Molecular Design Strategies for Next-Generation Organic Photovoltaic Materials

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Abstract. The molecular design strategy of the new generation of organic photovoltaic materials is an important direction of the development of photovoltaic technology. In this paper, the research progress of molecular design strategy of new generation organic photovoltaic materials is systematically summarized, and the importance of molecular design in the development of organic photovoltaic technology is deeply expounded. Starting from the basic principle and early development stage of OPV, this paper compares the performance of conjugated polymers and small molecules as active layers and then introduces the method to improve the charge transfer efficiency by adjusting the energy level. In addition, this paper focuses on analyzing the current advanced molecular design ideas of donor materials and acceptor materials, such as side chain engineering of molecules, the three-dimensional structure of control materials, etc., which lays a foundation for the improvement of organic photovoltaic performance. The paper offers insights into the trends and challenges of technological progress in three aspects: stability design, scalable synthesis, and environmentally friendly materials. In the future, improving the photochemical and thermal stability of materials through molecular design will be an important direction. Therefore, better molecular design strategies play a central role in advancing organic photovoltaic technology, and their potential and application prospects are broad.

Keywords: Molecular design, energy level adjustment, organic photovoltaic.

1. Introduction

Photoelectric polymerization solar cells (OPVs) constitute a significant breakthrough in renewable energy technologies. Distinguished by their incorporation of organic materials, OPVs emerge as a viable alternative to conventional solar cells, offering advantages in terms of reduced production costs and versatile application possibilities. OPVs convert light into electricity through a three-step process. Initially, organic molecules in the OPV absorb light, creating electron-hole pairs. These pairs are then separated by an internal electric field, directing electrons and holes to opposite layers. Finally, these charges migrate to different electrodes, generating electricity. The key to this process is the optimization of material and electrode energy levels to enhance charge collection and reduce loss through recombination.

The molecular design of early organic photovoltaic materials focused on improving their light absorption capacity, but usually ignored the effect of their molecular structure on the material's electron transport performance, which also led to the inefficiency of OPV. Now with the development of science and technology, researchers have begun to pay attention to the impact of molecular structure on electronic transport and have optimized accordingly. They modulate the molecular structure to optimize its light absorption properties and improve carrier dynamic performance, which is also the key to OPV technology advancement. For example, introducing conjugated structures into the molecular skeleton can expand the range of light absorption; The use of molecular hybrid design can increase the internal electron dynamics of molecules. The solubility and workability of the material can be improved by selecting suitable functional groups. By optimizing the molecular structure, the researchers have successfully improved the conversion efficiency of OPV, so that it has a good application prospect.

In recent years, with the continuous progress of organic material synthesis and molecular design technology, the performance of OPV has also been improving. At present, the important strategies to

explore the improvement of OPV conversion efficiency include the following aspects: First, the design of energy level matching organic absorption layer and conductive layer materials. The energy level alignment between materials can effectively improve photoelectric conversion efficiency. Control the binding pattern of organic material molecules to donor and recipient materials. The second is to explore new structural designs. For example, the effect of molecular symmetry and intermolecular spatial structure on performance, conjugated structures in molecules can improve the light absorption coefficient, so that it can use light energy more fully. The last is to improve the environmental stability of organic materials. The molecules need to have a certain resistance to solvent, humidity, and light degradation to ensure the reliability of OPV components in practical applications.

Herein, in this paper, the basic concepts and advanced strategies of organic photovoltaic molecular design are discussed. Further, the design strategies of donor and acceptor molecules are also analyzed. In addition, advanced methods including stabilizing groups and cross-linking design, as well as exploring biodegradable materials, are also used to promote the continuous progress of organic photovoltaics in terms of sustainable development. This paper illustrates the importance of molecular design from both theoretical and application levels, and puts forward innovative ideas on future development directions, providing an impetus for the research of molecular design strategies for the next generation of organic photovoltaics.

2. Basic Concepts of OPV molecular design

2.1. Typical Materials for OPV

Conjugated polymers and small molecules are commonly used organic photovoltaic active layer materials. There are some differences in their synthesis methods, molecular structures, and photovoltaic properties. Generally speaking, conjugated polymers are synthesized by polymerization, with long molecular chains and complex molecular structures. The advantage of the long polymer molecular chain is that it has a strong light absorption capacity and can form a thicker film. [1] However, conjugated polymers have large molecular gaps, making it difficult to control the purity and crystallinity of the material.

Small molecules are obtained by multi-step organic synthesis reaction, and the molecular volume is small, and the structure is simple. In contrast, small molecules are not only structurally simple and less difficult to synthesize but their purity and crystallinity are also easier to control. However, due to the small size of small molecules, the ability to absorb light is weak, so it is necessary to form a thicker film to improve the absorption efficiency of light. In addition, small molecule materials may produce more impurities during solution treatment, which will also have a certain impact on their properties [2].

2.2. Importance of Energy Level Tuning

The energy level structure is one of the key factors that determine the conversion efficiency of photovoltaic cells. Energy level structure refers to the relative position relationship between electron level and hole level in semiconductor material. The researchers found that adjusting the energy level structure can promote the transfer of light-generating electrons from the conduction band to the contact layer, achieving a more efficient photoelectric conversion.

The adjustment of energy level is mainly achieved by doping different materials. For example, the incorporation of silicon materials into materials such as identification can make the conduction band energy level decrease, while the valence band energy level increases, expanding the energy gap, and facilitating the separation and collection of electron-hole pairs. At the same time, the doped material can change the crystal structure of the new material, reduce the barrier between energy levels, and conduct the charge generated by light more efficiently. In addition, the level adjustment can also optimize the open circuit voltage of the photovoltaic cell. The open circuit voltage directly affects the

maximum output voltage of the battery. A more ideal open circuit voltage can be obtained, and the maximum voltage output can be achieved by adjusting the level spacing reasonably.

2.3. Strategies for Energy Level Tuning

The adjustment of molecular energy level will affect the photoelectric performance of organic photovoltaic devices. Molecular structure design is the main method to adjust energy levels directly. The researchers raise or lower the HOMO and LUMO levels by introducing different substituting groups to the molecular skeleton to change the electron density distribution of the molecule. For example, the introduction of an electron donor group such as an amino group will reduce the LUMO level of the molecule; The introduction of electron acceptor groups such as cyanide groups will raise the HOMO energy level of the molecule [3]. In addition, expanding the π-conjugated system is also a common method to effectively reduce the LUMO level of molecules [4]. In addition to the molecular structure design, the addition of cosolvents or additives can also indirectly affect the energy level structure of the molecular layer. Cosolvents can change the interaction between molecules and then affect the energy level structure. For example, the addition of dichloromethane as a co-solvent can increase the π-π stacking spacing and thus reduce the HOMO level; The addition of tetrafluoroacetic acid can also raise the LUMO level by electron attraction. What's more, adding certain metal ions to organic semiconductor films can also adjust their energy levels by forming complexes with molecules [5]. At the same time, changes in the passivation effect caused by interfacial chemical interactions also help to improve the performance of optoelectronic devices [6].

3. Advanced Molecular Design Strategies

3.1. Donor Materials

3.1.1 Push-pull structures

Push-pull structures enhance intramolecular charge transfer by placing donor and acceptor units close together: In push-pull structures, the donor and acceptor units are extremely close together, usually only a few atoms or a few chemical bonds apart. This greatly shortens the distance that electrons need to travel from the donor to the acceptor, resulting in an increase in electron transfer speed. At the same time, the spatial overlap of donor and acceptor units will enhance the electron cloud overlap between the two, thus increasing the probability of electron transfer between the donor and acceptor. Similar to the "electron cloud superposition" effect. In addition, the close proximity of donor and acceptor units can achieve strong electron cloud coupling through spatial overlap, thereby reducing the energy barrier of electron transfer from donor to acceptor and increasing the feasibility of improving electron transfer. Finally, the chemical bond or molecular orbital overlap between the donor and the acceptor unit creates a resonance effect, which further reduces the energy barrier between the donor and the acceptor, and in turn accelerates the transfer of electrons.

By photoexcitation of individual non-fullerene acceptor molecules and different molecular aggregates, Ji et al. investigated the details of photoinduced electron transitions and the resulting charge transfer kinetics. It is found that the electron push-pull potential of non-fullerene acceptor molecules promotes the IR of each transition peak and increases the transition probability of each transition peak. As the electron transition and charge transfer behavior occur simultaneously, the transfer charge increases with the increase of the electron push-pull potential of the molecule. After adding molecular aggregation, the researchers found that the electron transition pattern and peak site changed with the aggregation pattern (Figure 1). The effect of optical excitation intensity is further considered, and it is demonstrated that the optical excitation of materials with stronger optical excitation intensity will lead to a more obvious charge transfer phenomenon. The research results mentioned in this paragraph provide us with a deeper understanding of the microscopic behavior of different non-fullerene receptor molecular systems under light irradiation and guide subsequent work towards a more rational and efficient direction. For example, by increasing the electron push and pull

potential of molecules, light absorption can be expanded, and intermolecular effects can be improved. By improving intermolecular aggregation patterns, these light absorption and charge transfer effects can be further modulated in practical optoelectronic applications of non-fullerene acceptor molecules [7].

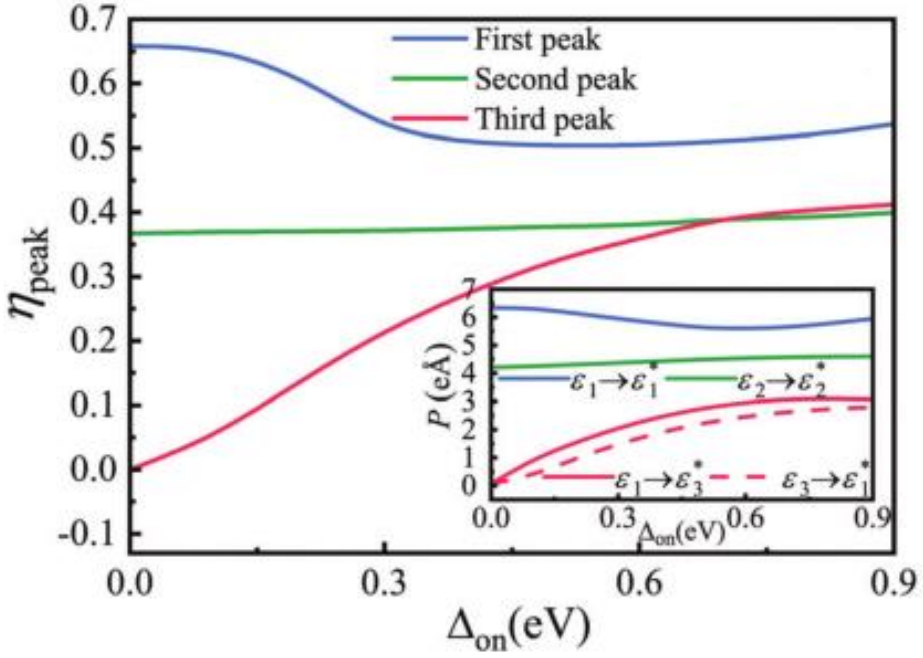

Fig. 1 Transition probability of different peak transitions as a function of the value of the electronic push-pull potentials [7]

3.1.2 Side chain engineering

Side chain design is an important means to control and optimize polymer properties. Through systematic research on the side chain of donor polymers, various key properties of polymers can be effectively regulated, and better polymer materials can be developed to promote the application of polymer materials in electronic devices, energy conversion, and other fields. In general, increasing the hydrophilicity of the side chain can improve the solubility of the polymer. At the same time, shortening the side chain can also increase the solubility, because the short-chain polymer has weaker intermolecular forces and is more soluble. The structure of the side chain also determines the morphology of the polymer film. Hydrophobic side-chain polymers form flat and uniform films in organic solvents, while hydrophilic side-chain polymers tend to form porous or rough film surfaces. By introducing hydrophobic and hydrophilic side chains at the same time, the porous properties of the films can be regulated. The porous membrane is more advantageous for electronic device applications because the porous structure can increase the contact area between the electrode and the active layer. In addition, side chains also affect the electron transport rate of polymer materials. In general, increasing the degree of conjugation of the side chains can improve conductivity. At the same time, shortening the length of the side chain is also conducive to the transition of electrons, thereby increasing the conductivity. Manipulating the polymer side chain can significantly improve photovoltaic performance, especially in non-fullerene receptor cells. Because the type, location, size, and length of the side chain significantly affect the solubility, intermolecular interactions, and charge transport properties of the molecule. The solar cell prepared by Zhang et al. using PBDB-ST and tic-sc2c6 polymer donors with four branched-chain substituents has a well-distributed nanofiber interpenetrating network, and the photoelectric conversion efficiency of the cell is as high as 9.16% and the maximum voltage is 0.92V compared with the receptor with linear side chain. These results indicate that the use of side-chain engineering is one of the most efficient methods to obtain higher photoelectric conversion efficiency by modulating the photoelectric properties of the receptor and the morphology of the blend [8].

3.2. Acceptor Materials

Non-fullerene acceptors, as a class of polymer materials with structural diversity, has shown high application potential in the field of organic photovoltaic. In the reported non-fullerene receptor batteries, many efforts have been made to change the structure of the conjugated backbone and electron-absorbing end group, so that it has excellent performance [9].

3.2.1 Diversity of non-fullerene acceptor structures

Non-fullerene acceptor molecules have a wealth of structural units. Non-fullerene acceptor materials with different structures can be designed by changing the types and connection modes of structural units. For example, the conjugation length of non-fullerene acceptor molecules can be changed by introducing different substituents to affect its light absorption range. Branching or star-shaped structures can also be constructed by connecting different polymerization units to increase the spatial spacing within the molecules. In addition, non-fullerene acceptors can also be chimeric with other organic materials such as fullerene to form composite structures. Through the above method, hundreds of non-fullerene acceptor materials with different structures have been synthesized, which also provides a broad space for the optimization of their optical properties [10].

3.2.2 Diversity of non-fullerene acceptor structures

The light absorption range of non-fullerene acceptor materials can be extended to the visible and near-infrared regions. By changing the structure, the maximum position of light absorption can be adjusted to better absorb the sunlight spectrum. Not only that, compared to other materials, non-fullerene acceptor only requires a thinner film thickness to absorb a lot of light. OPV using a non-fullerene acceptor has reached up to 20% light absorption. In addition, non-fullerene acceptor materials have good electrical conductivity, which is conducive to the transmission and collection of charges generated by light, and higher quantum yield means better photoelectric conversion efficiency [11].

3.2.3 Diversity of non-fullerene acceptor structures

Non-fullerene acceptor can not only be used as a photovoltaic material alone but also is often blended with other materials such as polymers or small molecules to form a blended film material. Its molecules can be effectively dispersed in the polymer matrix, making the film thinner and more uniform, changing its orientation, and promoting the contact area between the fluorescent material and the electron transport material. Not only that, but non-fullerene acceptors can also form self-assembled structures with other substances, such as nanowires, nanospheres, etc., to increase the mechanical strength of the film, but also conducive to the transmission of electrons or energy. Therefore, by using the ability of a non-fullerene acceptor to control the morphology of the blended film, new organic photovoltaic materials with excellent structure and performance can be designed. This is also an important direction of current research on non-fullerene acceptors.

3.2.4 Molecular acceptors with three-dimensional acceptance

The geometry of the receptor structure has a great influence on OPV performance. In conventional planar receptor structures, excitons must migrate a certain distance after formation to reach the contact surface for dissociation, which increases the probability of their recombination. If the three-dimensional spatial structure is used, the contact surface can be directly introduced into the acceptor material, thereby shortening the distance of the exciton to the dissociation point. In recent years, several research groups have begun to try to incorporate materials of different shapes and structures into the receptor materials to form three-dimensional network structures. For example, carbon nanotubes have been incorporated into polymer receptors to form a nanotube-polymer composite network structure. This structure takes advantage of the good electrical conductivity of carbon nanotubes and introduces the contact surface directly into the three-dimensional network, greatly reducing the migration distance of excitons. The experimental results show that the exciton dissociation efficiency and current output capacity of this structure are significantly improved

compared with the planar structure. Ihly et al. We used variable band gap carbon nanotube films paired with different fullerene derivatives to explore the influence of exciton dissociation driving forces and measured that the small recombination energy of three-dimensional systems can be used for charge extraction with relatively low carrier energy loss compared to some polymer/fullerene systems that exhibit greater recombination energy [12].

4. Future Technology Advancements

4.1. Designing for Stability

The method of improving the photochemical and thermal stability of OPV materials by molecular design can alleviate the free radical and photooxidation damage caused by the material under light by introducing stable groups. In addition, the thermal stability of OPV films can also be improved by cross-linking design. Crosslinking can effectively reduce the degree of movement of polymer molecules at high temperatures, thereby improving the shape stability and mechanical strength of the film. Finally, it is also possible to maximize the photochemical and thermal stability of OPV materials by introducing stable groups and cross-linked units at the same time and utilizing their synergistic effect.

4.2. Scalable Synthesis

In order to maintain the high performance of OPV materials while reducing costs, it is necessary to conduct systematic research on various aspects of synthesis process optimization, process automation, and cost control. Expanding the scale will bring about changes in many factors, such as the control of reaction conditions, the purity of raw materials, etc., which may affect the structure and performance of materials. Therefore, scalability needs to be considered at the laboratory stage to reduce the uncertainty brought about by scaling up by optimizing the synthesis process. At the same time, it is also necessary to simplify the synthesis route, reduce the intermediate products, and reduce the cost. In addition, we can also start from the selection of raw materials, give priority to cheap and universal raw materials, reduce the use of rare and expensive raw materials, and explore the reuse and recycling of raw materials to reduce raw material costs.

4.3. Eco-Friendly Materials

At present, researchers are working on the development of bio-based and non-toxic new OPV batteries to realize the true environmental protection of batteries. For example, use biodegradable polymers such as polylactic acid as organic layer materials, instead of the original PET and other plastics [13]; Pigments from natural plant extracts were used instead of traditional metal complexes as light-absorbing layer materials; OPV batteries are prepared from natural materials such as waste biomass such as waste food and waste pulp [14]. This can not only make full use of waste resources but also be non-toxic and pollution-free in the production process. Once scrapped, the battery itself will naturally break down. This new type of material not only has reliable performance, but also can be naturally decomposed and assimilated into the soil after being scrapped, without special treatment, and has little impact on the environment. It will greatly improve the sustainability of OPV batteries and achieve a true sense of "green" energy.

5. Challenges and Future Directions

5.1. Current Limitations

High efficiency is the primary goal of OPV molecular design. Researchers have been exploring how to design molecules that can achieve better series structures, thereby increasing the efficiency of photoelectric conversion. For example, the intramolecular series structure is used to extend the whole molecule through the conjugate π system, which is conducive to charge transport; Or the

intermolecular series structure is used to form ordered polymers through intermolecular π-π interaction to promote charge migration. These methods are expected to achieve high efficiency by optimizing the molecular structure. Another important issue is to improve the stability of OPV molecules. One of the drawbacks of current OPV technology is that molecules are prone to denaturation under environmental factors such as light, humidity, and oxygen, resulting in limited efficiency and lifetime.

5.2. Current Limitations

In the field of OPV molecular design, we can foresee several major trends where machine learning will be widely used in the discovery of new materials. By learning from large amounts of organic molecular structure and performance data, machine learning algorithms can identify key structural features that affect OPV performance, thereby providing references for material design. This will greatly improve the efficiency of material design. Second, non-traditional organic materials will become the new direction of design. At present, the organic materials mainly used in the OPV field still stay in the traditional aromatic materials. However, many new materials, such as polymer materials, two-dimensional materials, and composite materials, have broad application prospects in OPV. They can not only provide a new photoelectric conversion mechanism but also may bring higher conversion efficiency.

6. Conclusion

Organic photovoltaic technology is a sustainable new energy, its development potential is huge. In recent years, OPV technology has made great progress, thanks in large part to continuous innovation in the field of molecular design. By fine designing the structure of organic molecules, scientists can effectively improve the light absorption rate and electron transport efficiency of OPV materials, thereby improving the conversion efficiency of batteries. This paper mainly discusses the application of molecular design in OPV batteries. This class of materials achieves better molecular alignment and ordering through different molecular design strategies. The energy level adjustment strategies for different molecules have proved that molecular design has a great influence on the optimization of OPV material properties. In the future, the field of molecular design has great potential for development. For example, we can explore more complex polymers and low molecular materials, use quantum chemical calculations to guide experimental research, and constantly optimize material structural parameters. At the same time, it is also necessary to pay attention to the process control and stability of the material. Only through continued innovation can OPV technology be truly applied to a wide range of renewable energy sectors. It is believed that with the maturity of molecular design technology, OPV will become a mature sustainable energy alternative technology and make important contributions to the construction of a low-carbon society.

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