

Molecular Design, Crystallization Control, and Photoelectric Performance Comparison of High Mobility Organic Semiconductors

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Abstract. In recent years, organic semiconductors have shown broad application prospects in the fields of organic field effect transistor (OFET), organic photovoltaic (OPV), and organic light emitting devices (OLED) due to their adjustable molecular structure, flexible processing, and low cost. However, the contradiction between high mobility and excellent photoelectric performance is still the core problem restricting its development. Based on the research progress of typical organic semiconductor systems in recent years, this paper systematically analyzes the molecular design strategies, crystallization control methods, and the influence mechanism on photoelectric properties of high mobility organic semiconductors. In the theoretical part, the molecular structure characteristics, carrier transport mechanism, doping, and interface engineering principles of organic semiconductors are described. In the part of performance comparison, the mobility, luminous efficiency, and device performance of typical material systems are compared. According to previous studies, through molecular conjugate structure optimization, crystal orientation control and Interface Engineering collaborative design, the carrier mobility can be significantly improved and the photoelectric performance can be taken into account, which provides theoretical guidance for high-performance organic optoelectronic devices.

Keywords: Organic semiconductors, molecular structure, interface engineering, mobility, crystallization control.

1. Introduction

With the rapid development of flexible electronics and wearable technology, organic semiconductor materials have gradually become an important research object in the field of Optoelectronics due to their unique advantages. Compared with traditional inorganic semiconductors, organic materials have the characteristics of adjustable molecular structure, simple solution processing, and excellent mechanical flexibility. They have irreplaceable advantages in large-area electronic devices and low-cost manufacturing [1].

In recent years, the performance of organic semiconductors has been significantly improved. Typical materials such as DPP (diketo pyrrolopyrrole) and hmeoscs (high mobility emissive organic semiconductors) have improved their carrier mobility from $10^{-4} \text{ cm}^2/\text{V}\cdot\text{s}$ to more than $10 \text{ cm}^2/\text{V}\cdot\text{s}$ [2]. The efficiency of organic photovoltaic and organic light-emitting devices has been continuously improved to promote their commercial applications. In addition, the development of exciton control technology (such as triplet state management and triplet triplet annihilation up conversion mechanism) has also significantly improved the photoelectric conversion efficiency [3]. At the same time, from the perspective of the development of semiconductor optoelectronic materials in a broader sense, inorganic semiconductor systems have achieved high-performance devices through fine band engineering and epitaxial growth technology, which provides an important reference for organic semiconductors [4].

However, with the continuous improvement of performance, a fundamental contradiction gradually appeared. Enhancing the intermolecular $\pi - \pi$ stacking can effectively improve the charge transport capacity, but at the same time, it will enhance the intermolecular interaction, leading to the increase of exciton non-radiative recombination, thus reducing the luminous efficiency [5]. The trade-off between high mobility and high luminous efficiency has become the core issue of current organic

semiconductor research. However, with the improvement of performance, the structural contradictions within the material gradually appear. Enhancing π - π stacking can improve the charge mobility, but at the same time enhance the intermolecular interaction, resulting in the increase of exciton non radiative recombination, thus reducing the luminous efficiency [6]. Similar problems also exist widely in inorganic /organic heterostructure systems. For example, the balance between carrier separation and recombination also determines the performance of devices in wide band gap semiconductor heterostructures such as TiO₂/bdc [7].

In order to find out and solve the deficiencies between high mobility and high luminous efficiency, this paper will focus on the structure and performance control mechanism of organic semiconductors, the performance comparison of typical materials and devices, as well as the key challenges and improvement strategies for the collaborative optimization of high mobility and high luminous efficiency. This study aims to adjust the contradiction between high mobility and high luminous efficiency.

2. Theoretical Basis

Organic semiconductors are usually composed of conjugated molecules or polymers, and their electronic structure is determined by homo/lumo energy levels. Typical structures include donor acceptor (D-A) structure, π conjugated planar skeleton and alkyl side chain regulatory structure. For example, DPP based materials have a strong electron absorption core and excellent conjugation, which makes them have excellent mobility and a wide optical absorption range [2]. In addition, electronic defect structures (such as naphthalimide and anthraquinone) can effectively reduce the LUMO energy level and improve the n-type transmission performance [1].

The key physical properties of organic semiconductors include carrier mobility, exciton behavior, energy level matching, and molecular stacking. The carrier mobility determines the response speed of the device, which is the core index. The exciton behavior includes singlet and triplet excitons, which are very important to photoelectric performance. The matching degree of energy levels affects charge injection and interface transmission. The molecular stacking mode determines the charge transmission path (π - π stacking) [3].

Organic semiconductors can be regulated in four aspects: molecular design, crystal regulation, doping engineering and interface engineering. A D-A structure molecule can be designed by introducing rigid conjugate units and side chain engineering to adjust the band gap, improve mobility and crystallinity [2]. Crystallization control can use thermal annealing technology to promote the quality of single crystal, epitaxial growth can improve the quality of single crystal, and self-assembly and confinement crystallization can improve the orientation [3]. Doping engineering can regulate charge density and energy level structure through p/n type doping and energy transfer [7]. Interface engineering can use metal oxide to adjust charge injections and heterojunction to optimize carrier separation [3].

Excitons in organic materials exist in bound states, including singlet and triplet states. Singlet excitons and triplet excitons are exciting states formed by the binding of electron-hole pairs through Coulomb interaction after electrons are excited. Singlet states tend to emit fluorescence rapidly, while triplet states usually have lower energy, longer lifetime, phosphorescence, but limited transition. However, the proportion of triplet excitons is as high as 65%, which has an important impact on the device performance [3].

In recent years, studies have shown that low-energy excitons can be effectively utilized and the luminous efficiency and photoelectric conversion efficiency can be improved through the triplet to triplet annihilation (TTA) up conversion mechanism, which provides an important way to break through the traditional efficiency limit [3]. The performance of an organic molecule can be evaluated by mobility, switching ratio, external quantum efficiency, power conversion efficiency, and luminous quantum efficiency.

3. Performance Comparison

From a broader perspective, the development path of semiconductor optoelectronic materials usually follows the co-evolution law of "material design structure optimization device integration" [4]. Compared with inorganic semiconductors, organic semiconductors have advantages in structural tunability, but there are still gaps in carrier transport and stability. Therefore, it is necessary to carry out comprehensive optimization through structural design and device engineering.

The functional differences of typical organic semiconductor materials can be seen in Table 1. The five types of organic semiconductors have their own advantages and disadvantages. The differences in material properties are mainly divided into three aspects: mobility, luminescent properties and exciton radiation. Mobility mainly comes from strong π stacking and molecular planarity. Exciton quenching and aggregation induced effects are the main factors affecting the luminescent properties. High mobility is usually in contradiction with the close packing of molecules and the increase of exciton non radiative recombination. So, this is also the biggest challenge at present [5]. Organic single crystal heterojunction can realize bipolar transmission and improve charge separation efficiency [3]. At the same time, the interface electric field can promote exciton dissociation, thereby improving photoelectric conversion efficiency.

It is worth noting that in the inorganic semiconductor system, the carrier separation efficiency can be significantly improved, and the recombination loss can be reduced by constructing the heterojunction structure (such as TiO₂/bdc), so as to improve the device performance [7]. This idea can also be borrowed from the organic semiconductor system, that is, through the design of organic/organic or organic/inorganic heterojunction structure, to realize the collaborative optimization of charge transport and exciton behavior.

Table 1. Performance comparison of various organic semiconductors and inorganic semiconductors

Organic semiconductor category	Advantage	Defect
DPP-type materials	High stability, low cost, easy access	Average mobility and luminescent properties
Hmeoscs materials	High mobility, high luminescent properties	There are certain constraints, which is difficult to use on a large scale
Non-fullerene receptor	High mobility, Excellent photoelectric performance	High cost, difficult to popularize
Organic single-crystal heterojunction	Bipolar transmission, high charge separation efficiency	Difficult preparation and high regulatory requirements
TiO ₂ /BDD system	Improving carrier separation efficiency	Complex structure

4. Control Methods of Organic Semiconductors

Molecular design is the basis of realizing high mobility organic semiconductors. By adjusting the molecular conjugation length, introducing D-A structure and optimizing the side chain structure, the energy level structure and intermolecular interaction can be regulated at the molecular level. Taking DPP based system as an example, the pdppf-dtt composed of furan-flanked DPP and DTT, achieves a mobility of 3.56 cm²/V·s in top-contact/bottom gate transistors [2]. The mobility range of high mobility light-emitting organic semiconductors (hmeoscs) in OFET can cover 10⁻⁵-10 cm²/V·s, indicating that the charge transport and photoelectric response window can be improved simultaneously through the collaborative design of rigid conjugate skeleton and receptor unit [1,4].

The crystal structure directly determines the charge transfer path of organic semiconductors. The crystallinity and orientation of the materials can be significantly improved by thermal annealing, solution shear, epitaxial growth and confined self-assembly. The literature shows that the mobility of dif tes ADT 2D single crystal can be increased to 8.6 cm²/V·s by using anchored seed epitaxy; The average mobility of c8-btbt single crystal array obtained by microspating in air sublimation method

is 6.28 cm²/V·s, and the highest is 9.67 cm²/V·s; The mobility of flexible dpp-dtt transistors is 9.1 cm²/V·s with cross-linked PVA dielectric layer, and the working voltage is less than 1 V [8]. These results indicate that the construction of high-quality single crystal and highly oriented films is the key path to improving the mobility [2,8].

Doping is an important means to control the electrical and optical properties of organic semiconductors. The carrier concentration, energy level structure and interface contact resistance can be adjusted by p-type or n-type molecular doping; In the host guest doping system, the effective distance of Förster energy transfer is usually 3-10 nm, while Dexter energy transfer mainly occurs in the range of 1-2 nm. Therefore, the doping ratio and molecular spacing will directly affect the luminescence color, fluorescence lifetime, and carrier transport [9]. In addition, in terms of exciton regulation, triplet-triplet annihilation (TTA) can transform two low-energy triplet states into a high-energy singlet state, and its internal conversion efficiency can theoretically reach 62.5%, so it has important application potential in OLED and OPV [3,10].

At the device level, the interface properties have a decisive impact on the performance. By introducing metal oxide interface layers or constructing organic/organic and organic/inorganic heterostructures, charge injection efficiency can be improved, and charge separation can be promoted. The nanostructured WO_x/MoO_x interface layer can improve the hole or electron injection efficiency by adjusting the work function and interface energy level, while the low-dimensional organic single crystal heterostructure can optimize exciton dissociation and bipolar transmission by using the interface with fewer defects and more controllable energy band arrangement [8, 11]. In addition, TiO₂/BDD heterojunction also shows that the light response and environmental stability can be improved through the coordination of energy band matching and interface electric field, which provides a reference for the interface engineering of organic semiconductors [7].

5. Performance Optimization of Organic Semiconductor Devices

Organic semiconductors have been used in many fields, such as organic field effect transistors (OFETs). Their performance is closely related to the material structure, interface characteristics and device configuration. Carrier mobility is the core index for evaluating material properties [2]. High mobility organic semiconductors can significantly improve the switching speed and operating frequency of devices and are the key materials of flexible integrated circuits. The results show that the grain boundary defects can be effectively reduced by improving the crystallinity and molecular orientation of the materials, so as to improve the charge transfer efficiency [8]. For example, the mobility of DPP polymer pdppf-dtt in top contact/bottom gate transistors can reach 3.56 cm²/V·s; The mobility of dif-tes ADT two-dimensional organic single crystal was increased to 8.6 cm²/V·s after the growth of anchored seed epitaxy; The average mobility of c8-btbt single crystal array device is 6.28 cm²/V·s, and the highest is 9.67 cm²/V·s [2]. In addition, the ultra-low voltage flexible OTFT device based on dpp-dtt can still achieve a mobility of 9.1 cm²/V·s and a subthreshold swing of less than 100 mV/DEC when the operating voltage is less than 1 V, indicating that the material crystallization control and device structure optimization play a decisive role in improving the performance of OFET [2].

In organic light-emitting devices, the matching of charge transport and exciton recombination process has a decisive impact on the efficiency of the device. High mobility is conducive to rapid carrier injection and transport, thereby improving the charge recombination efficiency. However, due to the high proportion of triplet excitons in organic materials, their non-radiative recombination will significantly reduce the luminous efficiency [10]. In recent years, by introducing the triplet-triplet annihilation (TTA) up conversion mechanism, it can effectively use low-energy excitons to improve the luminous efficiency and break through the traditional efficiency limit; Relevant reviews point out that the internal conversion efficiency of this mechanism can theoretically reach 62.5% [3]. At the same time, the study of high mobility luminescent materials (hmeoscs) shows that the mobility of organic semiconductors in OFET has gradually expanded from 10⁻⁵-10 cm²/V·s to a higher level,

and after the collaborative optimization of energy level and luminescent properties, the external quantum efficiency (EQE) of OLED has reached about 40%, which provides an important basis for achieving high mobility and high luminescent efficiency [1]. In addition, the charge balance and radiation recombination efficiency of the light-emitting layer can be further improved by using molecular doping, energy-saving arrangement and carrier injection [9].

In organic photovoltaic devices, photoelectric conversion efficiency mainly depends on the process of exciton separation and carrier transport. Non fullerene receptor materials have made significant progress in recent years due to their excellent light absorption properties and energy level matching advantages [5]. Research shows that with the collaborative development of high mobility organic semiconductors and device engineering, the photoelectric conversion efficiency (PCE) of OPV devices has exceeded 20% [1]. In addition, triplet exciton management also provides a new idea for further improving photovoltaic efficiency; Relevant studies have pointed out that triplet triplet annihilation upconversion and singlet splitting are considered to be important ways to break through the Shockley-Queisser limit of single junction solar cells [10]. By optimizing the molecular structure, reducing the non radiation voltage loss and constructing a reasonable donor acceptor heterojunction structure, the charge separation efficiency and carrier transport capacity can be effectively improved, so as to achieve higher short-circuit current and filling factor [1,8].

In addition to traditional devices, multilayer organic semiconductor structures have been used in nerve stimulator devices to regulate biological tissues by converting optical signals into electrical signals; Previous studies have shown that such devices can effectively stimulate retinal ganglion cells in working areas as small as 50 μm in diameter [5]. In addition, using the advantages of inorganic semiconductor heterojunction (such as TiO_2/BDD system) in carrier separation and stability for reference, introducing it into the design of organic/inorganic composite devices is expected to further improve the device performance and environmental stability [5].

6. Limitations and Improvements

Although high mobility organic semiconductors have made significant progress, they still face a number of key challenges. First of all, the structural contradiction between mobility and luminous efficiency has not been fundamentally solved. Its essence lies in the competitive relationship between molecular stacking and exciton dynamics [11]. Secondly, the crystallization process of organic semiconductors is highly sensitive to environmental conditions and prone to defects, which affect the stability of devices [2]. In addition, organic materials generally have the problem of poor environmental stability and are easily affected by oxygen and moisture. Finally, the development of n-type organic semiconductors lags behind, which limits the further improvement of device performance [1].

In view of the above problems, four aspects can be improved. The asymmetric D-A molecular structure is developed to realize the coordinated regulation of charge transport and exciton behavior; A multi-scale crystallization control strategy was established to realize the orderly control from molecular stacking to macro orientation; Optimize interface engineering and doping technology to improve charge injection and transmission efficiency; Develop multi-functional integrated material system to achieve synchronous improvement of mobility, luminous efficiency and stability [1,8,9].

Develop multi-functional integrated material system to achieve collaborative performance improvement. At the same time, the advantages of inorganic semiconductor heterojunction (such as TiO_2/BDD system) in high stability and efficient carrier separation can be used for reference, and it can be introduced into the design of organic optoelectronic devices to improve the environmental stability and photoelectric conversion efficiency of devices [7]. In addition, future research should also strengthen the regulation of exciton dynamics, such as improving energy utilization efficiency through triplet state management and TTA upconversion mechanism [2,6]. At the same time, the mature experience of inorganic semiconductor material system in energy band engineering and device

structure design can be used for reference to realize the systematic improvement of organic semiconductor from material design to device optimization [4].

7. Conclusion

This paper focus on the molecular design, crystal regulation and photoelectric performance regulation mechanism of high mobility organic semiconductors and reveals the intrinsic coupling relationship between carrier transport and exciton dynamics. The results show that the performance improvement of organic semiconductors is not a single parameter optimization, but a multi-scale synergy of molecular structure, aggregation structure and interface physical processes.

It is further pointed out that the structural contradiction between high mobility and high luminous efficiency stems from the non radiative recombination enhancement induced by strong $\pi - \pi$ stacking, which constitutes the core bottleneck of the current organic optoelectronic material design. Therefore, the key to break through the traditional "mobility luminous efficiency" trade-off relationship is to build a new molecular system and aggregation structure with both ordered charge transfer channels and controlled exciton behavior.

Based on the above understanding, in the future, it should focus on the following four aspects to develop D – a molecular structures with asymmetry and fine-tuning ability of energy levels, so as to realize the collaborative optimization of charge transport and exciton management, establish multi-scale crystallization control strategies, realize the orderly control from molecular accumulation to macro direction, introduce interface engineering and controllable doping mechanism, build efficient charge injection and transmission networks, and explore integrated functional material systems to meet the requirements of high mobility, high luminous efficiency and environmental stability. In recent years, the development of exciton regulation mechanism (such as TTA up conversion) provides a new idea for improving the efficiency of organic optoelectronic devices.

In general, this study provides a new theoretical framework for the design of high-performance organic semiconductor materials. With the further integration of molecular engineering and device physics, organic optoelectronic devices are expected to break through the existing performance limits and achieve more extensive applications in the fields of flexible electronics, wearable systems and large-area low-cost manufacturing. In addition, successful experience of inorganic semiconductor heterojunction (such as TiO₂/BDD) in carrier regulation will provide new design ideas and development direction for organic semiconductor system.

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