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Charge Transport Mechanism of Organic Semiconductors Based on Molecular Dynamics Simulation

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Abstract: The aim of this paper is to investigate the charge transport mechanism in organic semiconductors based on molecular dynamics simulation. Molecular dynamics simulation, as an effective computational method, can reveal the microscopic mechanism of charge transport in organic semiconductors. The basic principles and methods of molecular dynamics simulation will be introduced in the paper, and its application in studying charge transport in organic semiconductors will be discussed. Through the simulation analysis, the effects of key parameters such as intermolecular interactions, carrier mobility and electron transport on the performance of organic semiconductor devices can be revealed, providing guidance for the design and optimization of organic semiconductor devices.

Keywords: Molecular dynamics, Organic semiconductors, Charge transport.

1. Research background

Charge transfer (CT) is an important research topic spanning several fields such as physics, chemistry, materials science, biology and information science, and has received much attention in recent years [1]. By applying charge transfer theory and related techniques, many difficult phenomena can be better explained.

Marcus's theory has played an important role in charge transfer between molecules and for his outstanding contribution he was awarded the Nobel Prize in Chemistry in 1992[1]. After unremitting efforts, Marcus theory has become an important theoretical framework which not only supports the related semiclassical theories, but also provides important theoretical support for the development of quantum chemistry. Usually, due to the difference in the strength of the electro-phonon coupling, the charge transport mechanisms in organic crystals are mainly classified into three categories: the energy band model, the polariton model, and the hopping model.

2. Overview of Organic Semiconductors

Organic semiconductors are materials made up of specific organic molecules that have excellent electrical conductivity and can transmit current to electronic devices, making them insulators of electrons. Organic semiconductors can be broadly classified into three categories: organic light-emitting diodes, organic solar cells, and organic field-effect transistors [4]. In recent years, organic electronic devices represented by organic field effect transistors have received increasing attention. Although devices based on such materials have characteristics such as simple preparation process and bendability, their carrier mobility is much lower than that of inorganic materials. Designing organic semiconductor materials with high mobility has been a cutting-edge topic in the field of microelectronics, and the charge transport mechanism of organic semiconductors is of great importance as a theoretical basis for material design.

2.1. Organic Light Emitting Diode (OLED)

Organic LED is an electroluminescent device, which operates in four steps: (1) the power supply is turned on, electrons are injected from the cathode into the lowest unoccupied orbital (LUMO) of the organic semiconductor while holes are injected from the anode into the highest occupied orbital (HOMO) of the organic semiconductor, and the two kinds of carriers are transported when subjected to a certain bias; (2) the two types of carriers are moved in the composite region, which forms the exciton of a single or triple-wire state; (3) the exciton is subjected to diffusive transport; and (4) the exciton decays the energy in a radiated or radiation-free form[5].

Figure 1. Organic Light Emitting Diode

2.2. Organic Solar Cell (OSC)

Organic solar cells are a highly efficient photovoltaic technology that achieves absorption and conversion of solar radiation in four steps[6]. It works as follows: (1) when exposed to light, the organic semiconductor material absorbs photons and converts them into excitons; (2) the excitons are transported and decay in the form of radiation (light) or no radiation (heat); (3) the excitons are separated at the organic interface and free holes and electrons are produced; and (4) after the holes and electrons are separated they are transported to the anode and cathode, resulting in the generation of an electric current.

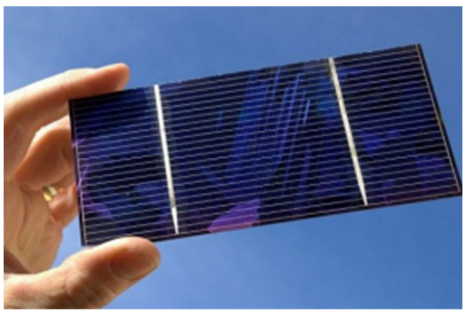

Figure 2. Organic solar cell

2.3. Organic Field Effect Transistor (OFET)

An organic field effect transistor is a field effect transistor that uses an organic semiconductor as the active layer, the source injects charge into the conducting channel, the drain collects the charge that flows out of the conducting channel, and the gate enables the organic semiconductor to generate charge at the interface with the insulating layer to form a conducting channel. When the gate voltage V>0, the LUMO and HOMO energy levels of the organic semiconductor material move downward, then the electrode injects electrons into the LUMO, applying a certain source-drain voltage, the organic material transmits the electrons; when the gate voltage V<0, the organic semiconductor layer of the LUMO and the HOMO energy levels move upward, the electrode injects holes into the HOMO, applying a certain source-drain voltage, then the organic material transmits holes , forming a current.

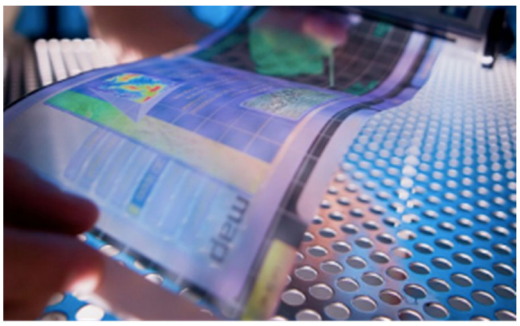

Figure 3. Display driven by organic field effect transistors

3. Molecular Dynamics Simulation

3.1. Introduction to Molecular Dynamics

Molecular dynamics simulation is a method of modelling the behaviour of an atomic or molecular system by numerically integrating Newton's equations of motion. It is based on the principles of Newtonian mechanics and simulates the time evolution of the system by calculating the forces and accelerations of the particles [7]. In molecular dynamics simulations, the positions and velocities of atoms or molecules are updated by solving the equations of motion to obtain the state of the system at different points in time.

Molecular dynamics simulations can model the behaviour of a system under different temperatures, pressures and chemical environments, and they require the definition of the initial state of the system, including the initial positions and velocities of the atoms or molecules, as well as the force field parameters [8,9]. Force fields are mathematical functions that describe the interactions between molecules, and different force field models can be chosen depending on the specific problem being studied. Commonly used force fields include classical force fields and quantum force fields. The classical force field model is based on empirical parameters and is suitable for describing the mechanical properties and interactions of molecules, while the quantum force field model is based on the principles of quantum mechanics and is suitable for describing the electronic structure and charge distribution of atoms and molecules.

3.2. Simulation process

3.2.1. Constructing the initial model

The success of an MD simulation depends on creating an effective initial model. If the initial model is not appropriate, it will not only delay the time for the system to reach a stable equilibrium, but also may lead to serious deviation of the simulation results, or even failure of normal operation. In general, in order to obtain the best initial model, we need to conduct a thorough research and develop the best configuration based on actual test data. To ensure the reliability and stability of the simulation programme, overly complex structures should be avoided as much as possible. The forces on the atoms in the MD are determined by their interaction potentials, but when they deviate from their equilibrium positions, or when they are too close to each other, the forces on the atoms increase dramatically, which will result in the simulation programme not being able to accurately track the motions of the atoms, which will make the data of the atoms lost or calculate physical quantities (e.g., system energy, temperature, and pressure, etc.) beyond what is expected. After completing the initial model construction, the initial energy consumption of the system can be effectively reduced by taking effective energy minimisation measures. Although energy minimisation optimisation can be effective up to a certain point, it still does not solve the problem completely, so it is important to keep in mind that the actual physical structure prevails when constructing the initial model as a way of ensuring that the model is reliable and operable.

3.2.2. Numerical integration of the equations of motion

With MD simulations, we can accurately determine the velocity v_i, position γ_i, and forces on each particle F_i and use this information as a basis for better predicting the characteristics of the next time step. During this motion, each particle motion can be characterised by Newton's second law:

$$m_i \frac{d^2 r_i}{di^2} = \sum_{\substack{i=1 \\ j=1}}^{N} F_{ij} \ (i = 1,2,3, \cdots N) \qquad (1)$$

Where m_i is the mass of the i-th particle, N is the total number of particles in the system, and F_{ij} is the force of the j-th particle acting on the i-th particle. By numerically integrating the equations of motion, the value of its potential energy can be estimated by using the time step of its previous step as a reference. Numerical integration methods for the equations of motion can be classified into Verlet's algorithm, Frog Hopper's algorithm, and Predictive Correction algorithm[9].

3.2.3. Analogue parameter setting

Successful implementation of MD simulations depends not only on the establishment of a reasonable initial model and the precise selection of the optimal numerical integration algorithm, but also on the precise tuning of a number of key parameters to ensure the validity and accuracy of the simulation.

(1) Initial speed: Before the MD simulation begins, the

initial speed that needs to be assumed for the simulated system. By adjusting the initial running rate of the system, the time for it to achieve stable operation can be greatly reduced. At the same time, its system temperature is also affected by the particle running rate, and usually an initial rate as close to the real temperature should be set for the system as possible.

(2) Potential Functions: Potential functions (or energy functions) are mathematical functions that describe the interactions between molecules. These functions are used to calculate the interaction energies between molecules in a simulated system and thus determine the motion and behaviour of the molecules. In organic matter, the parameter describing the interaction between them is often referred to as the force field. Different potential functions take into account different types of interactions, including bond energies, angular energies, van der Waals forces, Coulomb interactions, and so on. For the simulation of complex systems, a variety of hybrid potential functions can be chosen to describe the simulated system.

(3) Boundary conditions: when performing molecular dynamics simulations, some boundary conditions are needed to simulate the interaction of the system with the outside world, this is because in practical calculations, molecular dynamics methods are limited by finite observation time and finite system size, and the way to overcome this difficulty is to impose periodic boundary conditions [11]. The periodic boundary condition is one of the most widely used boundary conditions in molecular dynamics simulations, in which the simulated system is considered to repeat infinitely periodically, like an infinitely large crystal. When a molecule leaves one side of a simulation box, it re-enters from the opposite side to maintain the continuity of the system, which avoids the influence of surface effects on the simulation results. In addition to the periodic boundary conditions, there are also fixed boundary conditions and free boundary conditions. Fixed boundary conditions that the boundary of the simulation unit is fixed, the atomic coordinates can not exceed the specified boundary range. The free boundary condition means that the boundary of the simulation cell is unrestricted and the atoms are allowed to move freely.

(4) System of systems: under certain macroscopic conditions, a large number of properties and structures are identical, in various states of motion, the collection of independent systems, all known as statistical system of systems. The system is a basic concept introduced when describing the statistical regularity of the thermodynamic system by statistical method, and the system is a kind of expression of statistical theory. The choice of the system is based on the needs of the simulation to a reasonable choice. Some common types of system are: NVT (regular system, which fixes the number of particles, volume and temperature), NPT (isothermal and isobaric system, which fixes the number of particles, temperature and pressure), and NVE (micro-regular system, which fixes the number of particles, volume and total energy) [12].

(5) Time step: In MD simulation, the interval between numerical integration of particle position and velocity is the time step. The use of shorter time steps can significantly improve the accuracy of the computation, but at the same time it may lead to a large amount of computational resources being wasted. In order to obtain the best simulation results, it is often necessary to perform an accurate test of the time step to determine the optimal time step value.

(6) Heat bath: Its function is to regulate the temperature of the system, and it can help to control the operation of the system so as to achieve the best results.

4. Conclusion

Charge mechanism transport studies of organic semiconductors based on molecular dynamics simulations provide insight into the charge transport behaviour in organic semiconductor materials. Through simulation analysis, the microscopic mechanisms of charge transport in organic semiconductor materials can be revealed, including the influence of key parameters such as charge migration paths, carrier mobility, and interfacial effects. This information is important for the design and optimisation of organic semiconductor devices.

However, there are some limitations of molecular dynamics simulations, such as high computational cost and limited time scale. Future studies can combine other computational methods and experimental techniques to further improve the understanding and prediction of charge transport mechanisms in organic semiconductors.

In summary, organic semiconductor charge mechanism transport studies based on molecular dynamics simulations provide a powerful tool for in-depth understanding of the charge transport behaviour of organic semiconductor materials, and provide a theoretical basis and guidance for the design and optimization of organic semiconductor devices.

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