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Review

A theoretical approach for simulations of anisotropic charge carrier mobility in organic single crystal semiconductors

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ABSTRACT

Charge carrier mobility is important for organic semiconductor materials and mainly determines their device performance. Thereby how to improve carrier mobility lies at the heart of the development of organic electronics. Theoretical predictions and simulations can provide guidelines towards the possible realization of high mobility and the design of highly functional semiconductor materials and thus can help to achieve further discoveries in the field. In this paper, we review a recently proposed theoretical method (an effective one-dimensional diffusion equation model) which presents the first analytical expression for angular resolution anisotropic mobility of organic single crystal semiconductors. The method encompasses the hopping mechanism, Marcus-Hush theory and first-principles calculations and is suitable to characterizing the anisotropic transport behaviors in organic single crystal semiconductors as well as to studying the property-structure relationship in semiconductor materials. Illustration of applications of the method demonstrated its capabilities in description and understanding of the transport of charges, correct prediction of angular resolution anisotropic mobility, and assist in the design of n-type and p-type organic electronic materials.

1. Introduction

Organic semiconductors, generally categorized into small molecules (or oligomers) and polymers, promise the advent of fully flexible devices and thus have great potential in the applied research field [1], owing to that organic semiconductors have advantages such as chemical versatility, easy processibility, flexibility, low cost and low weight. Because the performance of all organic electronics devices critically depends on the transport efficiency of charge carriers (electrons or/and holes) within organic materials, characterization of materials' ability to transport charges is therefore important and essential. The charge carrier mobility with a unit of $cm^2/V{\cdot}s$ (it means velocity over electric field) is the key quantity to characterize a material's charge transport ability. However, due to the localization of electronic states on individual molecules or segments of molecules, charge carrier mobilities of organic semiconductors are usually several orders of magnitude lower than those of (silicon-based) inorganic materials [2]. Further advance in organic electronics technology should overcome the challenges arising from the low charge carrier mobility of organic materials and from our limited knowledge of structure-property relationship in organic semiconductors, for which, high-quality organic single crystals can offer higher carrier mobilities and exciton recombination yields and are thus expected to be good candidates [3].

The charge carrier mobility of organic semiconductors can be measured by various widely known methods including the time of flight (TOF), the field-effect transistors (FETs), and the diodes. For example, with the TOF technique [4], Kepler [5] and Leblanc [6] conducted the first measurement of charge mobilities in organic materials. Theoretically, several models, such as band model [4] and hopping model [7], etc., have been proposed and applied to explain the intrinsic carrier transport behaviors observed in organic FETs experiments.

Organic single crystals are those of highly conjugated organic molecules with well-defined morphology and high crystallinity where highly conjugated organic molecules offer fast charge carrier transport, rapid optoelectric response and reliable exciton manipulation. The electronic properties of organic single crystals strongly depend on the nature of molecules, their conjugations and conformations, their mutual distance and the orientation between adjacent molecules. As such, variations of intermolecular distances and conformation disturb the conjugation and perturb the delocalization of the charges [8]. Due to

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molecules of organic oligomers are generally aggregated by weak van der Waals forces which cause the more flexibility of molecules, hence, for most conjugated organic oligomers, the intermolecular electronic coupling (or the electron transfer integral) is weaker than the electron-vibration coupling (or the reorganization energy). Such relatively weak intermolecular interactions mean that the carrier transport, at room temperature or higher, is best described by hopping model rather than the band model. The band model is well established for inorganic covalently bonded materials and thus can rationally describe the transport behavior for well-ordered organic crystals at low temperatures, but it is not suitable for organic materials at high temperature. At high temperatures (e.g., ≥ room temperature), it is often assumed that the charge is localized due to the thermal disorders of molecules and that charge transport occurs through thermally activated hopping [9]. In such hopping model, the intrinsic charge transport rates of electrons or holes are determined by two parameters: the intermolecular electronic coupling (or the electron transfer integral) and the inner and outer reorganization energy. Note here that the two parameters are extremely dependent on the packing of the organic molecules and therefore the packing motifs, e.g., herringbone packing (edge-to-face), face-to-face packing, lamellar packing (1D or 2D π-stacking), etc., are very important for obtaining high mobility. Usually, larger transfer integral and smaller reorganization energy will give higher mobility.

Organic FETs (OFETs) are devices consisting of an organic semiconductor layer, a gate insulator layer, and three terminals (drain, source and gate electrodes) [10]. OFETs were firstly fabricated in 1980s using conjugated polymers or small molecules [11–14] and significant progress has been made in the performance of OFETs. Recently, the fabrication methods of OFETs based on single crystals and by soft-contact lamination have allowed for the direct measurement of carrier mobility at different transport direction in organic single crystals. The experiments with these fabrication methods have observed the anisotropic behavior of charge transport in organic single crystals and further revealed that the mobility anisotropy dependent on crystal axes is an intrinsic and common property of organic single crystals. For example, with the reversible sticking elastomer stamp, Sundar et al. explored the dependence of the field-effect mobility on the orientation of the transistor channel (or conducting channel) relative to the crystallographic axes and firstly observed a strong anisotropy of the field effect mobility within the *a*-*b* plane of single crystals of rubrene [15]. Later, with the prepatterned fan-shaped electrodes, Lee et al. succeeded in measuring the mobility in the *a*-*b* plane of a more fragile single crystal pentacene at intervals of 30° in angle [16]. Their room-temperature mobility shows the anisotropic behavior and they also imply that the mobility anisotropy reflects the intrinsic property of single crystal pentacene. From then, experimental studies based on the single crystal organic FET (SCOFET) continuously observed and showed the anisotropy of charge transfer in tetracene [17], dinaphtho [2,3-b:2′,3′-*f*]thiopheno [3,2-*b*] thiophenes (DNTT) [18], 4-hydroxy-cyanobenzene (4HCB) [19], b-tetraethyl(triisopropylsilylethynyl)pentacene (BTE-TIPS-PEN) [20], 4,4′-bis((E)-2- (naphthalen-2-yl)vinyl)-1,1′-biphenyl (BNVBP) [21], etc. Studies using other experimental techniques also found the anisotropic charge transport in naphthalene [22], and 8-hexyl-thiophene $(3HT)_8$ [8], etc. In addition, the angular distribution of the charge-carrier mobility usually exhibits a cocoon-like shape.

"Much of our understanding of the intrinsic charge transport properties in organic semiconductors originates from our studies of single crystals" [23]. Due to the highly ordered structures, minimized charge traps and absence of grain boundaries, organic single crystals are ideal materials for examining the efficacy of charge transport along different molecular orientations, and the development in fabrication of SCOFETs has realized the direct measurement of intrinsic charge transport, in particular the anisotropic charge transport, in organic single crystals. On the other hand, successful fabrication of SCOFETs has also offered the interesting and unique opportunity for revealing the relationship between the microscopic molecular packing and macroscopic anisotropic charge transport of the crystal organic materials, due to the origin of the anisotropic mobility arises from the sensitivity of electronic couplings to molecular packing, as a result from that the electronic couplings between adjacent molecules are closely related to the relative positions (including spacing and relative orientations) of interacting molecules. The above two points in relation to the inherent anisotropic behaviors of charge transfer in organic single crystals are very important for understanding the new organic materials at the macroscopic level and for facilitating the design and application of the next-generation devices, which therefore have attracted the world's attention since the development of the SCOFET techniques in 2004. For instance, since mobility of organic crystals is intimately related to electron cloud on molecule and the electron cloud splitting with its neighbor molecules, thus, how to achieve the largest orbital overlaps between adjacent molecules in organic crystal structures should be critical for designing and developing high-mobility organic semiconductors.

With the continuous development of the SCOFET technique, it becomes more and more evident that the electrical characteristics, charge carrier field-effect mobility, current on/off ratio, and other features of the highly–conjugated organic molecular systems in SCOFETs are strongly dependent on the organization of the conjugated molecules. To better understand the transport mechanism, it is necessary to gain knowledge of the anisotropic transport behaviors of organic molecular crystals that is closely related to stacking motifs and molecular structures. Further, understanding the anisotropic mobility can assist in controlling the directions of transistor channel relative to reference direction of molecular crystal to obtain the highest charge mobility. To date, both the theoreticians and experimentalists are facing this challenging task to understand the mechanism of the anisotropic charge carrier transport and the interplay between the crystallographic structure and the charge transport characteristics, e.g., along the π–π stacking direction, or the herringbone interaction direction, or along the backbones of conjugated molecules in a large molecular crystal, etc. However, before the publication of Ref. [24], a theoretical predication of the anisotropic charge transport in an analytical functional form cannot be found for organic single crystal semiconductors.

In this review article, special attentions are given to a theoretical method, developed in Han's laboratory, for carrier mobility calculations for organic semiconductor materials [24]. This method successfully presents the first analytical expression for the angular distributions of charge-carrier mobility for organic crystals. The fundamental merits of the method are summarized as follows, simplicity and ease implementation, ability to give the analytical expression of the mobility orientation function μ_Φ that shows the mobility in a specific conducting direction on a specific surface of the organic crystals, capability to well simulate and reproduce experimental measurements, good predication for charge carrier mobility for organic crystal materials, and good ability to offer clear physical insight. It is hoped that the development of this method will contribute to a better understanding of property-structure relationship of organic crystal materials in a way that will facilitate the design of new materials and devices to achieve the desired performance.

The following portion introduces the above-mentioned theoretical method for the simulation and predication of charge carrier mobility in organic semiconductor materials and describes the way to obtain the mobility orientation function μ_Φ as well as the method to obtain the electronic couplings and the reorganization energy. Then, Illustrations of this calculation method in simulating and predicting the characteristics of charge carrier mobility in both p-type and n-type organic semiconductor materials are given and shown in the subsequent portion. The last portion summarizes with an outlook.