



Review

Design and elaboration of organic molecules for high field-effect-mobility semiconductors



Kazuo Takimiya*, Masahiro Nakano, Hiroyoshi Sugino, Itaru Osaka

RIKEN Center for Emergent Matter Science, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

ARTICLE INFO

Article history:

Received 7 December 2015

Received in revised form 5 February 2016

Accepted 19 February 2016

Available online 21 March 2016

Keywords:

Organic semiconductor

Organic field-effect transistor

High mobility

Molecular design

Electronic structure

ABSTRACT

In this article, we focus on several high-mobility organic semiconductors so far reported, such as acenes, heteroacenes, and rylene diimides, in order to extract molecular and supramolecular factors, including molecular size, manner of π -extension, heteroatom, molecular shape, and substituent, which would enhance our understanding of the design strategy for the synthesis of molecules for high field-effect-mobility semiconductors. After performing a detailed inspection of these organic semiconductors, we arrive at the conclusion that the construction of a two-dimensional (2D) electronic structure with large orbital overlaps in the solid state is the key. This can be realized by tuning these molecular factors; for example, the use of linearly π -extended systems with fused aromatic ring structures, heteroatom incorporation, and the use of suitable substituents for 2D packing, such as herringbone or 2D bricklayer packing.

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1. Introduction

Optoelectronic devices based on organic π -conjugated molecules, often called organic semiconductors, have emerged in the 1980s as a technology that can be potentially utilized in practical applications, such as light emission (organic light-emitting diode, OLED), switching (organic field-effect transistor, OFET), and photovoltaic conversion (organic photovoltaics, OPVs) [1,2].

Although these organic devices have several advantages, such as light weight, flexibility, low production cost, and low environmental impact of the production process, their performances have been generally inferior to those of corresponding devices based on inorganic semiconductors. In the last two decades, intensive efforts have been made for the development of superior organic semiconductors and the betterment of device fabrication techniques. Among the several functions required for organic semiconductors in the devices, carrier transport is the most basic and important one, and therefore, the carrier mobility (μ) of organic semiconductors is regarded as a key property for determining device performance. For this reason, to experimentally evaluate carrier

* Corresponding author.

E-mail address: takimiya@riken.jp (K. Takimiya).

mobility, a metric that measures how quickly carriers (holes or electrons) can move under an electric field in an organic semiconductor and the pursuit of high-mobility organic materials are pivotal issues in scientific communities related to materials chemistry and physics.

OFETs that have emerged in the 1980s can afford a relatively easy method for the evaluation of mobility in the thin-film state of organic semiconductors [3]. In addition, OFETs have been regarded as an attractive alternative for amorphous silicon-based thin-film transistors [4]. Since then, numerous organic semiconductors have been synthesized and examined as the active materials in OFETs [5]. As a result, several superior organic semiconductors that are based on both small molecules and conjugated polymers have been developed, and the relationship between the molecular structure and the transport property of organic semiconductors has been discussed in an effort to establish a design strategy for high-performance OFETs.

2. Molecular semiconductors

In order to clarify structure-property relationships in organic semiconductors, not only the molecular structure but also the solid-state structure of a given organic semiconductor is indispensable, because mobility is not a molecular property but a property that is deeply related to the nature of a molecular solid [6]. In this regard, molecular structures with exact atomic coordinates can be experimentally determined by single-crystal X-ray analysis, in sharp contrast to semiconducting polymers that have a certain molecular weight distribution and lack quantitative information of the atomic coordinates in the condensed phases. The exactly determined atomic coordinates of semiconducting molecules in the solid state can be utilized for the estimation of the electronic structure. In fact, this approach has been quite effective to correlate the molecular/solid-state structures to the transport properties, including the mobility obtained from OFETs. Although there are arguments on the effect of the grain boundaries between crystallites in the thin-film state, the electronic structure based on the single-crystal X-ray analysis can be nicely correlated to the mobility in the thin-film transistor settings of many representative high-mobility organic semiconductors.

In this article, we first examine several representative semiconducting molecular systems and then focus on such molecular factors as molecular size, manner of π -extension, heteroatom, molecular shape, and substituent, which should be optimized for realizing high-mobility organic semiconductors. Furthermore, the packing structures of such molecular systems are discussed on the basis of reported X-ray crystal structures aided by theoretical calculations of intermolecular orbital overlaps (transfer integrals). By performing these analyses, molecular and supramolecular factors are extracted. Finally, molecular design strategies for realizing better organic semiconductors would be created.

3. Molecular and crystal structures: from the point of view of organic semiconductors

In general, organic semiconductors consist of π -conjugated systems, and most of them contain several aromatic and/or heteroaromatic ring structures, as represented by oligoacenes and oligothiophenes. The electronic structure of organic semiconductors is determined by the molecular size and shape, the extent of π -conjugation, the substituent, and so on. Recent rapid progress in computational chemistry has enabled us to predict the molecular electronic structures and properties with certain reliability before the actual synthesis of molecules. At the same time, such computation helps us understand better the molecular electronic structures of semiconducting molecules.

Organic semiconducting molecules are utilized as a semiconducting layer in the solid state, often in the thin-film state. In such a condensed phase, each molecule interacts with neighboring molecules via weak and often anisotropic intermolecular interactions that make each molecular solid quite different from others. Although the electronic structure of a molecular solid is largely determined by the intermolecular interaction in the solid state, the molecular electronic structure also plays an important role. Thus, for the design of better organic semiconductors, one should pay attention to the electronic structures at both molecular and solid-state levels.

The carrier transport mechanism in organic molecular solids is still controversial. Many approaches from both experimental [7] and theoretical points of view [8] have been carried out, and several transport models, such as the hopping and band-like models, have been proposed. Among them, the hopping model has been widely accepted as an appropriate mechanism describing carrier transport in molecular solids. At the same time, the model is intuitively acceptable for organic chemists who recognize molecules as an isolated entity. According to the Marcus hopping theory [9], which has reasonably explained the transport characteristics of many organic semiconductors, the carriers are localized on a single molecular site, and the charge-transfer reactions take place via inter-site hopping, i.e., self-exchange charge-transfer reaction between a neutral molecule and a neighboring charged molecule, M and M^+ (Eq. (1) and Fig. 1 for hole transport as example).



In this regime, the rate constant for charge hopping (k_{et}) is described by:

$$k_{et} = \frac{4\pi^2}{h} \frac{1}{\sqrt{4\pi\lambda k_B T}} t^2 \exp\left(-\frac{\lambda}{4k_B T}\right) \quad (2)$$

where T is temperature, λ is reorganization energy, and t is transfer integral between the molecular sites. From the equation, it is obvious that for k_{et} to be enhanced, λ should be as small as possible and t should be as large as possible. As depicted in Fig. 1, the reorganization energy in the self-exchange reaction corresponds to the sum of the geometry relaxation energies ($\lambda = \lambda_1 + \lambda_2$) for the neutral state to charged state ($M \rightarrow M^+$, λ_1) and vice versa ($M^+ \rightarrow M$, λ_2). Even though λ can be related to an intermolecular charge exchange reaction, it can be recognized as a molecular factor that is related to the “stiffness” of a π -conjugated framework during the charge exchange reaction. In fact, λ can be theoretically computed, and all the λ s discussed in this paper are estimated by using Gaussian 09 program at the DFT B3LYP/6-31g(d) level unless otherwise stated.

On the other hand, another important parameter, t , which is the transfer integral or the orbital overlap between neighboring molecules, is an intermolecular factor. Thus, it is expected that the magnitude of t should be related to the distance, the mutual position, and the orientation of molecules in the solid state. For the evaluation of t by theoretical calculations, the atomic coordinates of semiconducting molecules are required.

These two parameters, λ and t , can be recognized as the indexes of “molecular character”: an organic semiconductor with a large λ and a small t can be understood as a system with a strong molecular character, in which the carrier tends to stay on each molecular site because of the large energy dissipation (large λ) and the small intermolecular orbital overlap (small t). In contrast, an organic semiconductor with a small λ and a large t is more like an inorganic covalent compound in which band-like transport is likely to occur: the carrier can be smoothly moved through the effective orbital overlap between molecules (large t) without a large energy loss (small λ). It is interesting to note that in many organic

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