Research Progress on the Third Component Materials of Ternary Organic Solar Cells

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Abstract. As a type of solar cells, the costs of the construction of organic solar cells are much lower than silicon-based solar cells. Moreover, they also have greater potential than other solar cells in wearable electronic devices and flexible equipment. However, their energy conversion efficiency is not high. It is well known that use three materials to prepare the active layer instead of two may change this situation. The paper first intoduces the advantages and disadvantages of different kinds of solar cells and briefly summarizes the effect of third component. In this paper, the working principles of ternary organic solar cells are classified into different types according to different mechanism and briefly explained. Then the paper chooses some important results of the predecessors to briefly intoduce the development of ternary organic solar cells and some milestones in this domain. The paper also divides the third component into different types according to the molecular characteristics of the material and introduces some advantages of these kinds of materials.

Keywords: Organic solar cells; Energy conversion efficiency; Third component.

1. Introduction

1958 to 2023, the atmospheric carbon dioxide concentration increased from about 316 ppmv to about 421 ppmv, and the global average temperature in 2023 reached 15.3℃, an increase of 1.2℃ compared with 1951~1980 [1]. Fossil fuels are also being consumed at a rapid rate and they are not infinite. According to NASA, the average annual energy radiated by the sun to the earth is about 1.74×10^{17} J, which is an ideal energy source for humans to change the situation.

At present, silicon-based solar cells are the most matured solar cells in our daily life. They have high efficiency and high commercialization rate but their application is limited by expensive construction and complex processes. However, organic solar cells are easy to prepare and they have low costs [2]. Because of this, they have enormous application potential but they have their disadvantages too. Silicon solar cells can convert over 26% of the solar energy into electricity [3], while the organic solar cells can only convert at most 20% of the solar energy [4]. Therefore, how to improve the property has become one of the most critical research directions in organic solar cells. Binary system succeeded in enhancing the property. However, binary system can absorb only some specific wavelengths of sunlight. Because of the absorption range is small, the utilization rate of sunlight of this kind of solar cells is low. Besides, the stability of this type of cells is also poor. However, these disadvantages can be greatly improved by adding third component and it has been widely recognized by researchers as the most effective method [5-6].

2. The Working Principles of Ternary Organic Solar Cells

At present, the acknowledged working principles of ternary organic solar cells can be divided into four categories: charge transfer mechanism, energy transfer mechanism, parallel structure, and alloy-like mode. These theories can effect the solar cells in different ways and one device can have more than one working principle.

2.1. Charge Transfer Mechanism

If a device want to form charge transfer mechanism, it requires the materials in the active layer have similar HOMO and LUMO energy levels and the third component is in the middle. Then the three components can form a cascade arrangement which makes it easier for the excitons to be transmitted to the interfaces (D/A, A_1/A_2 or D_1/D_2) and separated. This method can reduce the charge trap and improve the separation and transmission of current carrier. Besides, by forming a charge transfer mechanism, the device will have more exciton dissociation interfaces and more electron transport channels. The operation of the mechanism is shown in the figure1 [2,7].

2.2. Energy Transfer Mechanism

Energy transfer requires similarity between the emission spectrum of energy donor and absorption spectrum of energy acceptor. In this way, when the donor is excited by light, part of the energy will be converted into light and emitted. Due to the similarity, the acceptor can absorb this part of the light energy, thereby improving the energy conversion efficiency. Förster and Dexter energy transfer are two forms of this working principle. Förster energy transfer occurs through a long-range dipole-dipole interaction and when the energy donor forms an excited state, the energy is transferred to the energy acceptor through the resonant form of the Coulomb interaction. Dexter energy transfer is the direct transfer of energy through the transfer of electrons. When the third component is divided into energy donors, the energy generated in D_1 is first transferred to D_2 through the above two energy transfer methods. D_2 absorbs the energy to generate excitons and the excitons will dissociate at the D_2/A interface. The transfer of electrons and holes after dissociation is shown in the figure1 [2].

2.3. Parallel Structure

The parallel structure can be simply understood that the device is composed of two binary organic solar cells and the materials which are used to construct the active layer do not require high similarity. There can be big differences in the key parameters of the materials like energy level positions. This model is equivalent to the merger of D_1/A and D_2/A two devices. The operation of the mechanism is shown in the figure1 [6].

2.4. Alloy-like Model

When the added third component has similar surface energy and electrical properties to one of the materials of the main system, the third component will be coupled with it to form an electronic alloy state, resulting in a new energy level. In this model, electrons and holes are transported along the common holes and electron transport channels that form [7].

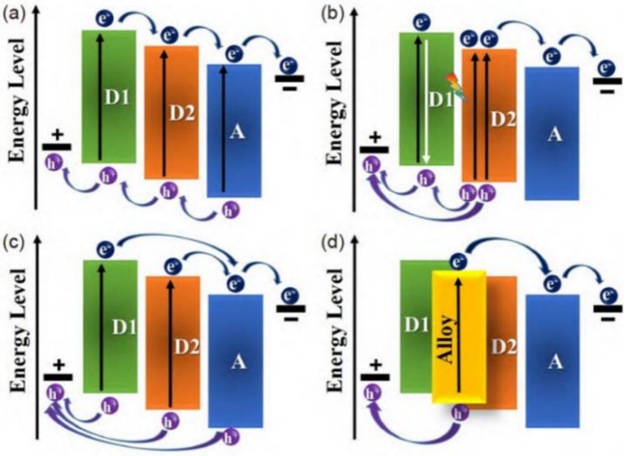

Fig. 1 the working principle of mechanisms in ternary OSCs: (a) charge transfer, (b) energy transfer, (c) parallel structure (d) alloy-like model [2]

3. Development of ternary organic solar cells

In 2010, M. Koppe et al. [8] introduced PCPDTBT into binary organic solar cells for the first time. By adding a third component PCPDTBT that is complementary to the P3HT:PC_{61}BM absorption spectrum, the group increased the efficiency by 12% compared with the original binary system. In this research, the project group succeeded in proving the advantages of the third component. It can boost efficiency as well as the exciton collection. Subsequently, T. Ameri et al. [9] added Si-PCPDTBT, a derivative of PCPDTBT, to the P3HT:PC_{61}BM binary system. Then the efficiency increased by 25% compared with the efficiency of the binary system. T. Ameri et al. controlled the ratio of the gross amount of P3HT and Si-PCPDTBT in the solar cell to the amount of PC_{61}BM to 1:1 and gradually increased the content of Si-PCPDTBT. With the improvement, the efficiency was also continuously improved until Si-PCPDTBT exceeded 60%. In this process, it was not until the Si-PCPDTBT exceeded 40% of the total P3HT and Si-PCPDTBT that the FF value of the cell decreased significantly which probably means that the microstructure of P3HT:PC_{61}BM will not be easily effected by third material. In 2011, B. C. Thompson's [10] group first introduced the fullerene acceptor ICBA to the P3HT:PC_{61}BM system. On the basis of previous research, B. C. Thompson's [11] group found that the HOMO and LUMO levels of materials change with the transformation of materials' content in 2013. Therefore, they proposed an alloy-like model for the first time to explain this phenomenon which provides an important direction for the subsequent mechanistic study of third component. In the same year, A. D. Taylor's group [12] used SQ to construct the solar cell with P3HT:PC_{71}BM and demonstrated that there is Förster energy transfer between SQ and P3HT. The transfer increases the efficiency of P3HT:PC_{71}BM:SQ system to 4.5% by increasing the absorbance range and enhancing charge transport. However, fullerenes and their derivatives can not absorb as much energy from the light as other photovoltaic materials. Even if the electron transport performance is good, the energy conversion efficiency of fullerenes and their derivatives as the main material of the solar cells is limited to 13% [2,7]. In 2015, Zhan et al. [13] developed a new material, ITIC. They use it to construct a organic solar cell and the efficiency successfully reached 11.4%, making non-fullerene materials as the main materials become a research hotspot. In 2016, Hou et al. [14] prepared a new acceptor material which was named IT-M and the research team introduced Bis[70]PCBM to the PBDB-T:IT-M system. By continuously adjusting the content of the Bis[70]PCBM, the energy conversion efficiency reached 12.20%. In 2018, Wang et al. [15] designed a low-bandgap acceptor COi8DFIC and fabricated a new device by adding PC71BM to the PTB7-TH:COi8DFIC system. The energy conversion efficiency of the cell was 14.62%. In 2019, Zhou et al. [16] synthesized a novel acceptor material Y6 to match PM6 and the efficiency reached 15.7%. This research makes the PM6:Y6 system a research hotspot. Many researchers have focused on PM6:Y6 and their derivatives. In 2020, Bao et al. [17] introduced DRTB-T-C4 to the PM6:Y6 system. DRTB-T-C4 has the advantages of high crystallinity and frontal orientation and it results in an efficiency of 17.13%. In 2021, Sun et al. [18] designed a new acceptor L8-BO-F and introduced it to the PM6:BTP-eC9 system. By controlling the amount of L8-BO-F, the project team successfully increased the efficiency of the cell to 18.66%. In 2022, Liu et al. [19] introduced the donor material D18 to the PM6:L8-BO system. D18 can form a refined double-fibril network morphology due to it can precipitate during the file-forming process and the precipitation can induce crystallization. This structure effectively helps the device gain an excellent performance. Today, the maximum efficiency of ternary organic solar cell is adding L8-ThCl to the D18:L8-BO system. The efficiency has exceeded 20% which has become another milestone in the domain of ternary organic solar cells [4].

4. Third component material

The third component material can greatly effect the performance and stability of the cells. The unique qualities of different kinds of materials will effect the device in many different ways. At present, the third component materials can be divided into four categories and the introductions are as follows.

4.1. Polymer material as the third component

The main functions of polymer materials as the third component are: Some polymer materials can improve the stability, heat resistance, stretchability and other properties of ternary organic solar cells. Organic polymers have good light absorption properties which can improve the utilization rate of sunlight. They can also complement the absorption spectrum of the main materials to improve the absorption range. Some polymer materials can form a cascade arrangement with the main materials to reduce charge recombination and energy loss. Some polymer materials can improve the morphology of the active layer. The enhancement of the morphology will lead to better exciton dissociation and charge transport [2].

In 2020, Wang et al. [20] added 30% PAE to the PM6:Y6 system, which increased the elongation at break of the cell by 4.4 times. The energy conversion efficiency of binary OPV is only 39% of that of unbent after multiple bending, while that of ternary OPV is still 73%. In 2022, Chen et al. [21] introduced the polymer PTO2 to the PM6:BTP-eC9 system, which improved the photon capture ability of the device and reduced the energy loss. In the end, the team succeeded in increasing the efficiency of PM6:BTP-eC9:PTO2 to 18.01%. When the efficiency of the ternary was 91.69% of the initial efficiency, the binary was 90.13％ under continuous illumination;At 85°C,when the initial efficiency of the ternary was 84.4%, the binary was only 77.8% after 528 hours. In 2023, Liu et al. [22] introduced the polymer FY1 to the PM6:BTP-eC9 system which can effectively improve the efficiency of exciton dissociation and charge transport due to a better mixture topography. The stability of the cells are also improved. By adding 5wt% FY1, the research team succeeded in increasing the energy conversion efficiency to 18.52%. The three-component device worked well within 800 hours while the two-component lost about 35% of the energy conversion efficiency after 400 hours.

4.2. Small molecule materials as the third component

Small molecule materials mainly have the following advantages in this domain: Some of them have high crystallinity which can more effectively improve the morphology of the active layer, and at the same time improve the energy conversion efficiency in terms of exciton dissociation. Small molecule materials can improve the absorbance range of the battery through their own wide absorption spectrum and complementation of absorption spectrum. Compared with polymer materials, small molecule materials have accurate chemical structure, accurate molecular weight, good reproducibility of photovoltaic performance and easy purification. Some small molecule materials can reduce the π–π stacking distance, making the front stacking more concentrated, and optimizing the morphology by enhancing the molecular stacking [2].

In 2020, Bao et al. [17] introduced DRTB-T-C4 to the PM6:Y6 system. Due to the high crystallinity of DRTB-T-C4, it can promote the charge transport by regulating the morphology of the active layer. Besides, the good compatibility makes it tend to be distributed at the interface of PM6 and Y6 which can also modify the morphology. When the ratio of DRTB-T-C4 to PM6 is 2 to 1, the energy conversion efficiency of the battery is increased to 17.13%. In 2022, Wei et al. [23] introduced BTID-2F to the PM6:L8-BO system. It can form a cascade arrangement and the energy loss of the three components is relatively low. After morphological characterization, the research team found that the introduction of BTID-2F enhanced the packing of molecules and optimized the morphology. The introduction also reduces the π–π stacking distance, enhances electron transport and achieves an energy conversion efficiency of 18.52% when BTID-2F accounted for 10% of the donor. In 2024, Hu et al. [24] designed ITOA and introduced it to the PM6:BTP-eC9 system.It can promote dense molecular packing, reduce domain size, and establish preferred vertical phase distribution to optimize morphology. Therefore, ITOA has excellent performance in inhibiting charge recombination and reducing energy loss. Due to these positive effects, ITOA raises the efficiency of the solar cell to 19.33% and it also enhances the stability.

4.3. Fullerene material as the third component

Fullerenes have good electron transport ability and they have been the main research objects of organic solar cell acceptor materials in the past. After the first addition of the third component, they are also explored possible applications in this domain. At present, using fullerene materials and their derivatives as third-component materials is not as attractive as other materials.

The introduction of fullerene materials into solar cells as a third component has the following advantages: Fullerene materials have good electron transport ability. Fullerene materials can optimize the distribution of each component, making charge transport more balanced and exciton dissociation more efficient [2].

In 2019, Hou et al. [25] introduced $PC_{61}BM$ to the PBDB-TF:Y6 system. $PC_{61}BM$ improved electron mobility by generating a more balanced charge transport while inhibiting charge recombination by reducing Y6 aggregation and efficiency reaches 16.5%. Subsequently, the fullerene material $PC_{71}BM$ was also introduced to the PM6:Y6 system and the cell efficiency was increased to 17.09% by optimizing the vertical miscibility of the cell.

4.4. Non-fullerene materials as the third component

After ITIC was developed, non-fullerene materials quickly became a research hotspot. They are often introduced as the third component. Non-fullerene materials mainly have the following advantages: Some non-fullerene materials can form nanofiber structures which provide more interfaces for excitons that can be used for dissociation. Non-fullerene materials can adjust the properties of the materials through chemical modification and other methods, and different non-fullerene materials can be designed according to the needs. Non-fullerene materials have good light absorption in the NIR region. At the same time, they also have good thermal and light stability. Some non-fullerene materials can form a uniform mixed phase with the acceptor materials in the host and improve the molecular packing .

In 2021, Sun et al. [18] synthesized L8-BO-F and introduced it to the PM6:BTP-eC9 system. It formed a homogeneous mixture of this non-fullerene acceptor and BTP-eC9 which improved molecular packing, light absorption and reduced voltage loss. The homogeneous mixture also inhibited charge recombination and efficiency of the solar cell was 18.66% after the addition of 15wt% L8-BO-F. In 2023, Zhang et al. designed $ZCCF_3$ by taking advantage of the easy change of the structure of non-fullerene materials. They replace the thiadiazole group on Y6 with trifluoromethyl group to produce $ZCCF_3$. Due to the similarity with Y6 structure, the project team introduced it to the PM6:Y6 system which limited the diffusion effect of the acceptor material under thermal stress by forming an alloy-like model. The model greatly enhanced the thermal stability. At the same time, the solar cell inhibited the charge recombination because of the formation of the alloy-like model, bringing the efficiency to 18.54%. In 2024, Wang et al. [4] synthesized L8-ThCl, a novel non-fullerene material. It shows amazing efficiency when it was mixed with D18 and L8-BO. L8-ThCl can bend and entangle with the D18-conjugated backbone through strong dipole-dipole interaction to form a tighter $\pi-\pi$ stack, allowing the donor and acceptor to form nanofiber morphologies. In this way, the efficiency of the solar cell exceeded 20% for the first time.

5. Conclusion

In summary, polymer materials can improve the stability and heat resistance of ternary organic solar cells. They can also greatly improve the energy conversion efficiency. Small molecule materials can effectively improve the morphology of the active layer because of their high crystallinity and their advantages of accurate molecular structure, clear molecular weight, and easy purification make the performance difference of each solar cell is not large. Fullerene materials have excellent electron transport ability and can also optimize the distribution of each component. Non-fullerene materials have the advantages of good absorption of near-infrared light, forming nanofiber structures and the improvement of molecular packing. These advantages make the ternary organic solar cells, which are added non-fullerene materials, have high energy conversion efficiency and make them a research hotspot. Charge transfer mechanism requires cascade arrangement and it will affect the efficiency through ways like reducing charge traps while energy transfer mechanism will affect the efficiency by boosting energy absorption. Parallel structure works like two devices and the materials which are used to construct the active layer do not need to be similar with each other. The materials needs similar surface energy and electrical properties to form alloy-like model. If the electronic alloy state appears, it will have new energy level and boost performance.

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