Graphical Abstract

Heavy metal complex containing organic/polymer materials for bulk-heterojunction photovoltaic devices

Ya-Nan Liu, Shi-Fan Wang, You-Tian Tao*, Wei Huang*

Key Laboratory of Flexible Electronics (KLOFE) & Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing Tech University (NanjingTech), Nanjing 211816, China

Bulk-heterojunction solar cells utilize heavy metal containing organic/polymer materials including platinum-acetylides, cyclometalated Pt or Ir complex containing conjugated oligomers and polymers as well as pure triplet small molecular cyclometalated Ir complex as electron donor materials have been illustrated.

Review

Heavy metal complex containing organic/polymer materials for bulk-heterojunction photovoltaic devices

Ya-Nan Liu, Shi-Fan Wang, You-Tian Tao*, Wei Huang*

Key Laboratory of Flexible Electronics (KLOFE) & Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing Tech University (NanjingTech), Nanjing 211816, China

ARTICLE INFO

Article history:

Received 30 May 2016
Received in revised form 29 June 2016
Accepted 1 July 2016
Available online

Keywords:

Platinum complex
Iridium complex
Bulk-heterojunction
Photovoltaic devices
Organic/polymer solar cells
Triplet

ABSTRACT

The application of heavy-metal complexes in bulk-heterojunction (BHJ) solar cells is a promising new research field which has attracted increasing attention, due to their strong spin-orbit coupling for efficient singlet to triplet intersystem crossing. This review article focuses on recent advances of heavy metal complex containing organic and polymer materials as photovoltaic donors in BHJ solar cells. Platinum-acetylide containing oligomers and polymers have been firstly illustrated due to the good solubility, square planar structure, as well as the fairly strong Pt-Pt interaction. Then the cyclometalated Pt or Ir complex containing conjugated oligomers and polymers are presented in which the triplet organometallic compounds are embedded into the organic/polymer backbone either through cyclometalated main ligand or the auxiliary ligand. Pure triplet small molecular cyclometalated Ir complex are also briefly introduced. Besides the chemical modification, physical doping of cyclometalated heavy metal complexes as additives into the photovoltaic active layers is finally demonstrated.

1. Introduction

Over the past few years, organic solar cells (OSCs) have attracted intense attention as renewable energy sources in both academia and industry, owing to their remarkable features such as flexibility, low cost, light weight, and large area mass production [1-5]. To date, the most efficient device structure for OSCs is utilized BHJ-type as the active layer [6-11], which consists of an interpenetrating blends of π -conjugated small molecules or polymers as electron donor (D) materials and typically fullerene derivatives [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) (Fig. 1) as electron acceptor (A) materials, providing efficient charge separation of the photogenerated excitons as well as favorable charge transport at the D/A interfaces [12-14]. The most common donor material in BHJ solar cells is regioregular poly(3-hexylthiophene) (P3HT) (as shown in Fig. 1), which can be used to achieve a power conversion efficiency (PCE) over 6% [15]. To acquire high performance BHJ solar cells, one of the most successful methods is to modify the chemical structure of the donor materials to achieve the desired electronic properties. Although a large amount of new photovoltaic donor materials have been developed, small molecular OSCs with PCE over 9% have been rarely reported [16,17]; on the other hand, only a few polymers show PCE exceeding 10% in single-junction [18-20] and $\sim$ 12% in multi-junction BHJ polymer solar cell devices [21-25]. In spite of the aforementioned success, after decades development of extraordinarily large number of organic/polymer donor materials, the possibility of further enhancements through chemical modification of designing new materials becomes a bottleneck [26,27]. Therefore, from the materials point of view, explore of new synthetic strategies affording extra approach to break through the PCE is particularly important. Since the mainstream of the previously reported organic/polymer materials all mainly based on singlet dominated pure organic materials, the introduction of organometallic heavy metal component with intersystem crossing is expected to better utilize the triplet excitons in devices to further improve the device performance. However, triplet concerning materials in organic photovoltaics (OPVs) have not been well investigated.

* Corresponding authors.

E-mail addresses: iamyttao@njtech.edu.cn (Y.-T. Tao); iamwhuang@njtech.edu.cn (W. Huang)

Fig. 1. Molecular structures of P3HT and PC₆₁BM.

In general, the mechanism of a typical BHJ solar cell involves four steps: light absorption and exciton generation at the photoactive materials, exciton diffusion to D/A interface, charge separation at D/A interface, and charge transport and collection [28]. Therefore, there are many aspects that can influence the performance of BHJ solar cells on the basis of the driving mechanism. Among, the average exciton diffusion length and charge separation are the most common factors to impact the power conversion efficiency. However, on one hand, the diffusion length (5-10 nm) [29,30] of singlet excitons in the most majority photovoltaic materials is usually significantly shorter than the absorption depth required for efficient light absorption. To increase the exciton diffusion length, the introduction of organic materials with high mobility and/or long lifetime is allowed [31,32]. On the other hand, in order to achieve high efficiency, eliminating geminate recombination of charge pairs that are formed by charge transfer (CT) at the donor-acceptor interface, which is competitive with charge separation should also be taken into consideration [33-36]. Besides, a major loss mechanism reported to limit the PCE of polymer solar cells is the “back reaction” in which the reverse energy transfer occurred from the photo-generated triplet charge transfer state (³CT) to the triplet state (¹T) of donor material when the triplet energy level values of CT state was lower than that of donor polymer [33,37]. Therefore, to reduce geminate charge recombination and facilitate charge separation, one possible way is to efficiently utilize the ³CT, as it is demonstrated that under strong magnetic field, the dark current of organic photovoltaic (OPV) devices could be increased by 45% due to the formation of triplet CT state [38]. In addition, ³CT with sufficiently long lifetime (micro-second scale or even longer) could increase the exciton diffusion lengths, making CT state more easier to separate and dissociate into free charges instead of recombination compared with the relatively shorter nano-second scale ¹CT state [31,33,39,40]. Thus, the formation of more ³CT based on heavy metal complexes is beneficial to increase the current and improve photovoltaic performance [31,39,40].

In the past decades, organometallic complexes have attracted extensive interests, owing to their specific interesting optoelectronic properties as the advanced characteristic to be widely applied as emitters in light-emitting devices [41,42], bioimaging [43,44] and sensitizers in dye-sensitized solar cells [45,46]. Whereas, organometallic complexes have been less investigated in organic thin film photovoltaics, and the initial studies have been focused on the donor/acceptor (*p/n* type) bilayer heterojunction device. For example, Tang et al. fabricated the first organic photovoltaic cell with a conversion efficiency of 1% in a two-layer-heterojunction device by using phthalocyanine (CuPc) (Fig. 2) as the *p*-type active material [47]. In a recent development, Roy and co-workers reported the synthesis of tetramethyl-substituted Cu(II) phthalocyanine (CuMePc) (Fig. 2) nanocrystals and BHJ ternary solar cells based on CuMePc:P3HT:PCBM, displayed excellent photovoltaic performance with a conversion efficiency of 5.3% [48]. Besides, Shao and Yang demonstrated a simple multilayer heterojunction photovoltaic device with the configuration of ITO/PEDOT/PtOEP(30 nm)/C₆₀(30 nm)/BCP(8 nm)/Al(100 nm) [31]. The work based on typical triplet heavy metal complex 2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*-porphineplatinum(II) (PtOEP) as *p*-type donor material, achieved relatively high performance with 2.1% of power conversion efficiency. Furthermore, heavy metal based cyclometalated Ir complex mer-bis(4',6'-difluorophenylpyridinato-N,C_{2'}) iridium(III) azaperylene (APIr) was also applied as the electron donor in a bilayer heterojunction device with a structure of ITO/APIr(5 nm)/C₆₀(30 nm)/*N,N'*-dihexyl-perylene-3,4,9,10-bis(dicarboximide) (PTCDI)(10 nm)/BCP(14 nm)/Al [49]. A fairly good PCE of 2.8% and considerably high open-circuit voltage (*V*_{OC}) up to 1.0 V was obtained.

Fig. 2. Molecular structures of CuPc, CuMePc, PtOEP and APIr.

In this review, recent progress on the development and application of heavy-metal complex containing photovoltaic donor materials for the bulk-heterojunction solar cells are presented. Low-bandgap platinum-acetylide [50-70] and the cyclometalated Pt or Ir containing polymers, oligomers or small molecules [71-77] as donor materials for the active layer of BHJ solar cells are successively demonstrated, in which the heavy metal complex was chemically bonded to the molecular backbone. Finally, physically doping of heavy-metal complexes as additives into the BHJ solar cells to enhance the photovoltaic performance are also discussed [78-81].

2. Heavy metal complex involved through chemical bonding

2.1. Platinum-acetylide containing polymers and oligomers

Platinum-acetylide containing derivatives is reported to be one of the effective *p*-type materials for organic solar cells, due to the square planar structure of Pt complex and fairly strong Pt-Pt interaction as well as excellent optoelectronic properties which is favorable to the performance of the photovoltaic devices [54,82]. The most promising and widely used platinum alkynyls have been a popular candidate for application into π -conjugated organometallic polymeric backbone [50-70]. The π -electron delocalization and the intra-chain charge transport along the entire polymer backbone is facilitated to be enhanced due to the *d*-orbitals (d_{xy} and d_{xz}) of the Pt atom overlaps with the π -orbitals (π_y^* and π_z^*) of the C $\equiv$ C unit to construct the one dimensional conjugated polymer chain, when the alkyne is coordinated with the electron-rich Pt(II) ions [83]. Additionally, the presence of bulky PBu₃ ligands which prevents strong aggregation improves the solubility of platinum-containing polyynes in organic solvents. Furthermore, by introduction of donor-acceptor (D-A) architecture to the platinum centered molecular backbone, broad absorption bands (even up to near-infrared region) attributed from the intramolecular charge transfer (ICT) between the electron donating and accepting units for small bandgaps are allowed to be achieved, making this kind of materials suitable for photovoltaic devices [84]. Therefore, the emerging use of low-bandgap soluble platinum-acetylide polymers and oligomers, which represent potential candidates for light weight solar energy conversion donor materials in OPVs, providing a new and versatile avenue to harvest sunlight for efficient solar power generation.

In 2006, Schanze and co-workers demonstrated the first report of a polymer-based photovoltaic device which involved a triplet excited state in the process of photoinduced charge separation [53]. Through blending a blue-violet absorbing platinum-acetylide polymer p-PtTh (polymer **1** as shown in Fig. 3) with PCBM to serve as the active layer in polymer photovoltaic device, a PCE of 0.27% was achieved. Due to the introduction of heavy metal Pt center in the platinum-acetylide, spin-orbit coupling enhanced, and thus rapid and efficient intersystem crossing from singlet to triplet occurred. The results from photophysical measurements provided the evidence that the charge carriers were produced in a photoinduced electron transfer (PET) process involving the triplet excited state of p-PtTh, which contributed to the device efficiency. The rather low efficiency could be attributed to the relatively wide bandgaps, and possibly unfavourable energy levels as well as poor charge-transport properties when blended with PCBM.

Fig 3. Molecular structures of platinum-acetylide containing polymers.

Then in 2007, Wong *et al.* reported 4,7-di-2'-thienyl-2,1,3-benzothiadiazole (TBT) containing π -conjugated platinum-acetylide containing polymer **2** (Fig. 3) [54]. The novel platinum metallopolyyne is based on planar conjugated segments with extended π -electron delocalized system throughout the polymer chain. Internal D-A functions between the electron-rich Pt-ethynyl groups and the electron-deficient benzothiadiazole rings in combination with two electron-donating thiophenes allowed a low-bandgap of ~ 1.85 eV with extended absorption that features unique D-A characteristics of the material. BHJ polymer solar cells based on metallopolyyne/PCBM blends as the photoactive layer, showed an average PCE of 4.1%. The significantly improved efficiency clearly demonstrated the potential of metallated conjugated polymers for efficient photovoltaic devices. Wong group also presented four π -

conjugated platinum(II) polyyne (**3-6**) containing bithiazole-oligo (thienyl) rings with solution-processable and strongly visible-light absorption [56]. By varying the oligothienyl chain length in the polymer backbone, optical and charge transport properties as well as the polymer solar cell efficiency could be tuned. Through gradually increasing the number of thienyl ring, the polymer bandgap reduced from 2.40 eV to 2.06 eV, thus the corresponding light-harvesting capacity enhanced and the intrachain charge carrier mobility improved. Therefore, in the polymer/PCBM blended systems, both polymer **5** and **6** exhibited carrier mobility on the orders of 10^{-4} $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ and comparable photovoltaic efficiencies, with high PCE of up to 2.7% and peak external quantum efficiency (EQE) of 83% for polymer **5** and PCE of $\sim 2.5\%$ for **6**. Unfortunately, heavy metal effect responsible for the intersystem crossing was reduced by the highly extended heteroaryl rings in the ligand. Therefore, it is described that the charge-transfer excited state mostly contributed to the efficient photoinduced charge separation in the energy conversion for **3-6** instead of the triplet state. This was different from the monothiophene based Pt-polyyne **1** blended films in which charge separation occurs *via* the triplet excited state of polymer platinum-acetylide.

Similar molecular design strategies have also been employed to synthesize a series of π -conjugated organometallic platinum-containing polymetallayne polymers which were functionalized with fluorine-oligothienylring (**7-10**), phenothiazine-oligothiophene (**11-13**) and triphenylamine-2,1,3-benzothiadiazole hybrids (**14** and **15**) [57-59], as shown in Fig. 3. The highest PCE of 2.88, 1.29 and 1.61% in each series were achieved for polymer **10**, **13** and **15** based BHJ devices respectively, owing to the presence of the most extended π -electron delocalized system along the polymer chain to efficiently harvest the solar energy. For example, the bandgaps of **7-10** successively reduced from 2.93, 2.60, 2.43 to 2.33 eV, accomplished by the gradual increase of PCE from 0.36, 1.54, 2.47 to 2.88%. The best performance of **10** based solar cell device was attributed to its considerably high charge mobilities and favorable light absorption characteristics [57]. In general, the design and synthesis of π -conjugated platinum-acetylide containing polymers *via* altering the number of thienyl ring, indicating a promising road to tune their optical absorption, electrochemical and electronic properties as well as the photovoltaic performance when applied as donor materials in BHJ solar cell devices. However, the utilization of the triplet excited states to promote an efficient photoinduced charge separation was not detected in these D-A platinum-acetylide polymers.

Besides, Wong *et al.* also synthesized a new D-A type organometallic polyyne **16** containing the more electron-rich 3,4-ethylenedioxythiophene (EDOT) and the electron-deficient benzothiadiazole hybrid spacer. The polymer exhibited a narrow bandgap of 1.76 eV, when used as the electron donor in the BHJ active layer only a relatively low PCE of 0.3% was obtained [60]. In addition, three amorphous π -conjugated organometallic polymers **17-19** (as shown in Fig. 3) were demonstrated by Jen and co-workers [61], which showed field-effect hole mobility as high as 1.0×10^{-2} $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$, therefore a relatively high level of performance was expected in BHJ photovoltaic devices based on the blends of organometallic polymers and PCBM. The best performance with V_{OC} of 0.79 V, fill factor (*FF*) of 51.4%, short-circuit current density (J_{SC}) at 10.12 mA/cm^2 and PCE up to 4.13% was achieved in a 1:4 weight ratio of polymer **18**:PC₇₁BM blends. Based on the 2,1,3-benzothiadiazole (BT) containing model polymer **2** (BT-BTPt), Luscombe *et al.* [63] reported a series of organometallic conjugated polyplatinynes comprising different electron-acceptors, such as pyrido[3,4-*b*]pyrazine (HPP-BTPt, **20**), thieno[3,4-*b*]pyrazines (TP-BTPt **21**, MTP-BTPt **22**, PTP-BTPt **23**). The optical bandgaps reduced from 1.96 of **20** to 1.86 (**2**), 1.66 (**22**), 1.54 (**21**) and 1.49 eV (**23**). BHJ solar cells based on the blends of polymers/PC₇₁BM gave PCE of 0.68% for **20** and 2.41% for **2**.

Near-infrared (NIR) absorbing platinum(II) metallopolyynes functionalized with fluorene and benzo[1,2-*c*:4,5-*c'*]bis([1,2,5]thiadiazole (**24**) or [1,2,5]thiadiazolo[3,4-*i*]dibenzo[*a,c*]phenazine (**25**) hybrid spacer were also presented [64]. Through the weak electron-donor and strong electron-acceptor strategy, both polymers exhibited narrow bandgaps of 1.54 and 1.65 eV, respectively, with absorption spectra extended down to 800-850 nm and up to 1% of PCE for bulk heterojunction solar cells. Besides, Pt(II) containing metallopolyynes **26** and **27** based the electron-deficient 4H-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-4-one were also reported [66], with extremely low bandgaps of 1.44-1.53 eV, representing the lowest optical bandgap yet reported for platinum(II) metallopolyynes to date. Similar to previous study, no triplet excited state occurs in photoinduced charge separation of the platinum-acetylide polymers/PCBM blends based BHJ solar cells. However, the work offers an attractive way towards conjugated heavy-metal complex containing photovoltaic materials with broad solar absorption and demonstrates the potential for both visible and NIR light power conversion.

Since the molecular weight of polymer active materials shows large impact on the performance and BHJ solar cells [20,76], compared to polymeric systems which intrinsically exhibits large structural variations in molecular weight, polydispersity, regioregularity and batch-to-batch reproducibility, small molecules or oligomers with well-defined structures are relatively easier to synthesize and purify. Kirk S. Schanze and co-workers designed and synthesized a novel fulleropyrrolidine end-capped platinum acetylide donor-acceptor triad assembly of **28** (Fig. 4) [85]. Employing **28** as the active layer consisting solely of a donor-acceptor dyad or triad assembly in the OPV devices, the PCE and J_{SC} as low as 0.056% and 0.5 mA/cm^2 was obtained, respectively, due to the singlet and triplet states of the platinum-acetylides were strongly quenched in the triad assembly. Then later in 2012, Wong *et al.* reported four π -conjugated small-molecular platinum(II)-bis(aryleneethynylene) complexes **29-32** which consist of the electron-accepting benzothiadiazole moiety and the electron-donating triphenylamine and/or thiophene units [84]. It was discovered that incorporating stronger electron-donor moieties into the π -conjugated metal-organic molecules could not only broaden the absorption bands, but also enhance the intramolecular charge transfer between the donor and acceptor units. Therefore, the best performance was achieved in oligomers **29** and **30**, with the hole mobility of up to 0.7 and 2.4×10^{-4} $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively. Solution-process BHJ photovoltaic devices by using them as donor active materials exhibited PCE of 2.37 and 2.34%, respectively.

Fig 4. Molecular structures of platinum-acetylide containing oligomers.

2.2. Cyclometalated Pt/Ir complex containing π -conjugated polymers

Besides on the linear platinum acetylides comprising photovoltaic materials, heavy metal organometallic polymers containing cyclometalated Pt or Ir complexes which was attached *via* the C^N or O^O diketonate ligands have been attracted gradually increasing attention due to better involvement from the orbitals of Pt or Ir center and the cyclometalated organic ligand to polymer backbone in both the ground and the excited states of the material [71-75]. Strong spin-orbit coupling on the heavy metal center allows for the mixing of singlet metal-to-ligand charge transfer state (¹MLCT) with the formally forbidden triplet metal-to-ligand charge transfer (³MLCT) and ³ π - π^* states. Therefore, cyclometalated Pt/Ir complex containing conjugated polymer donor materials are worth to investigate on better understanding the role of heavy atom effects on triplet formation in polymer photovoltaics. It is reported that materials with large triplet yields may provide favorable access to increase the current of OPV devices [31,51]. This enhancement in photovoltaic performance was attributed to the decrease of geminate recombination and increase of exciton diffusion length due to the forbidden nature of recombination from the triplet state. And it is demonstrated that triplet-forming polymers is beneficial to hinder geminate pair recombination and to improve the exciton diffusion length in BHJ solar cell devices [40,53,86].

Compared to the polyplatinyes, the cyclometalated Pt or Ir complex containing polymers demonstrated higher flexibility for tuning the optoelectronic properties through the modification of the chelated main ligands. In 2009, Fréchet *et al.* reported the two conjugated cyclometalated platinum-containing polymers Pt-T1 (**33**) and F8TZPt (**34**) (Fig. 5), in which the platinum center is adjacent to the conjugated backbone *via* a cyclometalated 2-(2'-thienyl)thiazole C^N ligand to form a coplanar conformation [40]. The polymers exhibited optical bandgaps of 2.1 and 1.65 eV according to different comonomers of fluorene and thiophene, thus both the two cyclometalated polymers showed a large overlap with the solar spectrum. The space charge limited current (SCLC) mobilities of **34** and **33** were measured to be 2.5×10^{-9} and $1 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. The SCLC mobility of Pt-T1 is significantly higher than polyplatinyes (10^{-8} to $10^{-7} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [39]. The improved charge transport properties of the cyclometalated platinum-containing conjugated polymers indicated an extra attractive route to organometallic polymers for photovoltaics. Triplet exciton formation was discovered indirectly by conducting the photosensitized emission behavior of singlet oxygen in both solution and solid film. Photovoltaic devices fabricated by blending the two polymer materials **34** or **33** with PCBM as the active layer gave PCE up to 1.3% and 0.4%, respectively, suggesting that cyclometalated platinum polymers are potential candidates of photovoltaic materials.

In 2013, Chien-Hong Cheng and co-workers synthesized two cyclometalated platinum polymers (**35** and **36**) and two Pt-free control polymers (**37** and **38**) as the comparison to characterize their photophysical properties and the photovoltaic performance [87]. It is found that the cycloplatinated polymers **35** and **36** exhibited significantly red-shifted absorption spectra and lower bandgap with respect to the Pt-free counter parts of **37** and **38**. The performance of the photovoltaic devices fabricated by Pt-based polymers and PCBM blends demonstrated PCE approximately more than twice of the corresponding Pt-free polymers, the best performance was achieved to be 2.9% for compound **35**. However, it was demonstrated that the higher current and PCE of cycloplatinated polymers based device than the Pt-free polymers was attributed to their significant red-shifted (80-90 nm) absorption bands to better harvest solar energy of the Pt-containing polymers instead of the triplet contribution.

Schanze group also presented a π -conjugated organometallic isoindigo-based polymer **39** (Iin-C18-Poly) that contains cyclometalated platinum unit was developed and applied as electron donor into BHJ solar cells with PCBM [74]. Isoindigo is an excellent acceptor in D-A type photovoltaic materials, attribute to its intrinsic electron-deficient nature [88-90]. The triplet excited state occurs in **39** with introducing cyclometalated platinum complex into the polymer backbone, could induce spin-orbit coupling and enhance singlet-triplet intersystem crossing. Since the singlet energy of the polymer (1.89 eV) is higher than the charge-separated states (Iin-C18-Poly⁺/PC₆₁BM⁻, *E*_{cs}: ~1.82 eV), therefore, PET from the singlet state of polymer to its charge separated state is favorable. Unfortunately, as the singlet and triplet energy levels of the charge transfer state are very similar, it is evidenced that the triplet state (1.09 eV) of the polymer was more than 0.5 eV below the charge separated state, and thus charge transfer for charge separation occurred *via* the triplet state is not at all likely to happen, while the triplet state energy loss from the triplet charge separation

state to the triplet of donor polymer might exist [33,37]. Together with the close lowest unoccupied molecular orbital (LUMO) (~ 4.2 eV) of the polymer to that of PCBM which lead comparatively low driving force for charge separation at the donor-acceptor interface, BHJ photovoltaic device performed a rather low PCE of 0.22%.

Fig. 5. Molecular structures of cyclometalated Pt/Ir containing polymers.

By chemically attaching the Ir complex into the π -conjugated poly(fluorine-*co*-phenylpyridine) (**43**) backbone through the cyclometalation of phenylpyridine with Ir center [86], the first cyclometalated heavy metal Ir complex containing polymer (**44**) for photovoltaics was presented by Holdcroft group. Blending the donor polymer with the electron acceptor of PCBM, a significant increase of EQE from 1.1% for **43** to 10.3% of **44** was observed. Despite the PCE of **44** based devices is considerably low as just 0.07%, whereas it is 35 times higher than the control Ir-free polymer **43**, exhibiting an enormously great improvement. It is demonstrated that introducing triplet forming Ir complexes into the poly(fluorine-*co*-phenylpyridine) polymer to function as donor materials for OSC, considerably enhanced photovoltaic conversion efficiencies was attributed to the formation of the triplet state and thus to extend the longer diffusion length. The rather low PCE of the Ir containing poly(9,9-dioctylfluorene-*co*-tris(2-phenylpyridine) iridium (III)) could be assigned to its unfavorable light harvesting ability and poor charge transport property.

compared to the Ir free control PTB7, enhanced J_{SC} , EQE and PCE have been achieved under various repeated experiments at lower Ir content of 1, 2.5% (batch 1) and 0.5, 1.5% (batch 2). Devices based on 1% of Ir embedded polymer **46**, the PCE was increased by 45, 39 and 31% at three different device fabrication conditions. From the materials point of view, besides on the exploitation of new conjugated photovoltaic materials, chemically bonding low content triplet heavy metal complexes to current high efficiency polymers could offer an extra approach to improve the PCE of BHJ polymer solar cells.

2.3. Phosphorescent triplet metal complexes

Cyclometalated heavy metal complexes bearing with large bandgap ligands have been extensively investigated as the phosphorescent emitter in high efficiency organic light emitting diodes [101-104]. However, the application of these small molecular pure triplet organometallic complexes as sole donor materials in BHJ organic solar cells has been rarely studied owing to the relatively poor charge transport and poor film-forming ability as well as narrow and weak light absorption capability. Zhen *et al.* designed and synthesized two red light-emission cyclometalated Ir complex **52** and **53** via harvesting triplet excitons in OSCs (Fig. 6) [77]. The film morphology, carrier mobility and light absorption were allowed to improve by introducing the 2,2,6,6-tetramethyl-3,5-heptanedione, *p*-methoxybenzene and triphenylamine into the ligand. The hole mobilities of **52** and **53** measured from field effect transistor (FET) are determined to be 3×10^{-6} and 3×10^{-5} $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, respectively, which is in good agreement with SCLC method of 2.0×10^{-6} and 4.3×10^{-5} $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$. A J_{SC} of 6.5 mA/cm^2 , V_{OC} of 0.74 V, FF of 0.42, and overall PCE of 2.0% was obtained in the conventional solution processed BHJ organic photovoltaic device by using the Ir complex **53** as the electron donor and PC₇₁BM as electron acceptor. The results indicated the possibility of involving phosphorescent dyes as single electron donors in solution processed BHJ OSCs, enriched the donor materials of OSCs and provided important guidance for the molecular design on new heavy metal complexes with low bandgaps, desired highest occupied molecular orbital (HOMO) and LUMO energy levels as well as suitable molecular packing to enhance the absorption and charge transport for triplet OSCs.

Fig. 6. Molecular structures of phosphorescent triplet metal complexes as sole donor materials.

Besides, Hong and co-workers also synthesized three isoquinoline-based Ir complexes (**54-56**) by changing the main ligands and studied their photovoltaic performance through fabricating BHJ solar cells [81]. By blending Ir complex with PCBM in a 1:4 ratio for the spin coated devices, **55** exhibited the highest PCE of 0.50%, compared to 0.43 and 0.34% for **54** and **56**, respectively. The higher PCE obtained from complex **55** mainly derived from the superior hole transport ability of the triphenylamine moiety.

3. Physically doping as additives

Morphology property of donor/acceptor blends in the active layer which includes domain sizes, D/A materials miscibility and molecular orientation, crystallinity *etc.*, directly affects the photovoltaic device performance especially J_{SC} and FF [105,106]. If the interfacial area between the electron donor and acceptor is too indistinct or the domains of the two phases within of the active composite layer are too large, exciton dissociation is unbeneficial. Therefore, several strategies including solvent additives, solvent annealing, thermal annealing or mixed solvent have been carried out to improve the morphology of the D/A blends to reach an optimal length scale of phase-separated interpenetrating networks between the electron donor and acceptor to maximize exciton dissociation and simultaneously minimize charge recombination, and thus to enhance photovoltaic performance [107-111].

Besides, incorporating of the heavy metal complexes as additives into the photoactive layer of the BHJ solar cells can also improve the J_{SC} and enhance the PCE of the devices. Loo and co-workers [78] reported the incorporation of fractional amounts of charged heavy metal Ir complex as nonvolatile additives to the photoactive layer of P3HT/PCBM blends. It was initially expected to induce the generation of triplet excitons which possess longer lifetimes and longer diffusion lengths from the heavy metal complex to enhance charge-carrier generation. However, detailed characterization suggested that it is not the generation of triplet excitons from the transition metal complex, whereas the Ir-based additives selectively partitioned into and remained in the P3HT phase, and thus to effectively increase the chemical incompatibility between the electron donor P3HT and acceptor PCBM. The strategy of involving of the nonvolatile additives efficiently altered the thermodynamics of phase separation between the electron donor and acceptor, resulting in the formation of more PCBM clusters. It was demonstrated that PCE could be enhanced from 1.01% to 1.81% through physically doping of 5 wt% Ir complex **57** to P3HT/PCBM blended photoactive layer in inverted bulk-heterojunction organic solar cell.

Kim and co-workers introduced a multifunctional Ir complex **58** (Fig. 7) as additives and polyethylene oxide (PEO) as an ion channel to strengthen the ionic mobility [112,113] to enhance the nanophase segregation of the photovoltaic active layer film and the compatibility of P3HT/PCBM blends [79]. Increased J_{SC} from 8.57 to 10.24 mA/cm² and PCE from 1.6% to 3.4% were observed. Besides on the influence of the additives to the morphology of the photoactive layer, they also discovered the obvious enhancement in J_{SC} was primarily attributed from efficient triplet to singlet energy transfer from the Ir complex **58** to P3HT.

Hornig *et al.* reported that greatly improved photovoltaic response was observed due to the enhancement of singlet-to-triplet conversion through physically doping of heavy-metal complex Iridium (III) tris[2-(4-totyl)pyridinato-N,C2] [Ir(mppy)₃] (**59**) into P3HT/CdSe hybrid organic solar cells [80]. It was found that the short-circuit current was increased by 100% with the 10 wt % Ir(mppy)₃, revealing a significant increased population of triplet excitons.

Fig. 7. Molecular structures of the organometallic additives.

4. Conclusion

We have summarized recent advances on the π -conjugated heavy metal complex containing small molecules, oligomers and polymers for their application in BHJ solar cells. Platinum-acetylide containing oligomers or polymers as donor materials exhibited PCE up to 5%. And the introduction of 1 mol% of Ir complex to the champion donor polymer PTB7 backbone, the PCE was up to 8.7% which was increased by 31-45% compared to the control polymer PTB7 under the same device fabrication condition. Involving pure triplet phosphorescent dyes as sole electron donors in solution-processed BHJ solar cells, gave overall PCE of 2%. It is believed that introducing appropriate long exciton lifetime organic materials is a very promising approach to improve the photovoltaic performance. The current pure triplet materials used in OPV displayed rather poor light harvesting ability and low charge carrier mobility. Therefore, high-mobility triplet materials with wide and efficient solar light absorption capability, high carrier mobility and well matched energy levels are highly desired to improve the efficiency of organic photovoltaic devices in the future. Furthermore, the confirmed detail mechanism of triplet content on the influence of organic solar cells is desired for future investigation, either for materials with very low ratio in current high efficiency D-A polymers or broad absorption of pure triplet organic small molecules or oligomers.

Acknowledgment

We thank The National Key Basic Research Program of China (973 Program, No. 2015CB932200) the National Natural Science Foundation of China (No. 21304047), NSF of Jiangsu Province (No. 13KJB430017), Research Fund for the Doctoral Program of Higher Education (No. 20133221120015) and Synergetic Innovation Center for Organic Electronics and Information Displays for financial support.

References

- [1] C. Li, M. Liu, N.G. Pschirer, et al., Polyphenylene-based materials for organic photovoltaics, *Chem. Rev.* 110 (2010) 6817-6855.
- [2] F.C. Krebs, Fabrication and processing of polymer solar cells: a review of printing and coating techniques, *Sol. Energy Mater. Sol. Cells* 93 (2009) 394-412.
- [3] M. Helgesen, R. Søndergaard, F.C. Krebs, Advanced materials and processes for polymer solar cell devices, *J. Mater. Chem.* 20 (2010) 36-60.
- [4] R. Søndergaard, M. Hösel, D. Angmo, et al., Roll-to-roll fabrication of polymer solar cells, *Mater. Today* 15 (2012) 36-49.
- [5] T.D. Nielsen, C. Cruickshank, S. Foged, et al., Business, market and intellectual property analysis of polymer solar cells, *Sol. Energy Mater. Sol. Cells* 94 (2010) 1553-1571.
- [6] J. Chen, Y. Cao, Development of novel conjugated donor polymers for high-efficiency bulk-heterojunction photovoltaic devices, *Acc. Chem. Res.* 42 (2009) 1709-1718.
- [7] G. Dennler, M.C. Scharber, C.J. Brabec, Polymer-Fullerene bulk-heterojunction solar cells, *Adv. Mater.* 21 (2009) 1323-1338.
- [8] S.H. Chan, C.-S. Lai, H.L. Chen, et al., Highly efficient P3HT: C60 solar cell free of annealing process, *Macromolecules* 44 (2011) 8886-8891.
- [9] E. Wang, L. Hou, Z. Wang, et al., An easily synthesized blue polymer for high-performance polymer solar cells, *Adv. Mater.* 22 (2010) 5240-5244.
- [10] J. Peet, J.Y. Kim, N.E. Coates, et al., Efficiency enhancement in low-bandgap polymer solar cells by processing with alkane dithiols, *Nat. Mater.* 6 (2007) 497-500.
- [11] L. Lu, T. Zheng, Q. Wu, et al., Recent advances in bulk heterojunction polymer solar cells, *Chem. Rev.* 115 (2015) 12666-12731.
- [12] Y. Zhang, X.-D. Dang, C. Kim, et al., Effect of charge recombination on the fill factor of small molecule bulk heterojunction solar cells, *Adv. Energy Mater.* 1 (2011) 610-617.
- [13] M.M. Wienk, J.M. Kroon, W.J.H. Verhees, et al., Efficient methano[70]fullerene/MDMO-PPV bulk heterojunction photovoltaic cells, *Angew. Chem.* 115 (2003) 3493-3497.
- [14] W. Chen, T. Salim, H. Fan, et al., Quinoxaline-functionalized C₆₀ derivatives as electron acceptors in organic solar cells, *RSC Adv.* 4 (2014) 25291-25301.

- [15] G. Zhao, Y. He, Y. Li, 6.5% Efficiency of polymer solar cells based on poly(3-hexylthiophene) and Indene-C₆₀ bisadduct by device optimization, *Adv. Mater.* 22 (2010) 4355-4358.
- [16] Q. Zhang, B. Kan, F. Liu, et al., Small-molecule solar cells with efficiency over 9%, *Nat. Photon.* 9 (2015) 35-41.
- [17] B. Kan, Q. Zhang, M. Li, et al., Solution-processed organic solar cells based on dialkylthiol-substituted benzodithiophene unit with efficiency near 10%, *J. Am. Chem. Soc.* 136 (2014) 15529-15532.
- [18] Y. Liu, J. Zhao, Z. Li, et al., Aggregation and morphology control enables multiple cases of high-efficiency polymer solar cells, *Nat. Commun.* 5 (2014) 1-8.
- [19] L. Dou, C.C. Chen, K. Yoshimura, et al., Synthesis of 5*H*-dithieno[3,2-*b*:2',3'-*d*]pyran as an electron-rich building block for donor-acceptor type low-bandgap polymers, *Macromolecules* 46 (2013) 3384-3390.
- [20] T.L. Nguyen, H. Choi, S.J. Ko, et al., Semi-crystalline photovoltaic polymers with efficiency exceeding 9% in a ~300 nm thick conventional single-cell device, *Energy Environ. Sci.* 7 (2014) 3040-3051.
- [21] C.C. Chen, W.H. Chang, K. Yoshimura, et al., An efficient triple-junction polymer solar cell having a power conversion efficiency exceeding 11%, *Adv. Mater.* 26 (2014) 5670-5677.
- [22] H. Zhou, Y. Zhang, C.K. Mai, et al., Polymer Homo-Tandem Solar Cells with best efficiency of 11.3%, *Adv. Mater.* 27 (2015) 1767-1773.
- [23] W. Cai, X. Gong, Y. Cao, Polymer solar cells: recent development and possible routes for improvement in the performance, *Sol. Energy Mater. Sol. Cells* 94 (2010) 114-127.
- [24] I. Etexbarria, J. Ajuria, R. Pacios, Polymer: fullerene solar cells: materials, processing issues, and cell layouts to reach power conversion efficiency over 10%, a review, *J. Photon. Energy* 5 (2015) 057214-057214.
- [25] H. Benten, D. Mori, H. Ohkita, et al., Recent research progress of polymer donor/polymer acceptor blend solar cells, *J. Mater. Chem. A* 4 (2016) 5340-5365.
- [26] T. Jiang, J. Yang, Y. Tao, et al., Random terpolymer with a cost-effective monomer and comparable efficiency to PTB7-Th for bulk-heterojunction polymer solar cells, *Poly. Chem.* 7 (2016) 926-932.
- [27] J. Lee, H. Ko, E. Song, et al., Naphthodithiophene-based conjugated polymer with linear, planar backbone conformation and strong intermolecular packing for efficient organic solar cells, *ACS Appl. Mater. Interfaces* 7 (2015) 21159-21169.
- [28] L. Lu, L. Yu, Understanding low bandgap polymer PTB7 and optimizing polymer solar cells based on it, *Adv. Mater.* 26 (2014) 4413-4430.
- [29] J.J. M. Halls, K. Pichler, R.H. Friend, et al., Exciton diffusion and dissociation in a poly(*p*-phenylenevinylene)/C₆₀ heterojunction photovoltaic cell, *Appl. Phys. Lett.* 68 (1996) 3120-3122.
- [30] D.E. Markov, C. Tanase, P.W.M. Blom, et al., Simultaneous enhancement of charge transport and exciton diffusion in poly(*p*-phenylenevinylene) derivatives, *Phys. Rev. B* 72 (2005) 045217.
- [31] Y. Shao, Y. Yang, Efficient organic heterojunction photovoltaic cells based on triplet materials, *Adv. Mater.* 17 (2005) 2841-2844.
- [32] J. Yu, J. Huang, H. Lin, et al., Exciton diffusion length analysis of mixed donor materials in organic solar cells by doping with phosphorescent iridium complex, *J. Appl. Phys.* 108 (2010) 113111.
- [33] M.K. Etherington, J. Wang, P.C.Y. Chow, et al., Recombination pathways in polymer fullerene photovoltaics observed through spin polarization measurements, *Appl. Phys. Lett.* 104 (2014) 063304.
- [34] J.D. Mihailescu, L.J.A. Koster, J.C. Hummelen, et al., Photocurrent generation in polymer-fullerene bulk heterojunctions, *Phys. Rev. Lett.* 9 (2004) 216601.
- [35] T. Offermans, S.C.J. Meskers, R. A. J. Janssen, Charge recombination in a poly(para-phenylenevinylene)-fullerene derivative composite film studied by transient, nonresonant, hole-burning spectroscopy, *J. Chem. Phys.* 119 (2003) 10924-10929.
- [36] S. Westenhoff, I.A. Howard, J.M. Hodgkiss, et al., Charge recombination in organic photovoltaic devices with high open-circuit voltages, *J. Am. Chem. Soc.* 130 (2008) 13653-13658.
- [37] T. Basel, U. Huynh, T. Zheng, et al., Optical, electrical, and magnetic studies of organic solar cells based on low bandgap copolymer with spin ½ radical additives, *Adv. Funct. Mater.* 25 (2015) 1895-1902.
- [38] J.P. Wang, A. Chepelianskii, F. Gao, et al., Control of exciton spin statistics through spin polarization in organic optoelectronic devices, *Nat. Commun.* 3 (2012) 1-6.
- [39] J.G. Mei, K. Ogawa, Y.G. Kim, et al., Low-band-gap platinum acetylide polymers as active materials for organic solar cells, *ACS Appl. Mater. Interfaces* 1 (2009) 150-161.
- [40] T.A. Clem, D.F.J. Kavulak, E.J. Westling, et al., Cyclometalated platinum polymers: synthesis, photophysical properties, and photovoltaic performance, *Chem. Mater.* 22 (2010) 1977-1987.
- [41] M.A. Baldo, D.F. O'Brien, Y. You, et al., Highly efficient phosphorescent emission from organic electroluminescent devices, *Nature* 395 (1998) 151-154.
- [42] R.D. Costa, E. Ortí, H.J. Bolink, et al., Luminescent ionic transition-metal complexes for light-emitting electrochemical cells, *Angew. Chem. Int. Ed.* 51 (2012) 8178-8211.
- [43] Q. Zhao, C. Huang, F. Li, Phosphorescent heavy-metal complexes for bioimaging, *Chem. Soc. Rev.* 40 (2011) 2508-2524.
- [44] D.L. Ma, H.Z. He, K.H. Leung, et al., Bioactive luminescent transition-metal complexes for biomedical applications, *Angew. Chem. Int. Ed.* 52 (2013) 7666-7682.
- [45] J.A.G. Williams, Photochemistry and photophysics of coordination compounds: platinum, *Top. Curr. Chem.* 281 (2007) 205-268.
- [46] W.T. Eckenhoff, R. Eisenberg, Molecular systems for light driven hydrogen production, *Dalton Trans.* 41 (2012) 13004-13021.
- [47] C.W. Tang, Two-layer organic photovoltaic cell, *Appl. Phys. Lett.* 48 (1986) 183-185.
- [48] Z.X. Xu, V.A.L. Roy, K.H. Low, et al., Bulk heterojunction photovoltaic cells based on tetra-methyl substituted copper(II) phthalocyanine:P3HT:PCBM composite, *Chem. Commun.* 47 (2011) 9654-9656.
- [49] T.B. Fleetham, Z. Wang, J. Li, Exploring cyclometalated Ir complexes as donor materials for organic solar cells, *Inorg. Chem.* 52 (2013) 7338-7343.
- [50] J.S. Wilson, N. Chawdhury, M.R.A. Al-Mandhary, et al., The energy gap law for triplet states in Pt-containing conjugated polymers and monomers, *J. Am. Chem. Soc.* 123 (2001) 9412-9417.
- [51] A. Kohler, J.S. Wilson, R.H. Friend, et al., The singlet-triplet energy gap in organic and Pt-containing phenylene ethynylene polymers and monomers, *J. Chem. Phys.* 116 (2002) 9457-9463.
- [52] K.S. Schanze, E.E. Silverman, X. Zhao, Intrachain triplet energy transfer in platinum-acetylide copolymers, *J. Phys. Chem. B* 109 (2005) 18451-18459.
- [53] F. Guo, Y.G. Kim, J.R. Reynolds, et al., Platinum-acetylide polymer based solar cells: involvement of the triplet state for energy conversion, *Chem. Commun.* (2006) 1887-1889.
- [54] W.Y. Wong, X.Z. Wang, Z. He, et al., Metallated conjugated polymers as a new avenue towards high-efficiency polymer solar cells, *Nat. Mater.* 6 (2007) 521-527.
- [55] K. Glusac, M.E. Köse, H. Jiang, et al., Triplet excited state in platinum-acetylide oligomers: triplet localization and effects of conformation, *J. Phys. Chem. B* 111 (2007) 929-940.
- [56] W.Y. Wong, X.Z. Wang, Z. He, et al., Tuning the absorption, charge transport properties, and solar cell efficiency with the number of thienyl rings in platinum-containing poly(aryleneethynylene)s, *J. Am. Chem. Soc.* 129 (2007) 14372-14380.
- [57] L. Liu, C.L. Ho, W.Y. Wong, et al., Effect of oligothiophenyl chain length on tuning the solar cell performance in fluorine-based polyplatinynes, *Adv. Funct. Mater.* 18 (2008) 2824-2833.
- [58] W.Y. Wong, W.C. Chow, K.Y. Cheung, et al., Harvesting solar energy using conjugated metallopolyne donors containing electron-rich phenothiazine-oligothiophene moieties, *J. Organ. Chem.* 694 (2009) 2717-2726.

- [59] Q. Wang, W.Y. Wong, New low-bandgap polymetallaynes of platinum functionalized with a triphenylamine-benzothiadiazole donor-acceptor unit for solar cell applications, *Poly. Chem.* 2 (2011) 432-440.
- [60] W.Y. Wong, X. Wang, H.L. Zhang, et al., Synthesis, characterization and photovoltaic properties of a low-bandgap platinum(II) polyyne functionalized with a 3,4-ethylenedioxythiophene-benzothiadiazole hybrid spacer, *J. Organ. Chem.* 693 (2008) 3603-3612.
- [61] N.S. Baek, S.K. Hau, H.L. Yip, et al., High performance amorphous metallated π -conjugated polymers for field-effect transistors and polymer solar cells, *Chem. Mater.* 20 (2008) 5734-5736.
- [62] W.Y. Wong, Metallopolyyne polymers as new functional materials for photovoltaic and solar cell applications, *Macromol. Chem. Phys.* 209 (2008) 14-24.
- [63] P.T. Wu, T. Bull, F.S. Kim, et al., Organometallic donor-acceptor conjugated polymer semiconductors: tunable optical, electrochemical, charge transport, and photovoltaic properties, *Macromolecules* 42 (2009) 671-681.
- [64] C. Qin, Y. Fu, C.H. Chui, et al., Tuning the donor-acceptor strength of low-bandgap platinum-acetylide polymers for near-infrared photovoltaic applications, *Macromol. Rapid Commun.* 32 (2011) 1472-1477.
- [65] X.Z. Wang, W.Y. Wong, K.Y. Cheung, et al., Polymer solar cells based on very narrow-bandgap polyplatinynes with photocurrents extended into the near-infrared region, *Dalton Trans.* (2008) 5484-5494.
- [66] X.-Z. Wang, Q. Wang, L. Yan, et al., Very-low-bandgap metallopolynyne of platinum with a cyclopentadithiophenone ring for organic solar cells absorbing down to the near-infrared spectral region, *Macromol. Rapid Commun.* 31 (2010) 861-867.
- [67] S.M. Aly, C.L. Ho, D. Fortin, et al., Intrachain electron and energy transfer in conjugated organometallic oligomers and polymers, *Chem. Eur. J.* 14 (2008) 8341-8352.
- [68] C. Qin, W.-Y. Wong, L. Wang, A water-soluble organometallic conjugated polyelectrolyte for the direct colorimetric detection of silver ion in aqueous media with high selectivity and sensitivity, *Macromolecules* 44 (2011) 483-489.
- [69] W.Y. Wong, C.L. Ho, Organometallic photovoltaics: a new and versatile approach for harvesting solar energy using conjugated polymetallaynes, *Acc. Chem. Res.* 43 (2010) 1246-1256.
- [70] Q. Liu, C.-L. Ho, Y.H. Lo, et al., Narrow bandgapplatinum(II)-containing polynyne with diketopyrrolopyrrole and isoindigo spacers, *J. Inorg. Organomet. Polym.* 25 (2015) 159-168.
- [71] Q.A. Alsulami, S.M. Aly, S. Goswami, et al., Ultrafast excited-state dynamics of diketopyrrolopyrrole (DPP)-based materials: static versus diffusion-controlled electron transfer process, *J. Phys. Chem. C* 119 (2015) 15919-15925.
- [72] S. Sekli, R.W. Winkel, E. Alarousu, et al., Triplet excited state properties in variable gap π -conjugated donor-acceptor-donor chromophores, *Chem. Sci.* 7 (2016) 3621-3631.
- [73] A.S. Gundogan, X. Meng, R.W. Winkel, et al., Platinum carbon bond formation *via* Cu(I) catalyzed stille-type transmetallation: reaction scope and spectroscopic study of platinum-arylene complexes, *Dalton Trans.* 44 (2015) 17932-17938.
- [74] S. Goswami, M.K. Gish, J. Wang, et al., π -Conjugated organometallic isoindigo oligomer and polymer chromophores: singlet and triplet excited state dynamics and application in polymer solar cells, *ACS Appl. Mater. Interfaces* 7 (2015) 26828-26838.
- [75] S. Goswami, R.W. Winkel, E. Alarousu, et al., Photophysics of organometallic platinum(II) derivatives of the diketopyrrolopyrrole chromophore, *J. Phys. Chem. A* 118 (2014) 11735-11743.
- [76] M. Qian, R. Zhang, J. Hao, et al., Dramatic enhancement of power conversion efficiency in polymer solar cells by conjugating very low ratio of triplet iridium complexes to PTB7, *Adv. Mater.* 27 (2015) 3546-3552.
- [77] H. Zhen, Q. Hou, K. Li, et al., Solution-processed bulk-heterojunction organic solar cells employing Ir complexes as electron donors, *J. Mater. Chem. A* 2 (2014) 12390-12396.
- [78] C.S. Kim, L.L. Tinker, B.F. DiSalle, et al., Altering the thermodynamics of phase separation in inverted bulk-heterojunction organic solar cells, *Adv. Mater.* 21 (2009) 3110-3115.
- [79] M.H. Yun, E. Lee, W. Lee, et al., Enhanced performance of polymer bulk heterojunction solar cells employing multifunctional iridium complexes, *J. Mater. Chem. C* 2 (2014) 10195-10200.
- [80] C.M. Yang, C.H. Wu, H.H. Liao, et al., Enhanced photovoltaic response of organic solar cell by singlet-to-triplet exciton conversion, *Appl. Phys. Lett.* 90 (2007) 133509.
- [81] W. Lee, T.H. Kwon, J. Kwon, et al., Effect of main ligands on organic photovoltaic performance of Ir(III) complexes, *New J. Chem.* 35 (2011) 2557-2563.
- [82] S. Archer, J.A. Weinstein, Charge-separated excited states in platinum(II) chromophores: photophysics, formation, stabilization and utilization in solar energy conversion, *Coord. Chem. Rev.* 256 (2012) 2530-2561.
- [83] H. Xu, R. Chen, Q. Sun, et al., Recent progress in metal-organic complexes for optoelectronic applications, *Chem. Soc. Rev.* 43 (2014) 3259-3302.
- [84] F.R. Dai, H.M. Zhan, Q. Liu, et al., Platinum(II)-bis(aryleneethynylene) complexes for solution-processible molecular bulk heterojunction solar cells, *Chem. Eur. J.* 18 (2012) 1502-1511.
- [85] F. Guo, K. Ogawa, Y.G. Kim, et al., A fulleropyrrolidine end-capped platinum-acetylide triad: the mechanism of photoinduced charge transfer in organometallic photovoltaic cells, *Phys. Chem. Chem. Phys.* 9 (2007) 2724-2734.
- [86] G.L. Schulz, S. Holdcroft, Conjugated polymers bearing iridium complexes for triplet photovoltaic devices, *Chem. Mater.* 20 (2008) 5351-5355.
- [87] C.Y. Liao, C.P. Chen, C.C. Chang, et al., Synthesis of conjugated polymers bearing indacenodithiophene and cyclometalated platinum(II) units and their application in organic photovoltaics, *Sol. Energy Mater. Sol. Cells* 109 (2013) 111-119.
- [88] J. Mei, K.R. Graham, R. Stalder, et al., Synthesis of isoindigo-based oligothiophenes for molecular bulk heterojunction solar cells, *Org. Lett.* 12 (2010) 660-663.
- [89] E. Wang, Z. Ma, Z. Zhang, et al., An easily accessible isoindigo-based polymer for high-performance polymer solar cells, *J. Am. Chem. Soc.* 133 (2011) 14244-14247.
- [90] J. Mei, D.H. Kim, A.L. Ayzner, et al., Siloxane-terminated solubilizing side chains: bringing conjugated polymer backbones closer and boosting hole mobilities in thin-film transistors, *J. Am. Chem. Soc.* 133 (2011) 20130-20133.
- [91] Y. Liang, Z. Xu, J. Xia, et al., For the bright future-bulk heterojunction polymer solar cells with power conversion efficiency of 7.4%, *Adv. Mater.* 22 (2010) E135-E138.
- [92] L. Huo, S. Zhang, X. Guo, et al., Replacing alkoxy groups with alkylthienyl groups: a feasible approach to improve the properties of photovoltaic polymers, *Angew. Chem.* 123 (2011) 9871-9876.
- [93] L. Dou, J. Gao, E. Richard, et al., Systematic investigation of benzodithiophene- and diketopyrrolopyrrole-based low-bandgap polymers designed for single junction and tandem polymer solar cells, *J. Am. Chem. Soc.* 134 (2012) 10071-10079.
- [94] W. Li, A. Furlan, K.H. Hendriks, et al., Efficient tandem and triple-junction polymer solar cells, *J. Am. Chem. Soc.* 135 (2013) 5529-5532.
- [95] M. Zhang, X. Guo, S. Zhang, et al., Synergistic effect of fluorination on molecular energy level modulation in highly efficient photovoltaic polymers, *Adv. Mater.* 26 (2014) 1118-1123.
- [96] L. Ye, S. Zhang, W. Zhao, et al., Highly efficient 2D-conjugated benzodithiophene-based photovoltaic polymer with linear alkylthio side chain, *Chem. Mater.* 26 (2014) 3603-3605.
- [97] S. Zhang, L. Ye, W. Zhao, et al., Realizing over 10% efficiency in polymer solar cell by device optimization, *Sci. China Chem.* 58 (2015) 248-256.
- [98] Y.J. Kim, M.J. Kim, T.K. An, et al., A new multi-functional conjugated polymer for use in high-performance bulk heterojunction solar cells, *Chem. Commun.* 51 (2015) 11572-11575.

- [99] Z. Ding, J. Kettle, M. Horie, et al., Efficient solar cells are more stable: the impact of polymer molecular weight on performance of organic photovoltaics, *J. Mater. Chem. A* 4 (2016) 7274-7280.
- [100] C. Liu, K. Wang, X. Hu, et al., Molecular weight effect on the efficiency of polymer solar cells, *ACS Appl. Mater. Interfaces* 5 (2013) 12163-12167.
- [101] Y. Chi, P.T. Chou, Transition-metal phosphors with cyclometalating ligands: fundamentals and applications, *Chem. Soc. Rev.* 39 (2010) 638-655.
- [102] W.Y. Wong, C.L. Ho, Functional metallophosphors for effective charge carrier injection/transport: new robust OLED materials with emerging applications, *J. Mater. Chem.* 19 (2009) 4457-4482.
- [103] W.-Y. Wong, C.-L. Ho, Heavy metal organometallic electrophosphors derived from multi-component chromophores, *Coordin. Chem. Rev.* 253 (2009) 1709-1758.
- [104] C. Ulbricht, B. Beyer, C. Friebe, et al., Recent developments in the application of phosphorescent iridium (III) complex systems, *Adv. Mater.* 21 (2009) 4418-4441.
- [105] L. Ye, S. Zhang, W. Ma, et al., From binary to ternary solvent: morphology fine-tuning of D/A blends in PDPP3T-based polymer solar cells, *Adv. Mater.* 24 (2012) 6335-6341.
- [106] H. Yan, S. Swaraj, C. Wang, et al., Influence of annealing and interfacial roughness on the performance of bilayer donor/acceptor polymer photovoltaic devices, *Adv. Funct. Mater.* 20 (2010) 4329-4337.
- [107] G. Li, Y. Yao, H. Yang, et al., "Solvent annealing" effect in polymer solar cells based on poly(3-hexylthiophene) and methanofullerenes, *Adv. Funct. Mater.* 17 (2007) 1636-1644.
- [108] F. Padinger, R.S. Rittberger, N.S. Sariciftci, Effects of postproduction treatment on plastic solar cells, *Adv. Funct. Mater.* 13 (2003) 85-88.
- [109] W.L. Ma, C.Y. Yang, X. Gong, et al., Thermally stable, efficient polymer solar cells with nanoscale control of the interpenetrating network morphology, *Adv. Funct. Mater.* 15 (2005) 1617-1622.
- [110] J.K. Lee, W.L. Ma, C.J. Brabec, et al., Processing additives for improved efficiency from bulk heterojunction solar cells, *J. Am. Chem. Soc.* 130 (2008) 3619-3623.
- [111] Y. Yao, J. Hou, Z. Xu, et al., Effects of solvent mixtures on the nanoscale phase separation in polymer solar cells, *Adv. Funct. Mater.* 18 (2008) 1783-1789.
- [112] T.W. Lee, H.C. Lee, O.O. Park, High-efficiency polymer light-emitting devices using organic salts: a multilayer structure to improve light-emitting electrochemical cells, *Appl. Phys. Lett.* 81 (2002) 214-216.
- [113] Y. Cao, G. Yu, A.J. Heeger, et al., Efficient, fast response light-emitting electrochemical cells: electroluminescent and solid electrolyte polymers with interpenetrating network morphology, *Appl. Phys. Lett.* 68 (1996) 3218-3220.