

Current Status and Advances for Polymers in the Active Layer of Organic Solar Cells

Haoxuan Zhang *

Department of chemistry, Shanghai University, Shanghai, China

* Corresponding Author Email: lihaidejj@shu.edu.cn

Abstract. Currently, the development and utilization of green energy is a hot research topic in today's society. Among the many new energy technologies, research on organic solar cell panels is receiving significant attention. In recent years, organic solar cells have made tremendous progress. They have evolved from their beginnings in 1839 to now achieving photoelectric conversion efficiencies exceeding 19%. They possess numerous advantages such as low cost, light weight, ultra-thinness, flexibility, and ease of large-area preparation. In the future, they have broad application prospects in fields such as flexible batteries and photovoltaic building power supply. The active layer in organic photovoltaic panels includes acceptors and donors, which are important factors determining the efficiency of photovoltaic cells. With the development of science and technology, many materials in the active layer have been significantly improved, such as thiophene compounds, graphene compounds, and non-graphene compounds. The development of these materials has expanded the spectral absorption range of the active layer, optimized energy level matching, and greatly improved device efficiency. Compared with traditional inorganic solar cell panels, their conversion efficiency is not yet outstanding, and there are still many problems to be solved.

Keywords: Polymer materials; active layer; thiophene compounds; graphene compounds.

1. Introduction

Energy issues are one of the primary challenges facing the socio-economic development of the world today. Due to the limitations of fossil fuels and the series of problems they bring, such as environmental pollution, the development and utilization of green renewable energy technologies have always been the focus of attention for governments and scientists worldwide. Among the many new energy technologies, the research on organic solar cell panels is of utmost importance. Compared with inorganic solar cells, organic solar cells have the characteristics and advantages of flexibility, semi-transparency, and large-area printable preparation. In recent years, the research community has witnessed tremendous progress in organic solar cells (OSCs), which have many advantages such as low cost, light weight, ultra-thinness, flexibility, and ease of large-area preparation. They have broad application prospects in fields such as portable and flexible batteries, and photovoltaic building power supply.

In 1839, the French physicist A. E. Becquerel first discovered the photovoltaic effect. However, it was not until 1959 that H. Kallmann and M. Pope successfully prepared the first organic photoelectric conversion device[1]. In 1993, it was demonstrated that opvs can achieve a better energy conversion efficiency by applying fullerene as an acceptor material in the active layer. In 1995, Heeger et al. creatively mixed a fullerene derivative (PCBM) and poly(phenylene vinylene) (MEH-PPV) solution for the first time, and obtained an organic solar cell active layer with a three-dimensional interpenetrating network structure by spin-coating processing, with a PCE as high as 2.9%. Since then, bulk heterojunction organic solar cells have become mainstream and entered a period of rapid development. In 2003, Sariciflci et al. used P3HT as the donor and a fullerene derivative (PC1BM) as the acceptor to prepare a bulk heterojunction organic solar cell with a PCE of 3.5%. With extensive research on molecular engineering, device optimization, and morphology control of photovoltaic materials, the PCE of bulk heterojunction (BHJ) cell devices based on polymer donors and small molecule acceptors (SMAs) has exceeded 18%[2]. Now, the development of non-fullerene acceptor (NFAs) materials has expanded the spectral absorption range of the active layer and optimized the

energy level matching of the heterojunction, making the material performance very high, and the light absorption efficiency is also close to around 20%.

Organic solar cells (OSCs) use a "donor-acceptor" blend film as the optical absorption layer. The working mechanism of the device includes the following four processes: (1) the active layer absorbs photons to generate excitons; (2) excitons diffuse to the interface and dissociate into free carriers; (3) free carriers are transported in the donor/acceptor phase to reach the corresponding electrodes; (4) carriers are collected at the [3]. The phase separation morphology of the active layer in organic solar cells is the bridge connecting material properties and device performance, and is an important parameter for high-efficiency photoelectric conversion processes. Sufficient donor/acceptor interfaces are conducive to exciton dissociation, which largely determines the performance of OPVs [4].

The active layer, primarily composed of donor and acceptor materials, is a critical component for photovoltaic conversion in solar cells, where the material choice significantly impacts overall cell performance. Consequently, research into active layer materials is crucial for enhancing the power conversion efficiency (PCE) of organic solar cells[5]. Polymer materials not only improve the performance of organic solar cells but also offer extensive possibilities for designing and manufacturing new photovoltaic devices. With ongoing advancements in materials science and device engineering, the application of polymer materials in OPVs' active layers is expected to expand, driving the technology towards higher efficiency and broader application.

2. Introduction of Key Material Structures

The principle of photovoltaic conversion in organic solar cells is similar to that of inorganic ones; the difference lies in the use of organic materials for the active layer in organic cells to convert light into electricity, as opposed to semiconductor devices made from silicon in inorganic cells. Organic solar cells adopt a stacked device structure which is shown in Fig. 1, consisting of a positive electrode, a hole transport layer, an active layer, an electron transport layer, and a negative electrode.

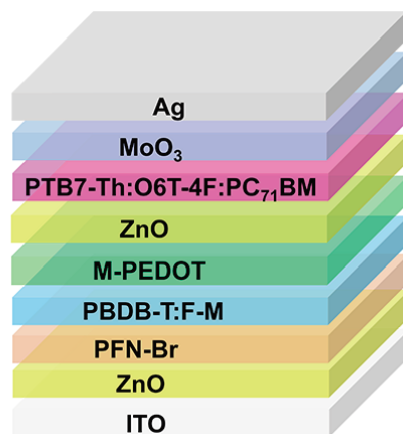


Fig 1. Schematic diagram of the device structures [11].

Commonly used polymers in the study of polymer solar cells include derivatives of polythiophene (PTH), polyphenylene vinylene (PPV), polyaniline (PANI), and other polymer materials. These polymers have a large π -conjugated system and a wide bandgap between π and π^* bands, adjustable through doping or chemical modification, typically ranging from 2.0 to 2.2eV, allowing effective solar light absorption. Among these polymers, PTH and PPV are particularly active in polymer solar cell research due to their photovoltaic performance and unique molecular architecture.

Besides conjugated polymers, fullerene materials are also favored in polymer photovoltaic cell research for their excellent π -conjugated system, high electron affinity and ionization potential, significant visible light absorption coefficient, and strong photostability. Some polymer materials are extensively studied and applied due to their unique optical and electronic properties.

Next, this article will mainly introduce some common polymer materials in the active layer.

2.1. Donor and Acceptor Polymer Materials

The active layer typically consists of donor and acceptor materials: these mainly refer to conjugated polymers or small molecule organics with high light absorption capacity and good electron donation characteristics. Initially, donor materials were simple homopolymers, with MEH-PPV being the first polymer used as a donor material. Since then, more high-performance donor materials have been developed. P3HT is a classic material in the history of organic solar cells, known for its simple chemical structure and low synthesis cost, with device efficiency reaching 10.82%[6]. Other common donor materials include poly(3-hexylthiophene) (P3HT), poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene) (PBTTT), etc.

Acceptor materials are used to accept electrons from donor materials, with common acceptors including fullerene derivatives (like PCBM) and non-fullerene acceptors (such as ITIC, Y6, etc.), typically characterized by good electron transport ability. Polymer donor materials play a key role in light absorption, exciton generation and transport, and morphology control, working in tandem with acceptor materials for efficient photovoltaic conversion. Molecular design and optimization can enhance the PCE of organic solar cells.

2.2. Polythiophenes

Fused Ring Thiophenes, and Their Derivatives PM6, D18, and their derivatives are currently the most successful wide-bandgap polymers, widely used to evaluate the photovoltaic performance of new non-fullerene acceptors. These polymers are characterized by an alternating donor-acceptor (D-A) conjugated backbone, with benzodithiophene (BDT) as the donor unit, and heterocyclic benzodithiophene-4, 8-dione (BDD) and dithienobenzothiadiazole (DTBT) as acceptor units. BDT, BDD, and DTBT's structural formulas, as illustrated in Fig. 2, serve as multifunctional donor units for constructing polymers. BDT's rigid and planar conjugated structure facilitates high hole mobility, while different side chain modifications allow fine-tuning of the polymer's energy levels and aggregation behavior.

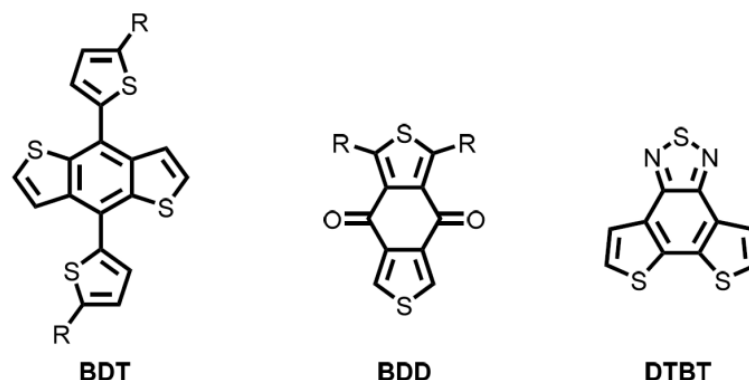
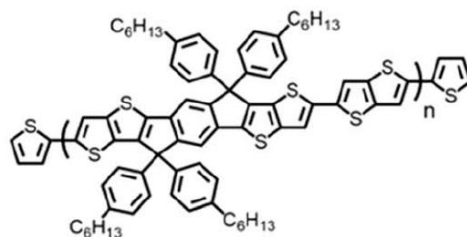


Fig 2. Molecular structure of BDT, BDD and DTBT [2].

In active layer materials, most materials opt for wide-bandgap polymers because such polymers generally have energy levels conducive to achieving higher VOCs in devices. Additionally, wide-bandgap polymers can serve as crucial components like short-wavelength photosensitive layers. Indacenodithiophene and benzothiadiazole (IDTT) is a favorable choice for constructing conjugated polymers. IDTT effectively extends the effective conjugation along the polymer backbone. Furthermore, the fusion of multiple seven-membered rings promotes the overlap of p-orbitals along the polymer backbone, enhancing strong intermolecular interactions and improving charge transfer. Polymers based on the highly conjugated nature of IDTT form coplanar and rigid backbones, resulting in low-energy disorder and thus facilitating efficient charge transport along the polymer backbone.

Recently, IDTT has emerged as a fundamental component for high-performance conjugated polymers, targeting enhanced mobility in organic field-effect transistors (OFETs) and PSC devices. This type of wide-bandgap polymer, PIDTT-TT (whose structure is shown in Figure 3).



PIDTT-TT

Fig 3. Molecular structure of PIDTT-TT [7].

This wide-bandgap polymer, PIDTT-TT, benefits from the strong electron-donating properties of IDTT and TT, making it a Dmure D' type alternating copolymer, distinct from D-A type low bandgap polymers. Notably, PIDTT-TT exhibits characteristics of a wide bandgap and deep energy levels. Moreover, PIDTT-TT surpasses P3HT with a higher extinction coefficient, compensating for the narrow absorption spectrum typical of wide-bandgap polymers. Through meticulous optimization of the photosensitive layer's morphology, PIDTT-TT achieves a power conversion efficiency (PCE) of 7.10%, one of the highest reported for broadband gap polymers. Importantly, devices based on PIDTT-TT demonstrate greater environmental stability compared to those using P3HT, primarily due to PIDTT-TT's deep energy levels, suggesting its potential as a highly stable material for PSC applications involving wide-bandgap polymers.

2.3. Fullerene-Based Acceptor Materials

Typically, electron acceptor materials are n-type semiconductors with relatively low HOMO / LUMO energy levels. The lowered LUMO level endows the acceptor materials with strong electron affinity, and their charge transport capability primarily relies on a large π -conjugated system. Currently, the dominant electron acceptor materials are fullerenes and their derivatives. Fullerene materials possess high electron mobility and excellent electronic properties, making them widely used in the active layer of organic solar cells. These mainly include mono-adduct, bis-adduct, and multi-adduct fullerene derivatives.

PC₆₁BM exhibits good thermal stability and exceptional electron transport performance, making it the most extensively used fullerene acceptor material at present. However, PC₆₁BM has weak absorption in the visible light region, leading to a lower short-circuit current density. Additionally, its low LUMO level results in a lower open-circuit voltage, ultimately affecting the conversion efficiency of organic solar cells. Subsequently, researchers developed PC₇₁BM to improve absorption in the visible light region. Not only does PC₇₁BM have higher light absorption intensity than PC₆₁BM, but it also has slightly improved solubility in organic solvents. As a result, organic solar cells based on PC₇₁BM achieve higher PCEs compared to those based on PC₆₁BM[8]. The structures of PC₆₁BM and PC₇₁BM are shown in Fig. 4. Currently, by modifying the side groups, a PCE of 11.70% can be obtained for solar cells, which is the highest efficiency achieved to date for organic solar cells based on fullerene materials.

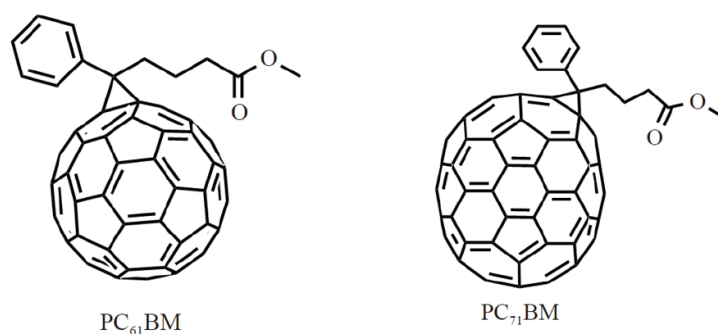


Fig 4. Molecular structures of fullerene materials as active layer receptors in organic solar cells [2].

2.4. Non-Fullerene Materials

Non-fullerene acceptors include polymers and organic small molecules. Researchers can design and synthesize organic small molecules and their oligomers with specific aggregation morphologies and excellent properties by using rich chemical methods. Currently, the highest power conversion efficiency of solution-processable bulk heterojunction solar cells based on non-fullerene organic small molecule acceptor materials has exceeded 6%, and is expected to be further improved by optimizing the morphology of the blended film and device structure [9]. In the development process of OPV technology, fullerene derivatives have dominated as electron acceptor materials for a considerable time, so the design of polymer donor materials has focused more on how to match with fullerene acceptor materials. In recent years, OPV cells based on polymer donors and non-fullerene organic acceptors, referred to as non-fullerene NF-OPVs, have developed very rapidly. In such cells, both the polymer electron donors and non-fullerene electron acceptor materials play a very important role.

2.4.1. Perylene Diimide Derivatives

Perylene diimide (PDI) derivatives, as a traditional n-type organic semiconductor, exhibit excellent optoelectronic properties, such as broad absorption in the visible region, high molar extinction coefficient, high electron mobility, easily tunable low LUMO level, and good chemical stability. PDI derivatives are one of the earliest studied electron acceptor materials, and their structure is shown in Fig.5. However, in the past few decades, those PDI-based OSCs have not achieved very high efficiency, mainly because the large π -conjugated plane of PDI exhibits a strong tendency to self-aggregate, forming sub-micron or even micron-sized crystalline structures in the solid state, which easily leads to the formation of exciton complexes, and excitons are easily captured by them, thus limiting the diffusion of excitons and the effective separation of charges.

Perylene imide-based electron acceptor materials overcome the defect of weak light absorption of fullerene materials, and their unique π -electron aromatic core determines the charge transport properties of the molecule in the solid state.

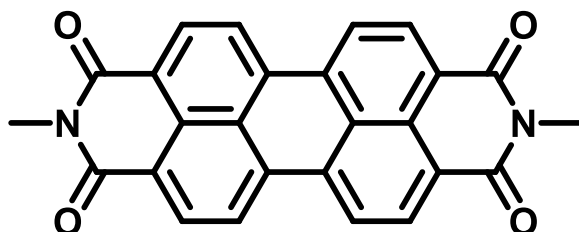


Fig 5. Molecular structures of perylene-3, 4:9, 10-tetracarboxydiimide [6].

2.4.2. Diketopyrrolopyrrole (DPP) Small Molecules

Diketopyrrolopyrrole materials have become excellent organic semiconductor materials due to their good photochemical stability, high molar extinction coefficient, good conjugated structure and other advantages. At present, due to the narrow bandgap and effective intermolecular π - π stacking of DPP materials, they are often used as charge transport materials in organic field-effect transistors and as donor materials in organic solar cells. DPP itself has relatively low LUMO and HOMO levels, and strong electron-withdrawing groups can be introduced to further increase the electron affinity of DPP materials, so that they can be used as an electron acceptor material[10].

3. Material Structure Optimization and Applications

3.1. Small Molecules for Active Layer Morphology Control

The morphology of the active layer is a crucial factor influencing device performance. Constructing a blend morphology with an excellent nanoscale interpenetrating network structure is vital for effective exciton dissociation and charge transfer in devices. Current technologies for

controlling film morphology mainly include the use of solvent additives, solvent vapor annealing (SVA), thermal annealing solvent vapor annealing (TASVA) combined with thermal annealing (TA), and the addition of a third component to construct ternary devices to adjust the film surface morphology[11].

Building on previous research, the intermolecular forces altered by the fluorine atoms in the terminal acceptor units of soluble small molecules which is shown in Fig. 6 were cleverly utilized to achieve the synergistic optimization of molecular energy levels and active layer morphology.

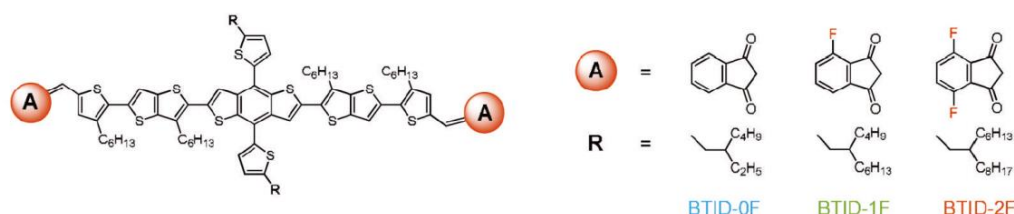


Fig 6. Chemical structure of fluorinated molecules [12].

On the one hand, fluorinated end groups can lower the highest occupied molecular orbital (HOMO) energy level and optical bandgap of the material. On the other hand, the introduction of fluorine atoms can reduce the surface energy of the molecule and its compatibility with the fullerene acceptor, thereby inducing a multi-level phase size distribution of the material in the horizontal direction: the coexistence of large-size particles (about 100 nm) with high phase purity and small-size particles (about 15 nm). This is conducive to charge transport while increasing the donor-acceptor interface area and exciton charge separation. In the vertical direction, the fluorinated end groups increase the enrichment of donor materials on the surface of the active layer, forming an electron blocking layer on the surface of the positive electrode, which is beneficial to improving the photovoltaic performance of inverted structure devices. This multi-level phase size distribution (as shown in Fig. 7) and surface enrichment effect make charge separation and transport more balanced, reducing charge recombination and energy loss, thereby achieving a significant improvement in device efficiency[12].

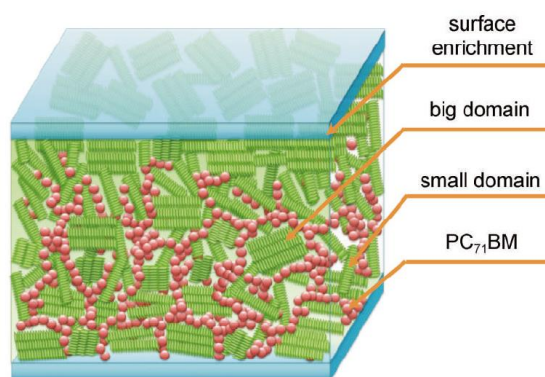


Fig 7. Schematic diagram of active layer phase structure [12].

3.2. Modification of Materials in the Active Layer

Optimizing materials in the active layer can be achieved not only by adjusting the number of π -conjugated bridging units and introducing side groups or side chains but also by introducing electronegative atoms such as Cl and Br at the terminal groups to tune the physicochemical properties of the materials, resulting in better bandgaps or morphologies[13].

Introducing appropriate heteroatoms such as O, S, N, F, and Cl into the backbone structure through precise molecular design strategies forms intramolecular interactions such as S--O, F--H, and S--N, resulting in conformational locking. Alternatively, introducing bulky substituents at appropriate positions on the conjugated main chain further suppresses single bond twisting, which is the main

approach to optimizing molecular geometry, achieving rigid backbone structures, and improving device performance.

In the future design and synthesis of non-fused ring acceptor materials, simpler structures and more straightforward synthetic steps can be. By synergistically utilizing intramolecular non-covalent conformational locking and introducing bulky side chains, control over material coplanarity and rigid backbone structures can be achieved. Furthermore, designing and introducing more diverse central cores, side chain units, and bridging units can be considered to further enhance the performance and stability of non-fused ring acceptor materials while simplifying the synthesis steps and reducing synthesis costs, which is the future direction of material design.

Material innovation is currently one of the main driving forces for improving PSC performance. Key issues in polymer design include designing bandgaps and energy levels to achieve high JSC and VOC, enhancing planarity to obtain high carrier mobility, and material processability and stability. All these issues are interconnected. Ideally, all factors should be optimized in a single polymer, but this remains a significant challenge. Over the past decade, understanding of the relationship between polymer design and these parameters has significantly improved[14].

Optimization of polymer solid-state thin-film solar cell devices can be achieved through further optimization of device physics: (1) selecting appropriate metal electrodes to achieve ohmic contact, thereby effectively collecting photogenerated carriers; (2) optimizing D/A matching while adjusting the bandgap of conjugated polymers for better absorption of sunlight; (3) optimizing the network morphology of phase-separated composites to improve carrier generation and transport efficiency, while requiring charge carriers to achieve maximum absorption and migration in different components of the composite heterojunction.

4. Limitation and Future Prospects

4.1. Issues to be solved

Currently, opvs have lower conversion efficiencies and short lifetimes and have not yet entered the utilization stage. There are issues such as low carrier mobility, disordered structures, high bulk resistance, and poor durability of the cells. The main reasons for the poor performance of organic solar cells are as follows:

(1) Due to the weak intermolecular interactions in organic materials, most of them are amorphous. Even if there is crystallinity, it is a mixture of amorphous and crystalline forms.

(2) Organic semiconductor materials have a narrow absorption band of sunlight. Most materials have a maximum absorption band of 350 nm to 650 nm. Therefore, the absorption spectrum does not match the solar spectrum, resulting in low photoelectric conversion efficiency.

(3) When organic semiconductors absorb sunlight, they produce bound hole-electron pairs called "excitons". The separation and migration of excitons are not entirely effective. Firstly, their diffusion distance is short, typically only about 10 nm. Secondly, the transport rate of electrons and holes generated after exciton separation is not high in general organic materials, resulting in low actual conversion efficiency of organic solar cells.

(4) Organic semiconductor materials are often unstable in the presence of oxygen and water.

4.2. Prospects for the application of materials in the active layer

Currently, significant progress has been made in the research of polymer photovoltaic cells. Researchers from various countries mostly focus on overcoming the above difficulties. For example, they improve light absorption by using polymers or dyes with near-infrared or infrared absorption, or improve photocurrent generation by using polymers with high fluidity and highly ordered liquid crystalline materials. The focus of research in photovoltaic cells is on creating materials and production methods that are both highly efficient and cost-effective. Organic polymer photovoltaic cells, which utilize conjugated polymers for photovoltaic purposes, are noted for their straightforward,

economical production process that supports large-scale manufacturing. This has heightened interest in the study of organic polymer photovoltaic cells.

The improvement of organic polymer photovoltaic cell efficiency can be achieved through material selection and device structure optimization. In addition, theoretical simulations of the influence of the active layers' thickness, the microstructure formed by the donor and acceptor on the photocurrent and exciton splitting efficiency, and the influence of the series and parallel resistance of the cell on the current-voltage characteristics of the cell also provide an important approach to obtaining high-conversion-efficiency organic photovoltaic cells.

In recent years, considerable progress has been made in the research of organic small-molecule electron acceptor materials applied in solution-processable, bulk-heterojunction organic solar cells, and the understanding of rational molecular structure design, device structure, and device performance optimization has been deepened. Designing and synthesizing novel n-type organic small molecules to replace fullerene-based acceptor materials is a promising and feasible approach.

After a series of improvements, polymer photovoltaic cells are expected to be used for certain commercial purposes. Due to performance parameters approaching the level of amorphous silicon photovoltaic cells, as well as the advantages of inexpensive raw materials and simple manufacturing, polymer photovoltaic cells can already be applied in all application fields of amorphous silicon photovoltaic cells.

5. Conclusion

In today's era, people's demand for energy is growing, and the development of new energy is imminent. Among them, organic photovoltaic cells are a very popular research direction. However, compared with traditional inorganic silicon solar panels, the efficiency of organic solar panels is significantly lower, and there are still many problems to be solved. The intermolecular interaction forces of organic materials are very weak, the absorption of sunlight is not wide, and the appearance of "excitons" interferes with efficiency during the conversion process. They also cannot exist stably in the air for a long time. However, with the continuous research and improvement of scientists, organic photovoltaic panels are also constantly progressing. In terms of material selection, scientists have found that polythiophene can be used as a very good donor material because they are wide-bandgap polymers that effectively improve charge transport efficiency. On the acceptor side, the selection from fullerene to non-fullerene materials has also greatly improved the photoelectric conversion efficiency. There are also other compounds such as DPP and PDI, which can be used as good organic semiconductors in the active layer.

With the continuous progress of research, the use of small molecules to regulate the morphology of the active layer, such as adding fluorine-containing molecules to the end groups, can effectively improve the compatibility of fullerene acceptors. Alternatively, by introducing suitable heteroatoms into the backbone structure through precise molecular design strategies or introducing side groups to greatly increase the conjugated structure. The application fields of organic solar panels are very wide. As photovoltaic materials, they have simple manufacturing processes, low cost, and can be manufactured in large areas. If high-efficiency and stable-performance photovoltaic cells can be obtained, the successful commercialization of polymer photovoltaic cells can be achieved.

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