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Jin, Y., Zhang, Y., Liu, Y., Xue, J., Li, W., Qiao, J., Zhang, F., (2019), Limitations and Perspectives on Triplet-Material-Based Organic Photovoltaic Devices, *Advanced Materials*, 31(22), 1900690.
<https://doi.org/10.1002/adma.201900690>

Original publication available at:

<https://doi.org/10.1002/adma.201900690>

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<http://eu.wiley.com/WileyCDA/>

DOI: 10.1002/((adma.201900690))

Article type: (Progress Report)

Limitations and perspectives on triplet materials-based organic photovoltaic devices

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This contribution is dedicated to Prof. Olle Inganäs on the occasion of his retirement.

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Keywords: triplet materials, organic photovoltaic cells, triplet excitons, exciton lifetime, exciton diffusion length

Abstract

Organic photovoltaic cells (OPVs) have attracted broad attention and become a very energetic field after the emergence of nonfullerene acceptors. Long-lifetime triplet excitons are expected to be good candidates for efficiently harvesting a photocurrent. Parallel with the development of OPVs based on singlet materials (S-OPVs), the potential of triplet materials as photoactive layers is explored. However, so far, OPVs employing triplet materials in a bulk-heterojunction have not exhibited better performance than S-OPVs. Here, the recent progress of representative OPVs based on triplet materials (T-OPVs) is briefly summarized. Based on that, the performance limitations of T-OPVs are analyzed. The shortage of desired triplet materials with favourable optoelectronic properties for OPVs, the tradeoff between long lifetime and high binding energy of triplet excitons, as well as the low charge mobility in most triplet materials are crucial issues restraining the efficiencies of T-OPVs. To overcome these limitations, first, novel materials with desired optoelectronic properties are urgently demanded; second, systematic investigation on contribution and dynamics of triplet excitons in T-OPVs is necessary; third, close multidisciplinary collaboration is required, as proved by the development of S-OPVs.

1. Introduction

As a promising renewable energy source, bulk-heterojunction (BHJ) organic photovoltaic cells (OPVs) consisting of electron-donating and electron-accepting materials are under a rapid development for their unique advantages of solution processing, large area, light weight, flexibility and robust devices allowing broad applications. The power conversion efficiencies (PCEs) of OPVs have been continuously increasing over the past decades enabled by close collaboration among chemists, physicists and material scientists; mass novel material synthesis, specially of nonfullerene acceptors; optimized device processing; and detailed understanding on the mechanisms involved.^[1] Very recently, PCEs over 15% in single-junction OPVs and 17% in a tandem device have been achieved,^[2] which make OPVs viable for large-scale industrialization in near future.

As a low-cost PV technology, solution processed OPVs possess very simple sandwich structures with thin photoactive layers (~100 nm) between two different electrodes fabricated on rigid or flexible substrates. At least one electrode is transparent, allowing incident photons into photoactive layers. In OPVs, converting photons to free charges (or electricity) via excitons is more complicated than that in silicon-based PVs. It involves four key steps, as shown in **Figure 1a**: 1) excitons are formed upon absorbing the photons with energy larger than the band gap of absorbers; 2) excitons diffuse to the interfaces between electron donor and acceptor; 3) excitons dissociate into free charge carriers (holes and electrons) at the interfaces; 4) the free charge carriers diffuse/drift by the built-in electric field and are collected at the corresponding electrodes. Consequently, the performance of OPVs is sensitive to many aspects, such as optoelectronic properties of the photoactive materials, the device structure, and the processing conditions.

To have high efficiency, first, the absorbers in OPVs must absorb as many photons as possible from the Sun to form excitons; the population of excitons is determined by the bandgaps, the absorption coefficients of absorbers, and the thicknesses of the BHJ layers. Second, excitons

need to dissociate into free charges before radiative or nonradiative decay, the dissociation rate of excitons is governed by the binding energy, the diffusion length of the excitons, and the energy-level alignment, as well as distribution (morphology) of donors and acceptors in the BHJ. Finally, the generated free charges must be extracted as quickly as possible at the collecting electrodes, and this extraction process is largely controlled by charge mobility of the active materials and the property of the interfacial layers between the BHJ and the electrodes. Charge-carrier generation, recombination, and extraction are three competitors in converting photons to free charges. Efficient charge generation, less charge recombination, and fast charge extraction are prerequisites for realizing high PCEs in OPVs. However, it is a big challenge in devices to simultaneously facilitate charge generation, hinder charge recombination, and accelerate charge extraction because the requirements of the above three competitors with regard to the active layer thickness and the interface area of the donor/acceptor (morphology) are conflicted. Absorbing photons needs thick absorber layers, which is unfavourable for extracting charges due to the long distance for charges to travel; a penetrating network of small donor/acceptor domains with a large interface in BHJs facilitates exciton dissociation, but also leads to large bimolecular recombination and obstructs the bicontinuous pathways for charge migrating to the electrodes.

There are two kinds of excited states, i.e. singlets ($S_1 \dots S_n$) and triplets ($T_1 \dots T_n$) in organic semiconductors as depicted in Figure 1b. In general, excitons directly formed by absorbing photons are singlets due to the selection rule in the electronic dipole transition processes.^[3] The singlet excitons generally have lifetimes in the range of 10-100 ps^[4] and diffusion lengths of 3-10 nm,^[5] which seriously constrain the thickness and domain sizes of donors/acceptors in BHJs. The extremely morphology-dependent performance in OPVs based on singlet materials (S-OPVs) not only compels the device processing involving harmful organic solvents (such as chloroform or chlorobenzene)^[6] or/and thermal treatments^[7] to enable the desired distribution of donor and acceptor, but also results in poor reproducibility of most highly efficient S-OPVs,

which may consequently impede their commercialization. Producing OPV modules with such fine nanostructured morphologies in large-area BHJs by industrial printing techniques for applications will be a big challenge. Besides, commonly used organic solvents for fabricating small area ($< 1 \text{ cm}^2$) highly efficient S-OPVs in the laboratory are neither environmentally friendly nor compatible for large-scale production.

Triplet excitons, in principle, have longer lifetimes/diffusion lengths than singlet excitons due to the forbidden nature of recombination from the triplet states.^[8] It is highly expected that harvesting photoinduced charge by dissociating triplet excitons may break the restrictions on the morphology and thickness of BHJs in OPVs and enable high-yield upscale OPV module production using less toxic or even environmentally friendly solvents with conventional printing technologies. Moreover, materials with large triplet yields may increase the photocurrent of OPVs by decreasing the geminate recombination.^[9] Therefore, the potential of triplet materials for high-performance OPVs, especially for high-yield industrial printing OPV modules, has stimulated extensive research on T-OPVs. How can triplet excitons be obtained if the excitons directly formed by absorbing photons are singlets? Triplet excitons can be obtained by either flipping the spin orientation of a singlet through the effective intersystem crossing (ISC) or bimolecular singlet fission.^[10] As shown in Figure 1b, effective ISC in organic molecules can be realized by either enhancing ISC rate or/and suppressing the radiative and nonradiative decay rate of S_1 .

Thin-film T-OPVs were initiated with a Schottky junction in the early 1970s,^[11] which attracted attention after good performance was demonstrated in a vacuum-deposited bilayer heterojunction in 1986.^[12] As shown in Figure 1c, during the past two decades, the progress of T-OPVs (the date is from Table 1 and ref.^[13]) is far behind that of S-OPVs (the date is from ref.^[14]). The speedy increase of PCEs in S-OPVs was mostly credited to developing novel building blocks for highly efficient photoactive materials, such as D-A copolymers^[15] and non-fullerene acceptors.^[16] At time of writing, we pondered why, so far, T-OPVs have not displayed

comparable PCEs with S-OPVs? What are the reasons for that: material properties or device morphologies? How can T-OPVs catch up S-OPVs? Which roles (donor, acceptor, or dopant) are triplet materials fit for? What can we do from the points of view of materials and devices? The materials play core roles in determining the performance of optoelectronic devices. The slower progress of T-OPVs than S-OPVs was mainly caused by a shortage of desired materials with favourable optoelectronic properties for OPVs. Currently, most triplet materials, either borrowed from organic light-emitting diodes (OLEDs) or newly synthesized, are undesired for T-OPVs due to their low charge mobilities, large bandgaps and small absorption coefficients. Highly efficient T-OPVs (8-9%) achieved only by doping small amount (1-5%) of triplet components also implies the restraint of triplet materials.

Presently, efforts are mainly focused on enhancing charge generation. The other two competing processes, recombination and extraction, are almost ignored, which are the main limitations for PCEs of T-OPVs indicated by the small fill factors (FFs) and the strong electric-field dependence of the photocurrent observed in most devices. In our opinion, the low charge mobilities of triplet materials are the main bottlenecks for T-OPVs.

The role of triplet materials in T-OPVs as donors or acceptors should be mainly determined by their electronic properties for facilitating either electron or hole transport in BHJs. Overall, to fully explore the potential of the long lifetime of excitons, novel materials designed for T-OPVs with favourable optoelectronic properties, especially comparable charge mobilities with singlet materials, are urgently needed.

OPV is a multidisciplinary field involving material synthesis, device engineering, and fundamental physics, which demands close collaborations among synthetic chemists, physicists, and material scientists. However, at present, most efforts on T-OPVs are mainly focused on introducing new materials and optimizing device performance by manipulating the morphologies of BHJs. A clear identification on the contributions of triplet excitons in T-OPVs

is missing. The major origins restricting the performance of T-OPVs are rarely systematically investigated, which we believe are essential to improve device performance.

There have been several reviews on various triplet materials.^[17] The significance here is that we try to provide a broader commentary than previous reviews on the development of various triplet small-molecules/polymers and the evolution of device architectures based on our complementary expertise in synthesizing PV polymers, metal complexes, and device engineering/physics. Our ambition here is not only to review the progress of the field, but also to analyse the performance limitations of T-OPVs, as discussed in Section 3. Keep all this in mind, several potential strategies to break the limitations are proposed in Section 4.

2. Triplet materials and performance of T-OPVs

Triplet materials employed in T-OPVs could be organometallic/heavy atom-containing small molecules or polymers. The molecular structures of representative small molecules and polymers introduced here are shown in **Figure 2** and **3**, respectively. Similar to S-OPVs, the performance of T-OPVs not only depends on the optoelectronic properties of the triplet materials, but also the device architectures and processing conditions. With progressive understanding of the mechanism of converting photons to electrons by triplet materials, the device structures of T-OPVs have experienced an evolution from single-layer Schottky-Junctions to bilayer heterojunctions, and even more sophisticated BHJs as shown in **Figure 4a-c**, which pronouncedly enhanced the device performance (Figure 1c).

2.1 Schottky-Junction T-OPVs

At a very early stage of OPVs, the PV properties of organic materials were investigated in the most succinct structure, i.e., the Schottky-Junction (Figure 4a) by sandwiching a p-type organic material between two different metals ($M_1/P/M_2$). The Schottky barrier cells were reported by Rowe and co-workers in 1974 with a configuration of Al/Mg phthalocyanine (MgPc)/Ag.^[11] To be noted, early in 1971, the phosphorescence of MgPc has been observed and clearly assigned to the molecular triplet states with essentially unity quantum efficiency of triplet

production. Albeit the phosphorescent yield was very low due to the overwhelming nonradiative decay.^[18] The Schottky barrier cells that Rowe and co-workers used to study the photovoltaic effects contained semitransparent Al and Ag electrodes. The photoactive area of the Al/MgPc/Ag cells was 1 cm² and the thickness was in the range of 150-500 nm. Unlike the method commonly used recording *J-V* characteristics today, the *J-V* characteristics of the Al/MgPc/Ag cell shown in **Figure 5a** were obtained by varying the load resistance at a constant incident-light intensity. An efficiency about 10⁻³% was reported for white light incident on the Ag electrode. The very low FF (about 0.25) indicated a high series resistance in the cell. Illuminated from Al with monochromatic light of 690 nm (the absorption peak of MgPc), the photovoltaic efficiency was about 0.01%, one of the highest efficiencies at that time. The authors could estimate or derive many parameters by combining experimental measurements and theoretical modeling. The carrier density and diffusion potential were derived from capacitance-voltage measurements. The Schottky barrier was identified at the interface of Al and MgPc by analyzing the action spectrum under illumination from either Al or Ag (Figure 5b,c). The electron lifetime was assessed to be ~ 10⁻⁹ s and the mobility ~ 0.1 cm² V⁻¹ s⁻¹. The electron diffusion length about 1.5×10⁻⁶ cm was also estimated from the photovoltaic action spectra. The quantum efficiency for carrier generation was ~ 1.5×10⁻³.

Besides small-molecular metal complexes, an organometallic polymer-based Schottky junction OPV was first reported by Lewis and co-workers in 1994.^[19] They fabricated devices by sandwiching a wide-bandgap platinum (Pt) poly-yne between indium-tin oxide (ITO) and Al electrodes. Measurements of the photovoltaic effect were carried out and the effect of triplet excitons on the photogeneration of charge carriers was discussed. The quantum yield for carrier generation at a peak wavelength (390 nm) of device with a thickness of 250 nm was 0.03%, which was comparable to the performance reported for a similar device based on poly(phenylenevinylene) (PPV) at that time. The spectral dependence of the photocurrents indicated that the electron mobility was lower than the hole mobility in the Pt poly-yne.

Therefore, the low electron mobility limited the number of electrons reaching the Al electrode and resulted in a low photocurrent. As nearly 99% efficient ISC to the triplet states in Pt polyyne, the authors supposed that a significant fraction of the photogenerated current would arise from those triplet excitons.

The first generation of T-OPVs employing Schottky junction exhibited poor performance with J_{sc} on the order of nA cm^{-2} and FF about 0.25 (Figure 5a) due to the intrinsic limitations of the Schottky structure and the few appropriate materials available. The field was not attractive because the application potential of T-OPVs was not convincing with efficiency only of the order of $10^{-2}\%$. The poor performance was improved with a new device configuration, i.e., the bilayer heterojunction by introducing an n-type material into the photoactive region.

2.2 Bilayer heterojunction and multilayer T-OPVs

A historical breakthrough of T-OPVs was made by Tang when they achieved an impressive PCE of 0.9% (**Table 1**) under simulated AM2 illumination (75 mW cm^{-2}) in bilayer-heterojunction devices (Figure 4b) employing copper Pc (CuPc) and perylene tetracarboxylic derivative (PV) as photoactive materials in 1986.^[12] CuPc is a triplet material, which was confirmed by the observed phosphorescence from CuPc in 1971.^[18] In a bilayer heterojunction, p-type and n-type semiconductors are sequentially stacked on top of each other by vacuum deposition. As shown in Figure 4a,b, the main difference of a heterojunction and a Schottky junction is the introduction of an “electron acceptor” layer between the organic semiconductor and the cathode, and thus the provision of an interface specific for facilitating exciton dissociation and preventing exciton quenching at metal electrodes. In addition, electrons and holes separately migrate in the donor and acceptor layers, which prevents bimolecular recombination. Consequently, the bilayer devices can achieve more efficient charge separation and extraction, leading to a much-improved J_{sc} and FF due to the existence of donor/acceptor interfaces and continuous pathways for charges transport to the electrodes. After more than a decade, different metal Pc-based materials have been developed and the performance of OPVs

has been enhanced in multilayer devices by including electron-blocking layers.^[20] Nevertheless, the exciton diffusion length and contribution of triplet excitons in the above OPVs have rarely been investigated.

In 2005, Shao and Yang reported bilayer-heterojunction T-OPVs based on Pt(II) octaethylporphyrin (PtOEP) as an electron donor and C₆₀ as the acceptor with a configuration of ITO/ Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/PtOEP (30 nm)/C₆₀ (30 nm)/ 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) (8 nm)/Al(100 nm). PEDOT:PSS and BCP are interfacial electron- and hole-blocking layers.^[21] PtOEP is a famous phosphorescent dye for OLEDs, which exhibits strong absorption at wavelength of 530 nm, and an emission peak at 650 nm with a long lifetime of 91 μ s.^[22] ISC from S₁ to T₁ is promoted due to the strong spin-orbit coupling (SOC) effect of Pt. A bilayer device with a PCE of 2.1% (V_{oc} = 0.66 V, J_{sc} = 5.6 mA cm⁻² and FF = 0.57) was realized after heating the device at 100 °C for 60 min under nitrogen in a glovebox. The exciton diffusion length of PtOEP was estimated to be about 30 nm by thickness-dependence experiment, which was comparable to the values for CuPc (10 nm) and C₆₀ (40 nm).^[23] Devices based on PtOEP showed relatively large electrical resistance, which was ascribed to the low charge mobility of PtOEP ($\sim 10^{-5}$ cm² V⁻¹ s⁻¹).

Li and co-workers developed an iridium complex, APIr, based on the azaperylene (AP) ligand as a donor material.^[24] AP was selected as the auxiliary ligand because of its similarity to common organic perylene-based materials. Difluoro-phenyl-pyridine (dfppy) was selected as the main ligand to lower the highest occupied molecular orbital (HOMO) level and improve the volatility of the complex. Intense absorption bands between 460 and 560 nm resulted from metal-to-ligand-charge-transfer (MLCT) transitions. The intensities of ligand-centered (LC) and MLCT transitions of APIr were higher than the other reported (dfppy)₂Ir-based complexes,^[25] indicating that the employment of the AP ligand increased the absorption of the Ir complex. A PCE of 2.8% (J_{sc} = 4.5 mA cm⁻², V_{oc} = 0.99 V, FF = 0.62) was achieved in a

bilayer device with a structure of ITO/APIr (5 nm)/C₆₀ (30 nm)/*N,N'*-Dihexylperylene-3,4,9,10-bis(dicarboximide) (PTCDI) (10 nm)/BCP (14 nm)/Al, while no PV performance was obtained in a control device containing AP/C₆₀ as a BHJ due to unstable amorphous film.

In comparison, devices based on ZnPc and PtOEP as donor materials had smaller PCE of 1.8% and 1.5% due to the small V_{oc} (0.62 and 0.43 V). The exciton diffusion lengths for APIr and PtOEP were 10.1 and 12 nm measured by the photoluminescent (PL) quenching, which were higher than that of ZnPc (5 nm). However, the devices for both PtOEP and ZnPc showed minimal changes in J_{sc} , V_{oc} , and FF with various donor layer thickness from 5 to 20 nm, whereas, APIr-based devices showed a decreased J_{sc} and FF with increasing APIr thickness. The dramatic decreased FF in APIr-based devices was attributed to minimal packing of octahedral APIr molecules, resulting in a reduced intermolecular orbital overlap. Thus, a slower charge-hopping process and a lower mobility restricted the benefit of a long exciton diffusion length and J_{sc} in APIr-based T-OPVs. Furthermore, the high V_{oc} of APIr devices showed minimal temperature and light-intensity dependence.

The improved performance, specifically in J_{sc} and FF, was achieved by developing bilayer heterojunction OPVs compared to Schottky devices. However, similar to Schottky devices, the efficiencies of bilayer solar cells are still limited by the short exciton diffusion length. In addition, the limited interfaces between the donor and acceptor in the bilayer structure have also hindered exciton dissociation and device performance.

2.3 BHJ T-OPVs

To harvest more photoinduced charges, the BHJ structure (Figure 4c) with interpenetrated donor-acceptor domains was developed to enlarge interfaces, for facilitating exciton dissociation. With such a nanoscale-interpenetrating network, the BHJ concept largely increases the interfacial area between the donor and acceptor phases and results in significantly improved PCE of OPVs via increasing J_{sc} . Compared with the bilayer heterojunction, donors and acceptors are well mixed in BHJs but separated on the nanoscale, which means there is no

preferred direction for separated charges to move as that in the bilayer heterojunction. Therefore, electrodes with different work functions and additional charge-extracting layers are essential to guide and selectively extract charges from BHJs. Furthermore, separated charges require continuous pathways towards electrodes. In other words, the donor and acceptor phases have to form nanoscale bicontinuous and interpenetrating networks for charge migration. Therefore, BHJ devices are much more sensitive to the nanoscale morphology in blends.

The BHJ structure can be formed by either codeposition of donor and acceptor materials in a high-vacuum chamber or solution-casting of donor/acceptor blends composed of small molecule/small molecule, polymer/small molecule or polymer/polymer.

2.3.1 Vacuum-deposited BHJ T-OPVs

Most small molecules used in T-OPVs at the early stages are not soluble. Vacuum deposition was a common way to fabricate T-OPVs. P-type and n-type molecules were co-deposited to realize a BHJ.^[26] In 2004, Chan's group developed a series of rhenium-based complexes for bilayer and codeposition BHJ devices.^[27] They found that complex Re-DIAN had a bipolar charge transport property with relatively high electron and hole mobilities of 2.5×10^{-3} and $2.3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$. The performance of the BHJ devices was always better than the corresponding bilayer devices. The effects of changing film thickness and ratio of Re-DIAN:C₆₀ on the performance of BHJ devices were investigated. For example, a best PCE of 1.29% for Re-DIAN:C₆₀ (1:1, 50 nm) was obtained in the BHJ device, which was one order of magnitude higher than the PCE (0.07%) of bilayer ones with Re-DIAN (25 nm)/C₆₀ (10 nm). The improved PCE was attributed to significantly enhanced J_{sc} from 0.42 mA cm^{-2} for bilayer device to 5.07 mA cm^{-2} for BHJ device. A thick active layer and large interfaces between the donor and the acceptor lead to more exciton dissociation in BHJ devices than in bilayer devices.

In 2014, three novel gold corroles (Au-Cs) complexes with long excited-state lifetime ($\geq 25 \text{ }\mu\text{s}$) were synthesized and codeposited with C₇₀ to fabricate BHJ T-OPVs.^[28] The corrole ligand is a negative trivalent tetradentate ligand and perfectly fits with trivalent Au ion, which was

further modified with different electron-withdrawing groups in order to tune the absorption energy. A pristine C_{70} device was fabricated as a reference, which showed a poor performance with $J_{sc} = 1.19 \text{ mA cm}^{-2}$, $V_{oc} = 1.23 \text{ V}$, $FF = 0.32$, and $PCE = 0.5\%$. After adding 3-7% of Au-Cs complexes as donor to C_{70} , all the PCEs were improved. A highest PCE of 3.0% was obtained by adding 5% of complex Au-C2 to C_{70} , which was further increased to 4.0% as shown in Table 1 by post-annealing, with a better molecular packing and increased interfaces of donor/acceptor as well as charge-transport property. Under illumination, nonradiative and radiative decay competed with exciton dissociation. The authors expected that the excitons-dissociation rate (k_d) could be increased by suppressing the radiative decay through using a weakly emissive donor.

2.3.2 Solution processed metal complexes T-OPVs

To fabricate BHJ OPVs, it is obvious that solution process is a more favourable method than vacuum codeposition for low-cost processing and easily manipulating the distributions of donors and acceptors. Since 1998, organic triplet materials with excellent emitting characteristics have been extensively developed and adopted in phosphorescent OLEDs.^[22] However, most of these small molecules have low solubility for solution processing. To be solution processible, the solubility and film-forming ability of the molecular metal complexes need to be improved by modifying molecular structures, such as decorating with alkyl or hydroxyl groups.^[29] Different metal complexes have been synthesized and utilized in solution processed T-OPVs, which exhibited relatively low efficiencies.^[30] Appropriate molecular modification were carried out and the related phosphorescent molecular metal complexes in BHJ T-OPVs were summarized by Wright.^[17g]

In order to harvest triplet excitons in OPVs, we made BHJ T-OPVs based on two cyclometalated Ir complexes, R1 and R2 as donors and [6,6]-phenyl- C_{71} -butyric acid methyl ester (PC₇₁BM) as an acceptor, in 2014.^[31] A moderate PCE of 2.0% was obtained by blending R2 with PC₇₁BM in a 1:2 weight ratio. The narrow absorption spectra and thin active layers

(~50 nm) limited the J_{sc} of the devices. The hole mobilities of R1 and R2 measured by space-charge-limited current (SCLC) method were 2.0×10^{-6} and 4.3×10^{-5} $\text{cm}^2 \text{V}^{-1} \text{S}^{-1}$, respectively. The lower hole mobility of R1 resulted in a lower FF of 0.35 compared to 0.42 for R2-based devices. The steady-state PL spectra showed phosphorescent emission peaks at 663 nm and 673 nm for pristine R1 and R2, respectively. The blend films showed complete PL quenching of pristine R1 and R2, indicating efficient charge transfer from the R1 and R2 to PC₇₁BM. Furthermore, new emission peaks around 1000 nm were observed in the blend films, which were assigned to the emission from the interfacial charge-transfer (CT) states formed between the complexes and PC₇₁BM. The EL spectra of the blends displayed emission about 1000 nm, which was similar with the PL emission. The T_1 energy was higher than CT state energy for both the R1 and the R2 systems, confirming the effective utilization of triplet excitons in photocurrent generation.

Conjugated small molecules containing Pt-bisacetylides with typical “dumbbell” shaped structures are mostly investigated for photophysical studies.^[32] A new “roller-wheel” type of Pt-bisacetylide complexes was designed by Qin and co-workers.^[33] Although no phosphorescence was observed for complex RWPt-1 and RWPt-2 in solution, the long-lived triplet state was confirmed by transient absorption. The T_1 energy for RWPt-1, RWPt-2, and RWPt-3 were estimated to be ca. 1.06, 1.12 and 1.67 eV, respectively, from time-dependent density functional theory (TDDFT) calculations. They pointed out that photocurrents of the devices mainly originated from charge separation of singlet excitons due to closed energy levels between T_1 of both compounds and the intermolecular CT states. Consequently, the domain sizes of the complexes need to be small enough for singlet excitons to be captured by nearby fullerenes before being converted to triplet excitons. BHJ devices based on RWPt-1 and RWPt-2 displayed impressive PCEs up to 3.9% and 5.9%, respectively, which were among the highest reported values for T-OPVs based on Pt-acetylide compounds. Comparable V_{oc} (0.8 and 0.85 V) and J_{sc} (12.9 and 14.4 mA cm^{-2}) were obtained due to the similar absorption and bandgaps,

while a distinct difference in FF (0.39 for RWPt-1, 0.63 for RWPt-2) resulting in the difference in PCEs. The low FF for RWPt-1 device was due to the molecularly mixed morphology, which was beneficial for charge dissociation but limited the charge transportation. RWPt-3 devices showed poor performance due to the larger bandgap (2.53 eV) and the absence of π - π interactions between organic chromophores confirmed by the single-crystal results.

Recently, for the first time, Huang and co-workers reported three triplet nonfullerene acceptors (PTP, HFPTP, BFPTP) based on tellurophene (the heaviest Group 16 heterocycle) with different degrees of ring fusing for OPVs.^[34] The unique properties of tellurophene, including its metalloid nature and large SOC effect, contribute to the generation of triplet excitons and charge separation. The lowest unoccupied molecular orbital (LUMO) mainly distributes on **perylene diimide planes**, while the electron-rich tellurophene can tune the overall electron delocalization. Changing the extent of ring fusing could effectively manipulate conjugation and geometries of molecules. These molecules exhibited strong absorption in the region of 300-600 nm, in which the light-absorbing capability was improved by increasing the extent of ring fusion. The differential pulse voltammetry measurement indicated that electron-accepting ability increased from PTP to HFPTP to BFPTP. Room-temperature and low-temperature transient PL spectra suggested the production of triplet states for all three molecules. OPVs based on PTP, HFPTP, and BFPTP blended with electron donor PBDB-T (0.8:1 w/w ratio) were fabricated and investigated. BFPTP-based device displayed an outstanding PCE of 7.52%, which was the highest value so far for tellurophene-based T-OPVs. The enhanced V_{oc} from PTP (0.77 V) to HFPTP (0.85 V) to BFPTP (0.94 V) was consistent with the rise of their LUMO levels. The increased J_{sc} and FF from PTP (4.48 mA cm⁻², 0.42), HFPTP (7.96 mA cm⁻², 0.48) to BFPTP (12.83 mA cm⁻², 0.62) were interpreted by their active-layer morphologies, which were investigated by grazing-incidence X-ray diffraction (GIXD), atomic force microscopy (AFM) and transmission electron microscopy (TEM). A more face-on orientation of PBDB-T and bicontinuous interpenetrating networks was observed in blend films of BFPTP from the GIXD

and TEM results. The exciton diffusion length of BFPTP was estimated to be 34 nm by a thickness-dependence experiment, which was comparable to that of fullerenes (ca. 40 nm). The existence of triplet excitons in the devices was verified by magneto-photocurrent measurements, which showed a typical triplet-polaron-interaction fingerprint profile. This pioneering work demonstrated that triplet excitons played a critical role in the enhancement of T-OPV performances.

At time of reviewing, Tao and co-workers online published a work based on a new octahedral heteroleptic Ir complex, TBzIr.^[35] The best PCE of 3.81% (V_{oc} of 0.92 V, J_{sc} of 8.91 mA cm⁻², and FF of 0.47) was achieved when the organic perylene diimide functionalized with amino *N*-oxide (PDINO) as cathode interface layer for TBzIr as the donor and PC₇₁BM as the acceptor. The controlled devices composed of organic TBz ligand and PC₇₁BM displayed with a very low PCE of 0.002%. The enormously enhanced PCE for the TBzIr based device was attributed to a combination of enhanced optical absorption, longer decay lifetime, more efficient PL quenching, and favourable film morphology, in comparison to those of controlled TBz-based devices.

2.3.3 Polymeric T-OPVs

To date, Pt containing polymers based on the Pt poly-yne building block have been extensively studied in T-OPVs.^[36] The breakthrough of this type of polymers based T-OPVs came from Wong et al. and Jen et al.. In 2007, Wong et al. exploited a novel π -conjugated narrow-bandgap polymer, P1 (about 1.85 eV) containing 4,7-di-2'-thienyl-2,1,3-benzothiadiazole as a core component,^[37] which showed a strong absorption band at 554 nm and an intense emission at 680 nm. A PCE of 4.9% (J_{sc} = 15.43 mA cm⁻², V_{oc} = 0.82 V, FF = 0.39) was achieved based on P1 blended with [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) (1:4 w/w ratio) BHJ T-OPVs, which was comparable with the highest singlet-material like poly(3-hexylthiophene) (P3HT)-based solar cells with efficiency of around 5% at that time. The transient PL measurement of P1 displayed a short lifetime in the nanosecond range and no vibronic structure

was observed in low-temperature PL spectra. Therefore, it was concluded that the emission was from the singlet excited state rather than the triplet excited state. The absence of triplet emission for Pt poly-yne-based polymers has also been found by other groups, which could be understood by the energy gap law (the non-radiative decay rate for the triplet state increases exponentially with decreasing T_1 energy).^[38] Later, three amorphous Pt-based polymers derived from P1 were designed and synthesized by Jen et al..^[39] The amorphous nature of these conjugated polymers confirmed by the X-ray diffraction measurement was less sensitive to the post-annealing process compared to polycrystalline polymers. Despite its amorphous nature, P3 and P4 showed good charge-transporting property with high hole mobility up to $1.0 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$. The best PCE of 4.13% ($J_{\text{sc}} = 10.12 \text{ mA cm}^{-2}$, $V_{\text{oc}} = 0.79 \text{ V}$, FF = 0.51) was obtained by blending P4 with PC₇₁BM in a 1:4 weight ratio. The performance was decreased at a lower fullerene ratio (1:1 and 1:2 w/w ratio) in the blend films, especially with a reduction in J_{sc} due to the inefficient charge separation and transportation. The devices showed better performance for PC₇₁BM compared to PCBM as the acceptor, which could be attributed to the better absorbance and charge-transport properties of PC₇₁BM.

In addition to the linear Pt poly-yne-containing polymers, several cyclometalated polymers containing Pt or Ir complexes were also investigated due to the demand of a deeper understanding of the roles of triplet excitons in T-OPVs. The first photovoltaic study on covalently incorporated Ir complexes into a conjugated polyfluorene polymer was carried out by Holdcroft.^[40] In order to investigate the triplet excitons in T-OPVs, the polymer without Ir was also synthesized for comparison. The absorption was slightly improved between 400 and 450 nm due to the introduction of Ir. The employment of Ir leads to a large red-shift of emission (from 442 to 596 nm) and a long PL lifetime of 0.26 μs , indicating the triplet nature of emission. BHJ OPVs were fabricated using polymer PDFN-PPD (refer to 1 in ref. 40) or PDFN-PPD-Ir (refer to 2 in ref. 40) as donors and PCBM as the acceptor. Nevertheless, the PCE of PDFN-PPD-Ir-based devices was considerably low as just 0.07%, whereas it was 35 times higher than

that of control polymer PDFN-PPD (0.002%). Such great improvement was mainly from the J_{sc} enhancement from 0.01 to 0.44 mA cm⁻². The considerably enhanced PCE was attributed to the formation of the triplet excitons with longer diffusion length. The unfavourable light absorption of the polymer, PDFN-PPD-Ir, limited the performance of T-OPVs.

Tao and co-workers incorporated various concentrations of triplet Ir complexes (0, 0.5, 1, 1.5, 2.5, and 5 mol%) to the backbone of the champion polymer PTB7 denoted as PTB7Ir in 2015.^[41] By blending PTB7Ir with PC₇₁BM as active layers, an enhanced PCE up to 8.71% was achieved at lower Ir content (1 mol%) (PTB7Ir1) compared with that of 6.64% for PTB7, mainly caused by the increased J_{sc} , from 16.71 to 18.14 mA cm⁻². However, the absorption intensity of the blend films decreased slightly with increasing concentration of Ir complex to PTB7 polymers, which was contrary to device external quantum efficiency (EQE) trends. The identical PL spectra of the blend films indicated that polymers with or without Ir undergo similar geminate recombination. Therefore, they concluded that the improvement of J_{sc} and PCE for PTB7Ir1 might be caused by reducing the recombination loss from ³CT to the ¹T of the donor. This work provided an extra approach to improve the PCE of BHJ OPVs by chemically bonding low content of triplet heavy-metal complexes to well-known polymers for OPVs, although the performance enhancement mechanism for this type of materials was unclear. A similar approach by the same research group of introducing Pt complex or Ir complex in low ratios to the well-known polymer PTB7-Th was exploited to make metallopolymers.^[42] The devices based on polymers containing 1.5% Pt (PTB7-ThPt1.5) and 1% Ir (PTB7-ThIr1) showed enhanced PCEs of 8.45% and 9.19%, respectively, compared with 7.92% for the control PTB7-Th devices. The authors attributed the enhanced PCE to the higher hole mobility, reduced bimolecular recombination, and more efficient charge separation.

In 2018, the first cyclometalated polymer acceptor PNDIT2Pt was designed and synthesized by Tao and collaborators.^[43] They introduced a small amount of cyclometalated Pt complex (0, 1, 2, and 5 mol %) as the third monomer to the conjugated acceptor polymer backbone of

poly[[*N,N'*-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-(2,2'-bithiophene)] (PNDIT2) through a random terpolymer approach. PNDIT2Pt exhibited a slightly higher melting point, crystallization temperature, HOMO and LUMO levels than the control PNDIT2 copolymer due to the introduction of a small amount of weaker electron-withdrawing Pt complex. The absorption of the polymers showed a huge redshift from solution to film, indicating the existence of π - π stacking and intermolecular interactions in the solid states. All-polymer PVs based on PTB7-Th as the donor and PNDIT2Pt as the acceptor exhibited an improved PCE of 4.51% for a polymer containing 1 mol% Pt (PNDIT2Pt1) relative to a control PNDIT2 (3.88%) in the same inverted device configuration. Higher hole and electron mobility and more efficient charge separation in the Pt-containing polymer were found to be responsible for the improved PCE. Tao et al. made another effort by replacing the naphthalene diimide unit with a very small amount of phosphorescent Pt complex to the PNDIT2 backbone.^[44] The terpolymers P(dbm)PtPyTPAx (x is refer to 1, 2 and 5 mol%) exhibited comparable optical and electrochemical properties to those of the PNDIT2 copolymer. By blending with PTB7-Th, the terpolymer acceptor P(dbm)PtPyTPA5 showed the highest PCE of 4.99% compared to 3.72% for PNDIT2 in the inverted device structures. The improvement in PCE was mainly ascribed to more efficient exciton separation, reduced charge recombination, and higher hole and electron mobilities with enhanced J_{sc} (from 10.41 to 11.99 mA cm⁻²) and FF (from 0.45 to 0.52) through a combination of photoelectric measurements. An increase in the maximum PCE from 3.79% for PNDIT2 to 6.18% for the P(dbm)PtPyTPA1 was also observed in all-Polymer PVs based on PBDB-T as the donor.

2.4 Ternary OPVs

The thin active layer (100 nm) in BHJ OPVs leads to a limited absorption and restricted J_{sc} of the devices. The tradeoff between charge dissociation and recombination in BHJs also hinders further improvement of PCEs. Ternary OPVs (Figure 4d), introducing a third component into the active layer of the BHJ OPVs, can enhance photon harvesting through complementary

absorption of three components. Incorporating heavy-metal complexes as additives or third component in the photoactive layer of BHJ OPVs has shown great potential in PCE enhancement.

Che and collaborators fabricated ternary OPVs by incorporating tetramethyl-substituted CuPc (CuMePc) nanocrystals into P3HT:PCBM OPVs.^[45] The complementary absorption of CuMePc and P3HT is shown in **Figure 6a**. With increasing CuMePc content in P3HT, the films showed an increased absorption of CuMePc and a decreased absorption of P3HT. The P1C1 film (1:1 weight ratio of P3HT:CuMePc) displayed a broader absorption than that of the pristine P3HT film. The hole mobilities of CuMePc and P3HT were 2.9×10^{-4} and $7.3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$, respectively, measured by the bottom-up thin-film transistors. The P1C1 composite film showed the highest hole mobility of up to $2.5 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$, which was attributed to the effect of the reduced traps in P3HT. Standard P3HT:PCBM and CuMePc:PCBM devices exhibited PCEs of 3.2% and 1.1%. The smaller V_{oc} of 0.54 V for the CuMePc:PCBM device could be explained by the smaller offset between the HOMO of CuMePc and the LUMO of PCBM, as shown in Figure 6b. The P1C1-based devices showed the highest PCE of 5.3%, with a V_{oc} of 0.58 V, J_{sc} of 16.3 mA cm^{-2} , and FF of 0.56. The improvement in J_{sc} and FF were attributed to the enhanced hole mobility and a broadened absorption of the P1C1 composite film.

Several advantages have been observed by doping a small amount of a metal complex in the active layer. Firstly, the long-lifetime triplet state in metal complex can result in an increased exciton diffusion length.^[46] Secondly, doping a small amount of a metal complex can tune the phase separation of the active layers.^[5c, 29] Thirdly, the energy transfer from the metal complex to the donor materials can enhance the photocurrent of devices.^[47]

Hsu et al. reported the increased diffusion length and improved morphology after doping an Ir complex in BHJ OPVs. They investigated the influence of Ir(ppz)₃ as a dopant in BHJ OPVs with P3HT and inden-C₆₀-bisadduct (ICBA) as active materials.^[48] An increased PCE from

5.41% to 6.08% was obtained after 0.1 wt% Ir(ppz)₃ was doped in a P3HT:ICBA blend without annealing treatment. The detailed parameters indicated that the enhanced PCE originated from the J_{sc} increasing from 10.09 to 11.76 mA cm⁻². The J_{sc} was further enhanced upon annealing at 150 °C for the 0.1 wt% Ir(ppz)₃-doped device, which boosted the PCE up to 7.08%. The enhanced performance by doping a small amount of Ir(ppz)₃ was attributed to the increased exciton diffusion length and the improved morphology of BHJs.

Cacialli et al. fabricated devices based on P3HT:PCBM with different amount of Ir(ppy)₃.^[5c] The enhanced charge transport properties of the active layers were observed from the J - V curves. When a certain amount of Ir(ppy)₃ was present in the P3HT:PCBM blend, the maximum J_{sc} , as well as the following PCE, were achieved for 5 wt% Ir(ppy)₃ doped devices. The detailed analysis of the EQE results showed that the singlet states of the Ir(ppy)₃ undergo a rapid ISC to the long-lived triplet states, and the excitons migration was facilitated with increasing Ir-dopants, especially for the case with 5 wt% Ir(ppy)₃. Besides, the morphology of the active layers showed that a large phase separation was formed at very high loads (above 5 wt%), which in turn lead to an overall reduced device performance.

In 2016, Kwon et al. identified the energy transfer from a variety of Ir complexes to the PTB7 or P3HT donors.^[49] The energy transfer from Ir-Orange to PTB7 was confirmed by the steady state PL and transient PL measurement. The PL intensity of PTB7 with 10 wt% Ir-Orange was twice that of pristine PTB7, while the emission of Ir-Orange almost quenched when excited in MLCT region (455 nm). These results indicated that the efficient energy transfer from the triplet excitons of Ir-Orange to the singlet excitons of PTB7, not the charge transfer from Ir-Orange to PTB7. Ir-Orange contributed to a significant improvement in J_{sc} from 13.3 to 16.1 mA cm⁻² with increased PCE from 7.31% to 8.70%. These improvements could be attributed to the efficient energy transfer between Ir-Orange and PTB7 as well as the morphological effect of doping Ir complexes. The amphiphilic nature of the Ir complexes facilitated the face-on orientation and the crystallinities of PTB7 and PC₇₁BM.

3. Main limitations in T-OPVs

The recent progress in T-OPVs summarized above clearly show that introducing triplet small molecules or polymers in OPVs can indeed improve the photovoltaic performance with particularly enhanced photocurrent, though the development of T-OPVs is far behind those of S-OPVs as shown in Figure 1c. Here we would like to analyse the main limitations of T-OPVs in charge generation and extraction.

3.1 Limitations on charge generation

It is well known that the lifetime of triplet excitons is usually about three orders of magnitude longer than those of singlet excitons^[50] while the binding energy of the triplet excitons is higher than those of singlet excitons due to the attractive exchange interaction of the same spin orientation. The long lifetime of triplets may facilitate charge generation and enhanced J_{sc} . On the other hand, the high binding energy of triplets will need large energy to dissociate. The trade-off between longer lifetime and higher binding energy of triplet excitons will determine whether significant numbers of charge carriers can be produced in T-OPVs. In general, the energy level of T_1 is lower than S_1 . As a result, the utilization of triplet excitons will lead to decreased V_{oc} because the S_1 -to- T_1 conversion will lower the energy level of excited states. Therefore, enhanced PCEs only can be achieved when the increased in J_{sc} is larger than the decreased of V_{oc} .

3.1.1 Inefficient photon absorption

The absorption spectra of the reported small molecular metal complexes mostly fall in the UV-visible region and their absorption coefficients in long wavelength are usually lower than the values of the well-known conjugated polymers employed in S-OPVs,^[21, 24, 27-28] which result in inefficient photon absorption in T-OPVs.

3.1.2 Debatable exciton diffusion length of triplets

There is a controversy on whether diffusion length of triplet excitons is longer than those of singlet excitons, although the diffusion length of triplet excitons in the range of 10-140 nm were

reported in literatures.^[51] Comparable diffusion lengths of triplet and singlet excitons were also demonstrated in some materials.^[52] The exciton diffusion length (L_D) is defined by equation $L_D = \sqrt{D \times \tau}$. Here, τ is the exciton lifetime and D is exciton diffusion coefficient or diffusivity, which describes the mobility of excitons inside a material. Therefore, a long exciton lifetime does not guarantee a long diffusion length, which also partly influenced by the crystallinity of materials.^[53]

Exciton diffusion is facilitated through either Förster or Dexter energy transfer.^[54] Förster resonance energy transfer (FRET) relies on a dipole-dipole coupling and requires overlap of emission spectrum of donor and absorption spectrum of acceptor, which occurs in a range of 1-10 nm. Specifically, an excited electron on a donor molecule recombines with the hole and the energy is transferred non-radiatively to excite an exciton on another acceptor molecule as shown in **Figure 7a**.^[55] In general, only singlet excitons can be transported via the Förster mechanism. Dexter energy transfer refers to the actual exchange of electrons between donor and acceptor when they have overlapping wavefunction within 1 nm distance as shown in **Figure 7b**. Therefore, the probability of Dexter energy transfer exponentially decreases with the distance between donor and acceptor. The efficiency of FRET usually outperforms that of Dexter energy transfer for singlet excitons because the dipole-dipole coupling is more efficient than exchange interaction, while triplet excitons may be transferred between non-phosphorescent molecules only by the Dexter mechanism due to the forbidden transition. Thus, the diffusivity of triplet excitons can be several orders of magnitude smaller than those of singlet excitons due to the different (Förster or Dexter) energy transfer mechanisms. Therefore, exciton diffusion length is comparable for triplet and singlet excitons when triplet excitons undergo Dexter energy transfer. However, triplet excitons generated from a phosphorescent donor can also undergo FRET process,^[56] which may increase the diffusivity for triplet excitons. As a consequence, the exciton diffusion lengths of triplet excitons can be longer than those of singlet excitons.

3.1.3 Utilization of triplet excitons

The dynamics of singlet and triplet excited states in BHJ OPVs have been investigated by Schanze's group based on several Pt-based polymers. The device fabricated with polymer p-PtTh as donor and PCBM as acceptor giving a PCE of 0.27%.^[9] The transient absorption measurements indicated that the triplet excited state rather than the singlet excited state of polymer p-PtTh was involved in the photoinduced electron transfer process. The energy level diagram shown in **Figure 7c** provides the mechanism of charge separation in the p-PtTh/PCBM system. The energy gap between T_1 of p-PtTh and the charge separated state was sufficiently large, which benefited the electron transfer from T_1 of p-PtTh to PCBM. Later, relatively efficient ISC was observed by the photophysical studies of polymer p-PtBTD-Th.^[57] However, after blending with PCBM, the singlet state emission of p-PtBTD-Th was quenched efficiently and the triplet state emission was not quenched, indicating only the singlet state has contribution to charge carriers. The energy of the T_1 was slightly below that of the charge separated state as shown in the Jablonski diagram of the p-PtBTD-Th/PCBM system (**Figure 7d**). This work revealed that although a triplet excited state was produced, it was too low in energy to undergo electron transfer to PCBM. Furthermore, the competition between ISC from S_1 to T_1 in p-PtBTD-Th and electron transfer process will decrease charge generation. Therefore, to harvest the triplet excitons in photovoltaic device, it would be necessary to manipulate the energy levels of either the polymer donor or the acceptor in order to match the energy levels between T_1 and charge separated state.

3.2 Limitations on charge extraction or FF

The competition between free charge carrier extraction and recombination determined the photocurrent and FF in the condition of bimolecular recombination dominated the recombination process.^[58] The FF is typically decreased with increasing the active layer thickness, resulting in a trade-off between extraction and absorption. The optimal active layer thickness for most OPVs is around 100 nm, while 200 nm is needed for complete absorption

across the spectrum.^[59] In our previous review, a guideline was proposed for the dependence of FF on the active layer thickness d , mobility μ and free carrier recombination rate constant κ in OPVs.^[60]

$$\frac{(\mu_{eff}[\text{cm}^2\text{V}^{-1}\text{s}^{-1}])^2}{(d[\text{nm}])^3(\kappa[\text{cm}^3\text{s}^{-1}])} > 40 \quad (1)$$

Where $\mu_{eff} = (\mu_e\mu_h)^{1/2}$, the geometric mean of the electron and hole mobility μ_e and μ_h .

As shown in **Equation 1**, the mobility of active layer is crucial to have a high FF. Reduce κ is another option for the low mobility materials to obtain a high FF. It has been reported that reducing the D/A interface with increased carrier lifetime leads to a reduced κ .^[61] Large domain separation in BHJs which reduced D/A interfaces and thus κ can be pursued by employing materials with long exciton diffusion lengths.

Unfortunately, the charge mobilities of most triplet materials are fairly low, which resulting in most FFs in BHJ T-OPVs are lower than 0.6 (**Figure 8a**) (except for the systems where very little triplet materials were employed) clearly indicates the extraction limitation of the charges in T-OPVs. The main restriction in T-OPVs is the low charge mobility of the existing triplet materials, which lead to unwanted charge recombination (**Figure 8b**). Given a J_{sc} and V_{oc} , extraction will make huge differences in FF and output power at maximum power point (P_{mpp}) as displayed in **Figure 8c** because overall P_{mpp} depends on extracted charges, not generated charges. You may argue that charge mobility did not hinder using triplets in OLEDs, why hinder them in T-OPVs? Requirements for material properties are very different or even contradictory in OLEDs and OPVs. In OLEDs, triplet materials are usually used as dopants in emitting layers with the thickness only 20-30 nm, charges are injected and driven by strong electric fields in hole and electron transporting layers. In OPVs, the thickness of BHJ layers needs to be thicker than 100 nm; triplet materials as donors or acceptors in most cases must play two roles: generating and transporting charges, which demands their charge mobility is high and less electric field dependence.

4. Perspectives

To address above limitations in T-OPVs, here we propose several potential strategies based on material designing and device engineering for high-performance T-OPVs.

4.1 Strategies for designing novel triplet materials

Feasible strategies are expected to design novel triplet materials synchronously possessing long triplet lifetime, high absorption coefficient, appropriate triplet energy, high charge mobility, low-cost and good processability for high performance T-OPVs. There is no doubt that it is a formidable challenge to synthesize such ideal triplet materials. Nevertheless, there are other hills whose stones may serve to polish the Jade and we could get some inspirations from the existing research.

4.1.1 Increase population of triplet excitons

Since the triplet excitons are usually generated through ISC between singlet excited states and triplet excited states in conventional organic materials, which is favoured by the strong SOC effect of heavy atoms, the involvement of heavy atoms especially heavy transition metals, such as Ir(III), Pt(II), has been demonstrated as the most efficient way to obtain triplet materials with high quantum efficiency of triplet production. Considering the high cost and limited resources of noble metals, it is indispensable to develop metal-free organic triplet materials with low cost, versatile molecular design, and good processability for further practical applications. However, it is still challenging for exploring metal-free organic triplet compounds with long lifetime because of the inefficient ISC caused by weak SOC and rapid non-radiative relaxation processes of the triplet excited states.^[62] According to El-Sayed's rule,^[63] the SOC is allowed between states of different symmetry and electronic configurations. Fast ISC has been observed in the low-lying $^1n\pi^*$ state of N-heterocyclic aromatic hydrocarbons and carbonyl compounds, where n represents a nonbonding electron of the nitrogen or oxygen atom.^[64] In recent years, metal-free room-temperature phosphorescence materials have been realized by largely suppressing non-radiative decay transition of T_1 even with small ISC rate, which could be achieved by

specific molecular packing motifs such as H-aggregates or crystal engineering, host-guest doping method and so on.^[65] Accordingly, in addition to cheap heavy metals, n/π -groups such as N-heterocyclic aromatic hydrocarbons and carbonyl groups, and specific molecular packing motifs might be alternative to noble metal to design novel next-generation organic triplet materials for T-OPVs.

4.1.2 Increase absorption and charge mobility

To improve the charge mobility of organic materials, large conjugated backbone is needed, which meanwhile can extend their absorption spectra. This can be realized by introducing conjugated moieties, such as electron-donating and electron-deficient building blocks, which have been widely used to design low band gap D-A conjugated polymers.^[66] Another efficient strategy is to incorporate a certain amount of heavy atoms to the backbone of state-of-the-art organic semiconductors/conjugated polymers.^[41-43] The excellent properties of organic semiconductors could be maintained, meanwhile the introduction of heavy atoms would facilitate triplet excitons with long lifetime. There is plenty of large room to improve the overall properties of these adducts, which could be manipulated by the concentration and location of heavy metals, the conjugated backbone structures, and their combining ways, etc.

4.1.3 Decrease energy loss

There is a large energy loss, i.e., typically 0.5-1.0 eV for the electron exchange between the S_1 and T_1 states in a conventional organic molecule. So it is imperative to manage the T_1 level and the energy gap between the singlet and triplet states (ΔE_{ST}) of triplet materials to minimize the above losses. Just in recent years, organic thermally-activated delayed fluorescent (TADF) materials with small ΔE_{ST} have experienced rapid development as the third-generation OLEDs.^[67] Using twisted strong D-A molecular structures has been proven to be an effective way for small ΔE_{ST} by minimizing the overlap of HOMO and LUMO levels. Recently, Shuai et al. performed the theoretical study of conversion and decay processes of excited triplet and singlet states in a typical TADF molecule, which would provide useful insight into the

molecular design of high-performance TADF materials.^[68] Thus, careful molecular design with the aid of theoretical calculation is needed to control the conjugation length for appropriate T_1 energy and small ΔE_{ST} based on twisted D-A structures with right intramolecular CT states.

4.2 Strategies on device engineering for T-OPVs

Potentials of materials can only be realized by employing appropriate device architectures and optimal processing conditions. Present achievements in S-OPVs is not only made by good materials, but also matured device engineering developed in the last decades. Currently, the T-OPVs are at a similar stage before countless low band gap D-A copolymers were synthesized and introduced in S-OPVs. Desired D-A copolymers broke the bottleneck, triggered extensive research on S-OPVs. Recent years, the ceiling of PCEs in S-OPVs was further boosted up to 15% via simultaneously increased J_{sc} and V_{oc} by using non-fullerene acceptors with complementary absorption spectra with donors and the decreased energy loss for exciton dissociation. To break the limitations on performance of T-OPVs, synergy of materials and device engineering is necessary. From device point of view, specially from production point of view, we propose following approaches.

4.2.1 Diffused bilayer heterojunction

From device engineering point of view, new device architectures suitable for large scale production are preferred. In order to achieve efficient charge separation and transport at the same time, Inganäs et al. demonstrated the idea of “stratified multilayers”, which is a bilayer structure with diffused heterojunction.^[69] By selecting the solvent that have temperature-dependent solubility to donor and acceptor materials, the bilayer structure can be formed by solution process, then the upper layer will diffuse into the bottom layer during the spin-coating, which was proven by the PL data. In this diffused bilayer heterojunction (**Figure 9a**), diffused heterojunction responsible for charge generation and bilayer can provide uninterrupted charge transport pathways for electrons and holes to electrodes and decrease bimolecular recombination to enable a high FF and PCE. Since the relatively low FF becomes the bottleneck

of T-OPVs, the stratified multilayers might provide a feasible way to the realization of efficient T-OPVs. Moreover, this architecture allows to be laminated for up-scaling OPV module production.

4.2.2 Non-fullerene T-OPVs

Most of the currently reported triplet materials behave as donor materials in T-OPVs. Very few triplet acceptor materials have been reported.^[34, 43] In recent years, tremendous efforts have been directed on the development of non-fullerene acceptors, which have several advantages over fullerenes in terms of easily tunable energy levels for achieving higher V_{oc} , better absorption properties for yielding higher photocurrents.^[70]

There are two ways to develop non-fullerene T-OPVs. First, although non-fullerene acceptors have boosted the performance of S-OPVs dramatically since 2015, the performance of devices based on triplet donors and non-fullerene acceptors was rarely investigated until now. This combination might be a good opportunity for the future investigation on T-OPVs. Second, designing high-performance non-fullerene triplet acceptors based on the backbone of these well-known non-fullerene acceptors by molecular modification may also a feasible approach for T-OPVs.

4.2.3 Ternary T-OPVs employing charge transport components

As demonstrated in our recent report,^[71] the roles of three actors in a ternary OPVs can be divided into electron donor, acceptor and charge transporter where donor benzodithiophene terthiophene rhodanine (BTR) and acceptor NITI formed structures similar as alloys for charge generation and excluded PC₇₁BM from charge generation, but used it as electron transport phase (**Figure 9b**). Introducing a high charge mobility material as third component to only take care of charge transport and release the duty of triplet materials through morphology manipulation maybe decrease the impact of low mobility of triplet materials on the PCEs of T-OPVs.

4.2.4 Investigation on role of triplets in T-OPVs

Studies on device physics, such as the origin of V_{oc} and energy losses have been and will continuously play an important role in the progress of S-OPVs. There are many similarities between singlets and triplets, which may convince people that the theory relevant in S-OPVs can be all used in T-OPVs. However, the discrepancies between triplets and singlets may play key roles in devices. Interestingly, for organic semiconductors featuring small ΔE_{ST} and TADF, exciton transport may occur along both the singlet and the triplet excited states. Recently, Holmes et. al found that the magnitude of singlet and triplet exciton transport is concentration dependent in a TADF-active organic semiconductor and the enhanced triplet exciton transport can be achieved in dilute film.^[72] Therefore, study on exciton dynamics and mechanism of T-OPVs are still needed to push T-OPVs forwards.

5. Conclusions

The main performance limitation on this field is the lack of desired triplet materials with simultaneously long exciton diffusion length, high absorption coefficient, appropriate triplet energy, high charge mobility, low-cost and good processability. Meanwhile, the deeper understanding on the roles of the triplets in devices, and closer interdisciplinary collaborations are also required. In addition to the analysed objective limitations of T-OPVs, the main subjective reason for the slow growth is few researchers believe and involved in the fields. Therefore, the field of T-OPVs is waiting for more researchers involving; more novel materials synthesized with desired optoelectronic properties such as long conjugated lengths, high absorption coefficients and high charge mobilities; more systematic investigation on device physics and theoretical study on conversion and decay processes of excited triplet states. We believe that synergizing novel favorable triplet materials with sophisticated devices processing will accelerate the field. We are looking for the days when employing triplets will really enable efficient T-OPVs with large domain morphology processed from green solvents for facilitating up-scale OPV module production in near future.

Acknowledgements

Y. Jin and Y. Zhang contributed equally to this work. Y. Jin, Y. Liu and F. Zhang acknowledge funding from the Knut and Alice Wallenberg foundation under contract 2016.0059, STINT funds for the Joint China-Sweden Mobility programme, the Swedish Government Research Area in Materials Science on Functional Materials at Linköping University (Faculty Grant SFO-Mat-LiU No. 200900971) and China Scholarship Council (CSC). J. Qiao would like to thank the financial support from the NSFC of China (51711530040 and 51473086). W. Li acknowledges the financial support by MOST (2017YFA0204702, 2018YFA0208504) and NSFC (51773207, 91633301) of China.

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

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Table 1 Summary of photovoltaic properties of mentioned T-OPVs with bilayer device structure (light orange), vacuum deposit BHJ (light blue), solution processed BHJ (light green) and ternary T-OPVs (light purple).

Active layer	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF	PCE [%]	ref
CuPc/PV	0.45	2.3	0.65	0.9	[12]
PtOEP/C ₆₀	0.66	5.6	0.57	2.1	[21]
APIr/C ₆₀	0.99	4.5	0.62	2.8	[24]
Re-DIAN-4H:C ₆₀	0.51	5.07	0.51	1.29	[27]
Au-C2 (5%):C ₇₀	0.85	10.34	0.46	4.0	[28]
R1:PC ₇₁ BM	0.77	4.3	0.35	1.2	[31]
R2:PC ₇₁ BM	0.74	6.52	0.42	2.0	
RWPt-1:PC ₇₁ BM	0.80	12.9	0.39	3.9	[33b]
RWPt-2:PC ₇₁ BM	0.85	14.4	0.63	5.9	
RWPt-3:PCBM	0.35	0.06	0.50	0.01	
PBDB-T:PTP	0.77	4.48	0.42	1.45	[34]
PBDB-T:HFPTP	0.85	7.96	0.48	3.20	
PBDB-T:BFPTP	0.94	12.83	0.62	7.52	
TBzIr:PC ₇₁ BM	0.92	8.91	0.47	3.81	[35]
P1:PCBM	0.82	15.43	0.39	4.93	[37]
P2:PC ₇₁ BM	0.84	7.33	0.40	2.45	[39]
P3:PC ₇₁ BM	0.81	8.67	0.51	3.57	
P4:PC ₇₁ BM	0.79	10.12	0.51	4.13	
PDFN-PPD-Ir:PCBM	0.63	0.44	0.19	0.07	[40]
PTB7Ir1:PC ₇₁ BM	0.75	18.14	0.64	8.71	[41]
PTB7-ThPt1.5:PC ₇₁ BM	0.80	16.21	0.65	8.45	[42a]
PTB7-ThIr1:PC ₇₁ BM	0.80	16.6	0.69	9.19	[42b]
PTB7-Th:PNDIT2Pt1	0.79	11.73	0.49	4.51	[43]
PTB7-Th:P(dbm)PtPyTPA5	0.81	11.99	0.52	4.99	[44]
PBDB-T:P(dbm)PtPyTPA1	0.86	10.84	0.66	6.18	
P1C1:PCBM	0.58	16.3	0.56	5.3	[45]
P3HT:ICBA:0.1 wt% Ir(ppz) ₃	0.86	12.40	0.67	7.08	[48]
PTB7:PC ₇₁ BM:10 wt% Ir-Orange	0.74	16.1	0.73	8.70	[49]

Figure 1. (a) A diagram of four-step working mechanism in BHJ OPVs where 1. excitons are generated; 2. excitons diffuse to donor/accepter interface; 3. excitons dissociate into free charges at interfaces; 4. free charges migrate towards collecting electrodes. (b) A schematic Jablonski diagram for the photophysical process of organic materials under photoexcitation. A: absorption, R: radiative decay transition, NR: non-radiative decay transition, IC: internal conversion, ISC: intersystem crossing, VR: vibrational relaxation; $n \geq 2$. (c) Progress in PCE of T-OPVs and S-OPVs. The data of T-OPVs is from Table 1 and ref.[13]. The data of S-OPVs is from ref.[14].

Figure 2. Molecular structures of small molecular metal complexes used in T-OPVs and the obtained PCEs in the OPVs.

Figure 3. Molecular structures of representative polymers used in T-OPVs and the obtained PCEs in the OPVs.

Figure 4. The schematic diagram of different device architectures of OPVs. (a) Schottky-Junction with one type of semiconductor sandwiched between two different metals (b) Bilayer heterojunction by stacking a n-type semiconductor layer as electron acceptor on the top of a p-type semiconductor layer as electron donor. (c) Binary BHJ contains a blend of electron donor and electron acceptor. (d) Ternary BHJ contains a blend of three components, either two electron donors mixed with one electron acceptor or one electron donor mixed with two electron acceptors.

Figure 5. (a) J - V characteristics of Al/MgPc/Ag cell illuminated with white light from Ag electrode. (b) Absorption spectra of MgPc (circle represent the absorption spectra of a film with a thickness of 150 nm) and theoretical plot of the action spectra for light incident from Ag surface (triangle represent experimental points). (c) Energy level scheme of the Al/MgPc/Ag cell. The barrier is at the Al/MgPc interface. Reproduced with permission.^[11] Copyright 1974, American Institute of Physics.

Figure 6. (a) UV-Vis absorption spectra of CuMePc, P3HT and P3HT:CuMePc (weight ratio of 1:3, 1:1 and 3:1, denoted as P1C3, P1C1 and P3C1) films. (b) Energy level diagram of the device. Reproduced with permission.^[45] Copyright 2011, the Royal Society of Chemistry.

Figure 7. Mechanism of Föster energy transfer (a) and Dexter energy transfer (b). The horizontal lines are HOMO and LUMO energy levels of donor (D) and acceptor (A) molecules; the asterisk denotes excited state. The dashed arrows represent simultaneous rearrangement of the electronic configuration. **Reproduced with permission.**^[55] Copyright 2015, the Royal Society of Chemistry. (c) Energy level diagram for p-PtTh/PCBM system. **Reproduced with permission.**^[9] Copyright 2006, the Royal Society of Chemistry. (d) Energy level diagram for p-PtBTD-Th/PCBM system. **Reproduced with permission.**^[57] Copyright 2009, American Chemical Society.

Figure 8. (a) Summarized FFs (data from Table 1) of T-OPVs with bilayer (black square), vacuum deposited BHJ (orange circle), solution processed BHJ (red circle), solution processed BHJ with no more than 5% metal complex content (green circle) and ternary (blue triangle). (b) Low charge mobility and inefficient extraction result in bi-recombination, in turn a low FF and PCE for T-OPVs. (c) Schematic diagram of the extraction effect on FF and P_{mpp} of OPVs for a given J_{sc} and V_{oc} .

Figure 9. (a) Device architecture of diffused bilayer heterojunction. (b) Illustration of the hierarchical morphology in the ternary film. The green circles represent PC₇₁BM, the blue rods represent NITI and the orange rods represent BTR. Reproduced with permission.^[71] Copyright 2018, Springer Nature Publishing AG.

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To harvest large photocurrent in bulk-heterojunction organic photovoltaic cells (OPVs), materials with long lifetime triplet excitons are expected to be potential candidates for providing sufficient time for excitons diffusion to donor/acceptor interfaces. Recent progress of various triplet materials based OPVs (T-OPVs) are briefly summarized, performance limitations and strategies to further enhance the performance of T-OPVs are discussed.

Keyword

triplet materials, organic photovoltaic cells, triplet excitons, exciton lifetime, exciton diffusion length

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Title

Limitations and perspectives on triplet materials-based organic photovoltaic devices

ToC figure