The Design and Performance of Non-Fused Ring Acceptors for Organic Solar Cells with High Power Conversion Efficiency

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Abstract. Organic solar cells (OSCs) have gained widespread applications in fields such as wearable devices, portable power and building-integrated photovoltaics because of their inherent flexibility, lightweight, and potential to lower production costs. Among the various components of organic solar cells, electron acceptor materials are one of the essential factors in attaining high power conversion efficiency (PCE). Traditionally, fullerene-based acceptors dominated the field, but their limitations in tunability and performance have led to the rise of non-fullerene acceptors (NFAs), particularly non-fused ring acceptors (NFREAs). NFREAs have attracted significant attention in recent years due to their easily adjustable molecular structures, simplified synthesis processes, and lower costs compared to fused-ring acceptors (FREAs). This review provides a detailed introduction to the development history and latest advancements achieved in NFREAs, with a focus on their classification based on different molecular backbones. Some key modification strategies are also discussed, offering insights into future directions for designing high-performance non-fused ring acceptors in OSCs.

Keywords: Organic solar cells; Power conversion efficiency; Non-fused ring electron acceptors.

1. Introduction

Since 1958 Kearns' team used Magnesium Phthalocyanine (MgPc) to build the first organic photovoltaic device which takes homojunction as the structure of its active layer, (OSCs) have been developed for nearly 70 years. During this period, significant breakthroughs have been made, the structure of the active layer has evolved from homojunction to bilayer heterojunctions and finally to bulk heterojunctions, together with Power Conversion Efficiency (PCE) increasing from less than 1% initially to nearly 3% [1–3]. This progress has successfully brought OSCs into the focus of researchers and quickly led to their advancements. Compared with traditional silicon-based solar cells, OSCs feature simple fabrication processes, flexibility, light weight and so on. Although they still cannot match the most advanced silicon-based solar cells in terms of the PCE, the rapid development of acceptor materials in recent years has shown that OSCs hold considerable potential and irreplaceable advantages in fields such as portable power solutions, flexible cells and building-integrated photovoltaics.

In the early days of acceptor materials, soluble fullerene acceptor PC60BM dominated the field of organic photovoltaics because of its outstanding electron-accepting abilities and isotropic electron transport properties. However, due to its highly symmetric molecular structure, PC60BM exhibits very limited absorption in the visible light region, and its energy levels are difficult to effectively adjust through chemical modifications to achieve optimal matching with different donor materials. This has become a major bottleneck in further improving the PCE. Although researchers have developed a series of modified fullerene acceptor materials based on PC60BM, only a few have demonstrated better photovoltaic performance. For example, PC70BM significantly enhances absorption in the 350–550 nm range, making it more widely used in OSCs where narrow-bandgap conjugated polymers serve as the donor. Li and colleagues developed an indene-C60 bis-adduct (IC60BA), which increased the LUMO energy level of PC60BM by 0.17 eV, significantly improving the PCE to 6.48% using P3HT as the donor[4]. Nevertheless, several such attempts experienced declines in short-circuit current (Jsc) and fill factor (FF) despite successfully improving the LUMO level of the acceptors. As a result, their overall performance fell short of PC60BM [4,5]. On the other hand, devices based on NFAs initially did not attract much attention in the industry due to their relatively low PCE. Compared to the rapid development of polymer donors, improvements in acceptor materials have been relatively slow.

This impasse was finally broken in 2015 with the discovery of the reputed molecule ITIC by Zhan and his team [6]. They developed this fused ring acceptor by using IT as the core and INCN as the end groups. With its broad and effective absorption in the visible region and well-matched energy levels with low-bandgap polymer donors such as PTB7-TH, ITIC achieved a PCE of up to 6.8%, demonstrating superior photovoltaic performance compared to fullerene acceptors. This breakthrough marked a significant shift in organic solar cell research, from fullerene derivatives to NFAs. Subsequently, the efficiency of OSCs based on NFAs rapidly increased to nearly 16% [7].

Although the series of FREAs, represented by ITIC, has achieved significant success, there are still certain limitations, leaving room for further breakthroughs. The synthesis process for large fused-ring structures is complex, resulting in high production costs and low yields [8]. Additionally, the flexibility of molecular design for fused-ring structures is limited, and their inherent structural instability poses challenges for commercialization. To solve these problems, Li et al. first introduced the concept of NFREAs in 2018, simplifying the complex structure of fused-ring molecules by connecting different structural units through single bonds, opening up new avenues for the advancement of NFAs [9]. In recent years, NFREAs have developed rapidly, with their photovoltaic performance gradually approaching that of fused-ring acceptors, while simultaneously reducing production costs and improving yields.

2. Composition and Working Principles of OSCs

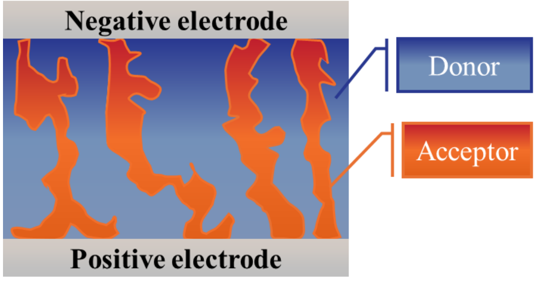

Fig. 1 The structure of a typical OSC with bulk heterojunction

As is shown in Figure 1, OSCs are typically composed of an anode, a cathode, and an active layer. The electrodes are selected based on energy level matching and transparency requirements, using metals or transparent conductive materials with appropriate work functions. To ensure sunlight reaches the active layer efficiently, at least one of the electrodes needs to be transparent while maintaining conductivity. The active layer is made of blended donor-acceptor materials, forming a bulk heterojunction structure to effectively shorten exciton diffusion distance and enhance charge separation efficiency. Typically, an electron transport layer (ETL) and a hole transport layer (HTL) are inserted between the active layer and the electrodes. These transport layers can minimize charge loss and improve charge extraction efficiency since they can optimize energy level alignment, reduce interfacial barriers, and prevent electrons and holes from leaking into the opposite electrodes.

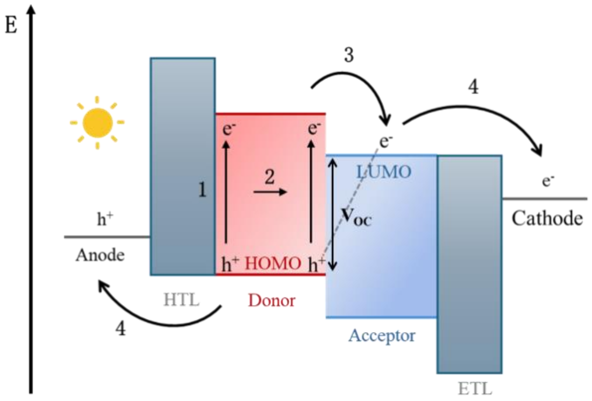

Fig. 2 The structure of a typical OSC with bulk heterojunction

As depicted in Figure 2, the operation of OSCs can be broken down into four phases: (1) Photon absorption: When sunlight passes through the transparent conductive electrode and reaches the active layer, the active layer material (donor or acceptor) absorbs the energy from sunlight. Electrons are then activated into the LUMO level, while holes are also generated at the HOMO level, forming excitons. (2) Exciton diffusion: Excitons (pairs of holes and electrons) diffuse towards the donor-acceptor heterojunction interface due to concentration gradients. During this process, recombination can occur. The distance excitons travel before recombining is called the "diffusion length." A longer diffusion length allows more excitons to reach the interface, thus increasing Jsc. (3) Charge separation: Once the excitons diffuse to the interface, they are affected by the intrinsic electric field. Electrons and holes move towards the acceptor and donor, respectively, leading to charge separation. (4) Charge transport and collection: The charges are driven by the intrinsic electric field towards the respective electrodes, where they are collected, generating photovoltage and photocurrent.

3. Molecular Structure Design of NFREAs

In general, the molecular structure of NFREAs consists of a non-fused ring core and two electron-withdrawing terminal groups. The non-fused ring core can be further classified into two types, namely D-A'-D and D-D'-D, depending on whether the central unit is electron-withdrawing or electron-donating [10,11]. The D units which exist in both structures usually act as π-bridges, connecting the central unit with the electron-withdrawing terminal groups. These D units typically have a delocalized π-bond thus exhibiting strong electron-donating properties. This feature not only enhances intramolecular charge transfer (ICT) but also promotes π-π stacking between molecules, facilitating efficient electron transport in the aggregated state.

3.1. D-A'-D Core Structure

In acceptors with a D-A'-D non-fused ring core, the introduction of the A' unit produces a local electron-withdrawing effect, which promotes charge separation and reduces charge recombination losses. This design effectively adjusts the molecular energy level, narrows the band gap, and expands the absorption spectrum, thereby improving the light absorption efficiency. However, the introduction of the A' unit also destroys the continuity of the π-conjugated system, resulting in a decrease in charge mobility.

3.2. D-D'-D Core Structure

Unlike the D-A'-D structure, the D-D'-D structure, with its highly conjugated system, exhibits stronger π-π intermolecular interactions. This always leads to better molecular packing and enhanced electron transport properties, enabling more efficient charge transfer in the aggregated state.

3.3. Asymmetric Core Structure

Although the above discussion primarily focuses on symmetric non-fused ring cores, they can also be designed in asymmetric forms. The symmetry of the structure significantly affects the optoelectronic properties of acceptor materials, but which structure has a positive impact on power conversion efficiency (PCE) depends on the specific core unit. Generally, asymmetric cores, due to their larger dipole moments and stronger intermolecular interactions, can achieve tighter molecular stacking, leading to more orderly arranged molecules, thereby enhancing charge transport [12].

In 2022, Liu et al. made four simple NFREAs with symmetric and asymmetric cores based on dithiophene cyclopentadiene (DTC) and dithieno[3,2-b:2',3'-d]pyrrole (DTP) respectively [13]. They investigated the effects of symmetric and asymmetric structures on the conformations and optoelectronic properties of these acceptors, as well as their performance in solar cells. Experimental results showed that the symmetric DTC-based acceptors and the asymmetric DTP-based acceptors exhibited high planarity, which facilitated π-π stacking and charge transport, thus achieving higher PCEs.

3.4. Noncovalent Conformational Locks (NoCLs)

Compared with FREAs, NFREAs usually have problems with conformation distortions due to the single bonds connecting their units, which provides convenience for intramolecular rotation. This results in reduced planarity and rigidity of the acceptor, significantly affecting intermolecular stacking and charge mobility. To address this issue, Huang et al. proposed the concept of "Non-covalent Conformational Locks (NoCLs)" in 2011 [14]. This strategy restricts C-C bond rotation to the plane by introducing highly electronegative atoms such as oxygen or fluorine. Once these atoms are introduced, they form relatively weak intramolecular noncovalent interactions (INIs) with heteroatoms on the structural units but are still strong enough to maintain the planarity of NFREAs to approach the level of the FREAs.

Fig. 3 The structure of DT-BT, DTFBT, and DT-OBT [15]

Up to now, researchers have conducted extensive studies in this area, making NoCLs one of the most popular strategies to enhance planarity. Ma et al., for example, further investigated the working mechanism of NoCLs within individual molecules to explain its impact from a microscopic view [15]. They synthesized three structural units widely used in OSCs, that is DT-BT, DTFBT, and DT-OBT, as shown in figure 3, and then conducted comparative studies on their intramolecular charge transfer (ICT) properties. The results showed that the order of the conductivities was opposite to that predicted by tunnelling theory. Further research indicated that this reversal was due to the introduction of NoCLs, which induced hyperconjugation in the HOMO orbitals of the molecules, thus creating more efficient charge transport pathways within the molecule.

Zhang et al. [11] conducted an in-depth theoretical analysis of NoCLs and developed a simple descriptor (S) to quantify their strength. Their research demonstrated that the S values follow the order S⋯F < Se⋯F and S⋯O < Se⋯O, providing new insights and theoretical support for further restricting the rotation of C-C bonds.

4. Modification

After the basic molecular structure is established, various modification methods can still significantly impact the photovoltaic performance of acceptor materials. The following is a brief summary of these modification approaches.

4.1. Asymmetric Engineering

First, the introduction of asymmetry is an effective strategy. In addition to the asymmetric cores mentioned in Section 3.3, asymmetric side chains or terminal groups can also be introduced, providing more flexibility in tuning molecular conformation and electronic energy levels. For example, Liu and colleagues prepared acceptor materials with two different terminal groups, IC-2Cl and NC-2F[16]. These asymmetric acceptors exhibited superior performance compared to the two symmetric acceptors prepared with the same terminal groups.

4.2. Side Chain Engineering

The side chain engineering has been considered one of the most effective modification strategies due to its flexibility in adjusting electronic and aggregation behaviour of the acceptors. The size, length, shape and many other factors of the side chains can make things different. Zhou et al. [17] prepared an OSC with high PCE by adopting NFREAs with V-shaped side chains. These acceptors show far better performance in both charge transport mobility and film morphology than those with linear side chains, which can be attributed to improved $\pi-\pi$ stacking. Except for this, adjusting the length of the side chains can also significantly affect solubility, therefore affecting the film morphology of the acceptors.

4.3. Polymerization

All-polymer solar cells demonstrate vast prospects in practical applications due to their excellent flexibility and exceptional device stability. Inspired by the innovative strategy of "polymer fused-ring acceptors (PFREAs)", Zhang et al. [11] proposed applying a polymerization approach to NFREAs . Benefiting from the cost advantages of NFREAs, polymerized non-fused ring acceptors (PNFREAs) significantly improved the balance between efficiency, stability, and cost, paving a practical way towards the commercialization of OSCs.

5. Conclusion

According to the working principle of photovoltaic devices, achieving high PCE requires both high J_{SC} and high VOC. The V_{OC} primarily depends on the difference in the energy level between the HOMO of the donor and the LUMO of the acceptor, while JSC is influenced by the material's light absorption efficiency and charge losses. Among non-fused core structures, the D-A'-D type features a narrower bandgap, providing a broader absorption spectrum. In contrast, the D-D'-D type excels in charge transport performance, resulting in lower charge losses. Both structures offer distinct advantages.

Overall, non-fused ring acceptors, as an emerging research direction for acceptor materials, have shown great potential in improving photovoltaic performance and reducing production costs. Breakthrough research and innovative concepts such as PNFREAs continue to emerge. However, since this field has only been proposed relatively recently, there is still a lack of extensive experimental data, and most breakthroughs remain at the experimental stage. Compared to FREAs, the commercialization of these materials is not yet mature, but they exhibit significant application potential, and researchers remain enthusiastic about further exploration.

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