Exploring Organic Small-Molecule Solar Cells: From Fundamental Principles to Advanced Device Architectures

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Abstract. Organic small-molecule solar cells (OSCs) have gained attention as strong contenders for next-generation photovoltaics, thanks to their distinct advantages like adjustable energy levels, flexible molecular design, and the potential for low-cost production. This paper reviews the crucial elements of OSC technology, with an emphasis on its operational mechanisms, material innovations, device architectures, and the latest advancements in research. The working principles, including exciton generation, charge separation, and collection mechanisms, are discussed in detail. Furthermore, the review explores the donor-acceptor materials, with an emphasis on how molecular engineering has optimized the efficiency and stability of OSCs. The comparison between single-layer and bilayer device structures is analyzed, highlighting their respective advantages and limitations in terms of efficiency, stability, and recombination losses. Finally, the latest breakthroughs in OSCs are presented, underscoring the significant progress in power conversion efficiencies and long-term operational stability. This paper seeks to offer an in-depth analysis of the current advancements and future potential of small-molecule organic solar cells.

Keywords: Organic small-molecule, solar cells, exciton generation, donor-acceptor materials, device structures.

1. Introduction

Organic solar cells (OSCs) represent a promising technology in the field of photovoltaics that has attracted considerable attention due to a number of advantageous characteristics, including their lightweight construction, flexibility, low production costs, and suitability for large-area fabrication [1, 2]. Although substantial progress has been made with polymer-based materials, organic small molecules have recently attracted increasing interest. These materials are favored for their well-defined molecular structures, ease of purification, and reproducible performance, making them ideal candidates for further research. Through molecular design, organic small molecules can be optimized for light absorption, energy level alignment, and charge transport, all of which are crucial for enhancing power conversion efficiency (PCE). The incorporation of non-fullerene acceptors has recently led to significant improvements in small-molecule OSCs, paving the way for further advancements in device performance and stability [3, 4].

This paper presents a detailed review of the recent advancements in the field of OSCs. It is structured as follows: Initially, the fundamental working principles of OSCs are explored. Next, strategies for designing donor and acceptor materials are examined, highlighting their influence on device performance. The paper then delves into significant breakthroughs in the development of high-efficiency devices, such as the use of benzodithiophene-based donor materials and non-fullerene acceptors. Finally, challenges related to material innovation, device stability, and commercialization are discussed, along with future research directions and opportunities for growth in the field.

2. The operational mechanism of organic small-molecule solar cells

Figure 1 illustrates a number of crucial processes in the operating concept.

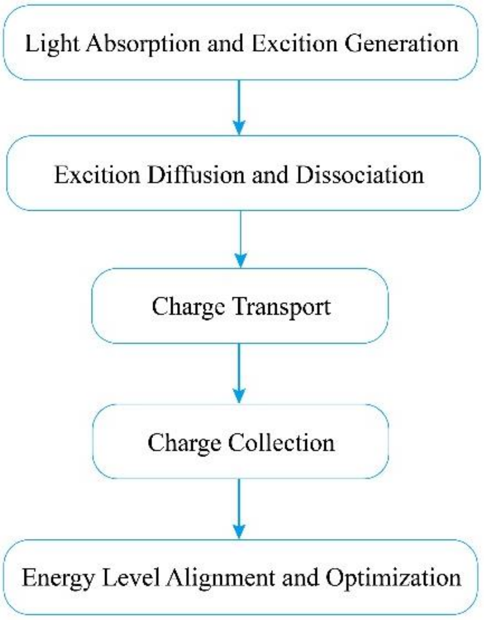

Figure 1. Basic steps of the working principle

2.1. Light Absorption and Exciton Formation

Donor material in the active layer of OSCs absorbs photons to start the device's functioning. This absorption event excites electrons from their ground state to a higher energy level, generating excitons—bound electron-hole pairs, held together by Coulombic forces due to the low dielectric constant typical of organic materials [1, 7]. These excitons have a higher binding energy than those in inorganic semiconductors, necessitating efficient dissociation into free charge carriers to contribute to current generation [2].

2.2. Exciton Diffusion and Dissociation

After being generated, excitons must migrate through the donor material toward the donor-acceptor interface before they can recombine. Given the limited diffusion length of excitons, typically between 10 and 20 nm, this process must occur rapidly [5]. At the donor-acceptor interface, the energy level difference facilitates exciton dissociation, causing electrons to transfer to the acceptor and leaving holes behind in the donor material [3]. The difference in energy levels between the lowest unoccupied molecular orbital (LUMO) of the acceptor and the highest occupied molecular orbital (HOMO) of the donor drives this dissociation process [4]. The effectiveness of exciton dissociation is a key factor that significantly influences the overall PCE of the device [6, 7].

2.3. Charge Transport

The liberated electrons and holes that result from exciton dissociation need to be moved to the appropriate electrodes. The mobility of the organic materials affects the efficiency of charge transport; this mobility can be enhanced by maximizing the active layer's crystallinity and molecular packing. [8]. Organic small molecules often exhibit lower charge mobilities compared to polymers, which can be a limiting factor for device performance. However, molecular engineering strategies, such as enhancing π-π stacking and minimizing energetic disorder, can improve charge transport properties [9, 10].

2.4. Charge Collection

The final step in the operation of OSCs is the collection of the free charges at the electrodes. Electrons are generally collected at a low work function cathode, such as aluminum, while holes are gathered at a high work function anode, commonly indium tin oxide (ITO) coated with PEDOT: PSS. The effectiveness of charge collection is significantly influenced by the alignment of energy levels at the junctions between the organic materials and the electrodes, which can be fine-tuned to minimize energy losses and reduce recombination. [11, 12].

2.5. Energy Level Alignment and Optimization

Effective charge separation and transport are intricately linked to the energy level alignment of materials, as well as the active layer and electrodes. To foster efficient charge transfer, it is imperative that the LUMO of the acceptor material is positioned lower than that of the donor, while the HOMO of the donor should be higher than that of the acceptor. The energy level offset enables the transfer of electrons from the donor to the acceptor, thereby facilitating the formation of charge carriers that can subsequently be extracted by the electrodes and employed to generate electrical power. In order to improve charge collection and lower energy losses, the electrodes' work functions should also match the energy levels of the materials. This will increase the solar cells' overall efficiency. [1, 2, 5].

3. Materials Design and Optimization in OSCs

3.1. Donor Materials Design and Optimization

Indeed, in the field of OSCs, the meticulous design and optimization of donor materials play a pivotal role in pushing the boundaries of PCEs. Donor materials must exhibit a strong absorption spectrum that overlaps with the solar spectrum to maximize photon absorption [2]. Molecular design strategies focus on extending the conjugation length, incorporating electron-donating or electron-withdrawing groups, and fine-tuning the molecular planarity of donor materials in OSCs is a strategic approach to enhance light absorption and facilitate charge transport. Additionally, the energy levels of the donor, specifically the HOMO and the LUMO, must be carefully tuned. A deeper HOMO level can enhance the Voc, while a well-optimized LUMO level can promote effective exciton dissociation at the interface [1, 5].

Additionally, morphological characteristics of donor materials are pivotal to device performance. Well-organized domains and optimal phase separation between donor and acceptor materials are key for facilitating efficient charge transport and minimizing recombination losses [8]. Molecular engineering strategies, including the modification of side chains to regulate crystallinity and phase separation, have been employed to optimize the morphology of the active layer. For example, adding alkyl chains or fluorine atoms can enhance molecular packing and strengthen π-π stacking interactions, resulting in improved charge carrier mobility [9, 10].

3.2. Acceptor Materials Design and Optimization

Acceptor materials are equally vital in determining the overall efficiency of OSCs. Traditionally, fullerene derivatives were widely used as acceptors, given their limited absorption capacity in the visible spectrum and morphological instability, researchers have shifted their focus to the development of non-fullerene acceptor (NFA) materials, aiming to overcome these limitations [5]. NFAs present a multitude of advantages, chief among them being their tunable energy levels. This characteristic allows for greater versatility in device design and optimization, enabling researchers to tailor the energy levels to match those of the donor material, thereby promoting efficient exciton dissociation and charge transfer. Furthermore, NFA exhibits a robust light-absorbing capacity and is capable of utilizing a more extensive portion of the solar spectrum than conventional fullerene acceptors. Furthermore, the potential for enhanced morphological stability offered by NFAs is another significant advantage, as it can lead to improved device performance and longevity. The design of NFAs focuses on creating acceptors with broad absorption spectra and appropriate energy levels to facilitate efficient charge separation and transport [7].

One successful approach in NFA design is the introduction of electron-deficient units, such as diketopyrrolopyrrole (DPP) or perylene diimide (PDI), which can be combined with electron-rich units to create a D-A-D structure. This structure not only allows for tuning of the energy levels but also enhances light absorption and charge carrier mobility. Moreover, optimizing the molecular packing and crystallinity of NFAs can lead to more favorable phase separation and improved charge transport [6, 11].

3.3. Donor-Acceptor Interactions and Morphological Control

The intricate interplay between donor and acceptor materials within the active layer holds paramount importance in dictating its morphology and, consequently, th e overall performance of the device. The careful selection and optimization of these materials, along with their interactions, can significantly enhance exciton dissociation, charge transport, and ultimately, the PCE. Careful control of the miscibility between donor and acceptor materials is essential to achieve optimal nanoscale phase separation, which promotes efficient charge transport while reducing recombination losses [11]. Too much miscibility can lead to large domains, which increase the likelihood of charge recombination, while too little can result in poor percolation pathways for charge carriers [3].

Morphological control in organic solar cells can be attained through several processing methods, including solvent optimization, thermal treatments, and the incorporation of additives during processing [4]. For instance, introducing solvent additives can facilitate the development of a more advantageous phase-separated morphology, which in turn boosts charge transport and improves power conversion efficiencies (PCEs) [5]. Another effective approach is thermal annealing, which enhances the crystallinity of the active layer and refines its morphology, ultimately improving both charge transport properties and overall device performance.

3.4. Stability and Optimization of Device Architecture

In addition to the molecular design of donor and acceptor materials, ensuring the stability of OSCs is essential for their practical deployment. Both materials and device structures need to be fine-tuned to resist environmental challenges like humidity, oxygen exposure, and fluctuating temperatures. Techniques such as effective encapsulation and the creation of more durable materials, which are less prone to degradation, can notably increase the operational lifespan of OSCs [8, 9].

4. Comparison of Single-Layer and Bilayer Devices in Organic Small-Molecule Solar Cells

4.1. Single-Layer Devices

Single-layer OSCs are among the earliest configurations studied in the field. In these devices, the active layer consists of a single organic material that serves as both the electron donor and acceptor [1, 6]. The simplicity of this structure allows for easier fabrication and processing, but it inherently suffers from significant limitations in efficiency. The primary challenge lies in the exciton dissociation process. Since both donor and acceptor functionalities are contained within the same material, the likelihood of excitons reaching a donor-acceptor interface before recombining is low [8]. As a direct consequence of the limited exciton diffusion and suboptimal charge separation within single-layer organic solar cells, these devices often exhibit lower power conversion efficiencies (PCEs) compared to their bilayer counterparts. Addressing these challenges through innovative material design, device architecture, and processing techniques remains a key focus of ongoing research efforts aimed at enhancing the performance of these promising renewable energy technologies [9].

Moreover, the charge transport in single-layer devices is often hindered by the lack of distinct pathways for electrons and holes. Without a well-defined interface, the probability of charge recombination increases, further reducing the device's efficiency [4]. Despite these drawbacks, single-layer OSCs have been instrumental in understanding the fundamental processes involved in organic photovoltaics and have provided a baseline for further device improvements [7].

4.2. Bilayer Devices

The advent of bilayer organic solar cells (OSCs) represents a pivotal advancement compared to their single-layer counterparts. In these bilayer systems, the active layer is meticulously crafted from two distinct components: an electron donor and an electron acceptor, intricately layered one atop the other [2]. This ingenious arrangement fosters a precisely defined interface between the donor and acceptor, significantly enhancing the efficiency of exciton dissociation and charge separation processes [1]. By employing the bilayer structure, excitons generated in the donor material are efficiently directed toward the donor-acceptor interface, where they dissociate into free charge carriers, enhancing the device's energy conversion efficiency [5].

Compared to their single-layer counterparts, bilayer OSCs exhibit enhanced PCEs stemming from improved charge transport mechanisms and mitigated recombination losses. The segregated paths for electrons and holes within the distinct donor and acceptor layers, facilitate more efficient charge collection at the electrodes. This separation of charge carriers not only reduces the likelihood of recombination but also promotes directed movement towards their respective collection points, ultimately leading to superior performance in terms of energy conversion [10]. Although substantial progress has been achieved in the development of bilayer OSCs, their performance is still somewhat constrained by the limited exciton diffusion length. This parameter, which denotes the distance an exciton can travel before recombining, must be commensurate with the thickness of the donor layer to ensure efficient exciton dissociation and subsequent charge separation. Failure to achieve this delicate balance can lead to a reduction in the overall PCE of the device [11]. If the donor layer is of excessive thickness, the probability of exciton recombination occurring prior to reaching the interface is increased, which subsequently reduces the efficiency of the device [5].

4.3. Comparative Analysis

A comparative analysis of single-layer and bilayer OSCs highlights the trade-offs involved in each device structure. While single-layer devices offer simplicity in design and fabrication, their performance is constrained by inefficient exciton dissociation and charge transport [1, 5]. On the other hand, bilayer devices provide better exciton dissociation and charge separation due to the distinct donor-acceptor interface, leading to higher PCEs [2, 8].

However, bilayer devices also face challenges, particularly related to the optimization of the donor and acceptor layer thicknesses. Achieving the right balance between sufficient thickness for light absorption and thin enough layers for efficient exciton diffusion is critical for maximizing the performance of bilayer OSCs [11]. Furthermore, the interfacial morphology between the donor and acceptor layers is of paramount importance in determining the overall PCE, as any imperfections at the interface can lead to increased recombination losses [4, 10]. A simple comparison of single-layer and bilayer devices is shown in Table 1.

Table 1. Single-layer devices vs. Bilayer devices

	Single-Layer Devices	Bilayer Devices
PCE	Higher	Lower
Fabricate	Simple	Hard
Stability	Less Stable	More Stable
Morphology Control	Difficult, challenging to control phase separation	Easier, distinct layers provide clearer material interfaces
Recombination Losses	Higher	Lower
Ideal Applications	Suitable for high-efficiency applications	Suitable for applications requiring higher stability

In summary, while bilayer OSCs represent a significant improvement over single-layer devices, both configurations have their inherent advantages and limitations. Single-layer devices, though limited in efficiency, are simpler to fabricate and provide valuable insights into the fundamental processes of organic photovoltaics. In contrast to single-layer devices, bilayer organic solar cells offer superior performance due to their heightened capabilities in exciton dissociation and charge transport. However, this performance enhancement comes with the necessity of meticulous optimization of material properties and layer thicknesses. The precise tuning of these parameters is crucial to ensuring that the bilayer interface remains optimal for exciton dissociation. Future research in this area will likely focus on further enhancing bilayer device architectures and exploring new materials that can overcome the current limitations, ultimately leading to more efficient and commercially viable OSCs [4].

5. A Review of Recent Advances in OSCs

5.1. Emergence of Non-Fullerene Acceptors (NFAs)

In recent years, a pivotal breakthrough in the realm of OSCs has centered on the emergence NFAs, marking a significant advancement in the field. Traditional OSCs primarily relied on fullerene derivatives as electron acceptors due to their excellent electron mobility and ability to form well-defined donor-acceptor interfaces. However, fullerene-based OSCs have limitations, including challenges such as inadequate absorption in the visible light spectrum, constrained tunability of energy levels, and morphological instability, these factors have posed obstacles to the widespread adoption of certain technologies [11]. To address these issues, researchers have developed NFAs, which have shown remarkable improvements in the performance and stability of OSCs. NFAs offer tunable absorption properties, allowing for better spectral matching with donor materials and enabling higher PCEs [1].

Among the various NFAs developed, ITIC and Y6 have gained particular attention due to their outstanding performance and compatibility with various donor materials. These NFAs have led to PCEs exceeding 18% in some OSCs, marking a significant milestone in the field [6]. Additionally, NFAs have been shown to improve the stability of OSCs, as they are less prone to degradation under light exposure and environmental conditions compared to fullerene-based acceptors [4].

5.2. Advances in Donor Materials

The emergence of new donors has also been a significant contributing factor to the recent advancements observed in OSCs. Traditional donor materials, such as P3HT, have been widely used but often suffer from suboptimal energy levels and limited light absorption. To overcome these limitations, researchers have focused on designing and synthesizing new donor molecules with enhanced properties, such as stronger light absorption, better energy level alignment with acceptors, and improved charge transport [10]. For example, benzodithiophene (BDT)-based donor materials have shown great promise due to their ability to achieve high PCEs when paired with NFAs [1].

Recent studies have also explored the use of non-conjugated donor materials, which offer unique advantages in terms of morphological stability and mechanical flexibility. These materials are particularly interesting for the development of flexible and wearable solar cells, which represent an exciting frontier in organic photovoltaics [8]. The combination of innovative donor with NFAs has led to a new generation of OSCs that exhibit not only high efficiency but also enhanced durability and flexibility [7].

5.3. Optimization of Morphology and Device Structure

Another noteworthy area of substantial progress in the realm of OSCs revolves around the optimization of morphology and device architecture. This endeavor involves meticulously refining the arrangement and properties of the various layers within the device, as well as exploring innovative structural designs, to enhance charge transport, exciton dissociation, and overall performance. The performance of OSCs is highly dependent on the nanoscale morphology of the active layer, which influences exciton dissociation, charge transport, and recombination. To attain the desired optimal morphology, a delicate equilibrium must be struck between the crystallinity of donor and acceptor, along with the intricate phase separation within the all-important active layer. This meticulous balancing act is crucial for maximizing performance [4]. Recent studies have concentrated on examining and regulating the factors that impact morphology, such as the choice of solvents, specific processing techniques, and the inclusion of various additives [11].

In addition to morphology control, researchers have also made strides in optimizing device structures to enhance performance. For instance, the inverted device architecture, which reverses the order of the electrode layers compared to the traditional structure, has gained traction due to its enhanced stability and greater compatibility with large-scale manufacturing processes [5]. Furthermore, the development of tandem and multi-junction OSCs, which combine multiple sub-cells with complementary absorption spectra, has pushed the boundaries of PCEs, offering a pathway to even higher efficiencies in the future.

5.4. Stability and Scalability

The commercial viability of OSCs depends not only on their efficiency but also on their stability and scalability. Recent research has focused on improving the long-term stability of OSCs by addressing factors such as photo-oxidation, thermal degradation, and mechanical stress [10]. To improve stability, it is imperative that more resilient materials be developed, more efficacious encapsulation techniques be implemented, and a stable interfacial layer be utilized. Additionally, scalable fabrication techniques have been explored to enable the mass production of OSCs at a competitive cost [4].

6. Conclusion

The conclusions obtained from the above study in this paper are as follows: The operating mechanism of organic small-molecule solar cells involves a sequence of interconnected processes, including light absorption, exciton creation, exciton diffusion, separation into free charges, charge transport, and finally collection at the electrodes. The efficacy of these critical steps is intricately tied to factors like the molecular architecture of the employed materials, the intricate morphology of the active layer, and the precise alignment of energy levels within the device. Ongoing research and innovations in these domains hold the key to unlocking even greater performance gains and bolstering the commercial viability of OSCs.

Moreover, recent breakthroughs in OSCs represent a comprehensive approach that integrates material innovation, device optimization, and processing techniques. These combined efforts have led to notable improvements in efficiency, stability, and scalability, bringing the technology closer to commercial viability. With continued research addressing the remaining obstacles, OSCs are positioned to contribute significantly to the global shift towards renewable and sustainable energy sources.

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