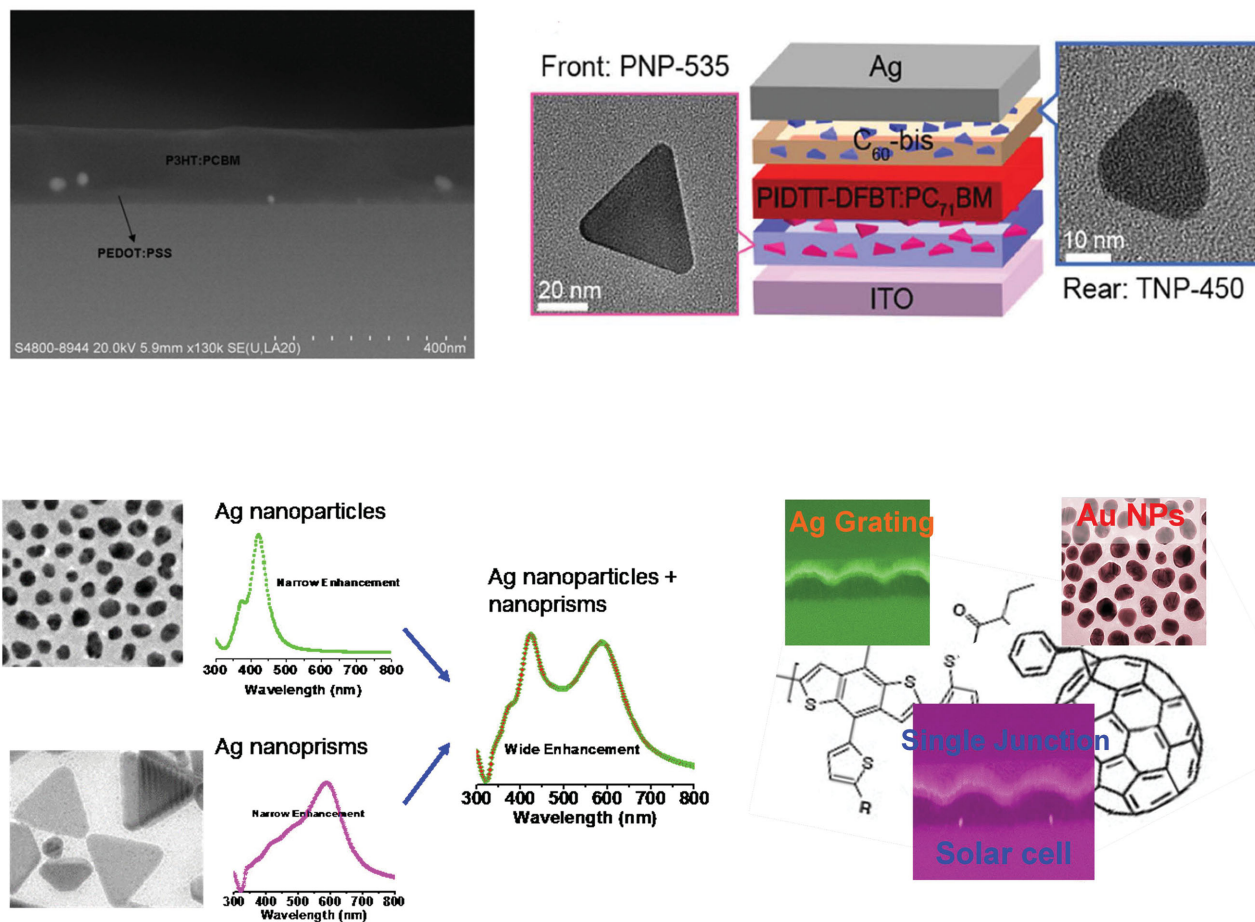


Figure 11. Representative cross section scanning electron microscopy (SEM) image of the film structure PEDOT:PSS+Au NPs/P3HT:PC₆₁BM+Au NPs. Reproduced with permission.^[154] Copyright 2011, AIP Publishing LLC. b) Scheme visualizing the dual interfacial layer strategy and device configuration incorporating TNP-450 nanoprisms (extinction peak around 450 nm) into C₆₀-bis layer and PNP-535 nanoprisms (535 nm) into PEDOT:PSS hole transporting layer, respectively. The insets show high-resolution transmission electron microscopy (HR-TEM) images of TNP-450 and PNP-535. Reproduced with permission.^[187] Copyright 2014, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. c) Schematic diagram showing the 20 nm Ag NPs and 60 nm Ag nanoprisms with different extinction peaks in ethanol. The combined Ag nanomaterials solution showed widened enhancement spectrum. Reproduced with permission.^[171] Copyright 2014, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. d) The SEM pictures of the Ag nanograting, Au NPs and cross-section SEM picture of the dual plasmonic device integrated by Ag nanograting and Au NPs. The background is the chemical structures of PDBTTT-C-T and PC₇₁BM. Reproduced with permission.^[155] Copyright 2012, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

absorption and device performance. Very recently, Yao et al. reported a maximum PCE enhancement from 7.7% to 9.0% by exploiting a dual carrier transport layer doping strategy (Figure 10b), in which Ag nanoprisms are incorporated in both front and rear transport layer (PEDOT:PSS as the front hole transport layer and C₆₀-bis as the rear electron transport layer) in poly(indacenodithieno[3,2-b]thiophene-difluorobenzothiadiazole) and [6,6]-phenyl-C₇₁-butyric acid methyl ester (PIDTT-DFBT:PC₇₁BM) based OPV devices.^[187] The plasmonic resonance of the nanoprisms in each carrier transport layer can be independently adjusted to obtain broadband optical absorption enhancement for the active layer. Ag nanoprisms are used instead of Au NPs as the smaller sized Au NPs exhibit higher absorption loss as compared to their scattering effect.^[187] The dual carrier transport layer doping strategy of Ag nanoprisms showed general compatibility with various PSCs materials and can provide universal optical enhancement without affecting the morphology of the active layer.^[187]

Additionally, the mixture of different NP materials is introduced to carrier transport layer of PSCs. Lu et al. incorporated both Ag and Au NPs into the PEDOT:PSS hole transport layer of PTB7:PC₇₁BM OPV devices and achieved a PCE enhancement from 7.25% (with no NPs) to 8.67% (with the dual NP scheme).^[191] After embedding the NPs of different materials into the hole transport layer, the absorption enhancement region by LSPs was significantly broadened.^[191]

Moreover, dual metal nanomaterials of different geometries that were directly incorporated into the active layer have been studied to achieve broadened absorption and improved device performance for OPV devices. Recently, Li et al. incorporated the combination of Ag NPs and Ag nanoprisms into the P3HT:PC₆₁BM active layer and achieved PCE enhancement from 3.60% to 4.30% (with 19.44% enhancement) (Figure 11c).^[171] The performance enhancement is a result of simultaneous excitation of low-order and

high-order plasmonic resonance modes, which can be tuned by material, size, shape and polarization and then further boost the device performance.

Furthermore, combining metal NPs embedded in the active layer and a nanograting electrode in OPV devices has been reported. Li et al. incorporated Au NPs in active layer and fabricated a Ag nanograting electrode as a back reflector in PBDTTT-C-T:PC₇₁BM-based OPV devices, achieving a high average PCE of 8.79%, with peak PCE up to 9.21% (Figure 11d).^[155] The PCE of the OPV devices with the same design recently reached 9.62%.^[149] The Au NPs embedded in the active layer exhibit strong absorption enhancement in the wavelength range of 480–600 nm, while the Ag nanograting showed relative higher improvement in the range below 400 nm and above 600 nm, indicating that broadband absorption enhancement is achieved as the metal NPs and nanograting complement each other in OPV devices.^[155,192]

3.3.5. Plasmonic OPV Devices Summary

Plasmonics contribute to the emerging field of organic photovoltaics and provide a promising approach for high performance OPV devices. High efficiency of plasmonic OPV devices have been reported to reach 9%^[155,186] and beyond (i.e., with the highest PCE recently reported reaching 9.62%.^[149] It is still under debate that the optical effects such as LSPRs, SPPs and light scattering induced by incorporating plasmonic nanomaterials particularly for small metal nanomaterials (< 20 nm) in the buffer layers may only contribute a minor contribution to device performance. Interestingly, the electrical properties and morphology enhancements are obtained from the metal nanomaterials embedded in carrier transport layer. Embedding metal materials into the active layer directly exploits the strong near-field of LSPs and the light scattering of the nanomaterials. The plasmonic optical effects of the metal nanomaterials and nanostructures are highly dependent on the material, size, shape, concentration of the nanomaterials. Several key considerations for designing plasmonic OPV devices should be addressed to maximize the benefits of incorporation of metal nanomaterials and nanostructures both optically (e.g., overlapping the plasmonic resonance with the absorption wavelength region of active layer) and electrically (e.g., better balanced transport path length of photocarriers.^[193] Also, the size of the nanomaterials and nanostructures should be chosen large enough (>20 nm) to promote light scattering and minimize metal absorption loss. Oversized NPs would introduce short circuit problems particularly in thinner films. In addition, the location of the plasmonic nanomaterial and nanostructure should be prudently selected such that the plasmonic OPV devices can achieve higher overall efficiency.^[194]

4. Summary and Outlook

In this review, we provided an overview on the recent progress in OPV devices through device structure optimization (including the emerging ternary organic solar cells, tandem solar cells, multiple-junction devices and novel interlayer

thin films) and optical engineering optimization from light-trapping scheme by incorporating periodic nanopatterns/nanostructures or incorporating metallic nanomaterials and nanostructures. Although significant progress has been made in the aforementioned aspects, further comprehensive optimizations are still required in order to push the PCE to a new high.

Among all of the approaches toward enhanced light absorption in the active layer, light trapping designs, which include geometric design and plasmonic design, have been successfully adopted in OPV to enhance light harvesting without physically increasing the thickness of the OPV active layer. Besides plasmonic-optical effects, metal nanomaterials and nanostructures incorporated with different layers in OPV devices will also exhibit other effects such as plasmonic-electrical effects,^[174] enhancement of electrical properties,^[146,148,195] charge carrier transport enhancement,^[153,161] absorption enhancement,^[150,169,186] morphology modification,^[196] energy alignment, and surface wettability.^[196] Consequently, the interplay of these competing effects of plasmonic OPV devices requires a comprehensive understanding for appropriate application in various types of OPV device. By exploiting optical and electrical effects, and other characteristics such as morphology modification and work function tuning of metallic nanomaterials and nanostructures, high performance plasmonic OPV devices can be realized.

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