Shuichiro Ogawa *Editor*

Organic Electronics Materials and Devices

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Preface

The Japanese Research Association for Organic Electronics Materials (JOEM) was established as an independent nonprofit organization in 1984. At that time, the electronics industry had been growing rapidly, and companies and their researchers were searching for the technologies and science of not only silicon and compound semiconductor materials but also organic semiconductor materials and organic conductive materials. Dr. Yoshio Taniguchi, who was working for Hitachi Ltd. then, had recognized that organic substances were promising materials in the field of electronics, and with his colleagues he coined the terms "organic electronics" and "organic electronics materials." Dr. Taniguchi and his colleagues founded the JOEM in order to stimulate the research activities of organic electronics materials among academia, governmental institutes, and industries by providing the opportunities for communication and discussion.

For the past 30 years, a large number of researchers in academia and industry have been studying and developing organic electronics. There are many unsolved obstacles, but there have been significant advances such as the development of organic light-emitting diodes (LED), organic thin-film transistors (TFT), and organic photovoltaic modules (PV). Notably, organic electronics technologies have attracted attention from the printing industries for application in flexible devices, wearable devices, and others, which may be commercialized in the near future.

The future of organic electronics is promising and growing, but there are still many challenges facing commercialization, such as material degradation involving oxygen, moisture, heat, process inadaptability, and cost. In order to solve these problems, there must be further advancement in our understanding of organic electronics, particularly in the basic sciences. We are concerned that researchers in industry who are involved in developing organic electronics may not be sufficiently educated in the basic principles and sciences of organic electronics materials and devices. This is an unfortunate result of a highly competitive global environment in industry, where most of the researchers and engineers have to focus so much on product development and commercialization. In order to avoid such

misfortune, we started an educational course called the "JOEM Academy" in 2011 for younger researchers and engineers, to promote better understanding of basic principles and sciences of organic electronics. Every year, eight to ten professors of organic electronics in Japan from the top universities are invited as lecturers at the JOEM Academy for 4–5 days. The number of participants is kept small (about 10 people) to encourage free discussion, which we believe to be the key to enhancing the understanding of basic principles and sciences. After the lectures, laboratory tours are held, where participants have the opportunity to see the latest research and facilities. We hope that participants have a valuable time with the lecturers and other participants. In 2014, Springer Japan contacted us concerning publishing some proceedings of the JOEM Academy, and we decided to compile this book.

This work is intended to be a resource and reference book for graduate students and researchers in the industry who are new to organic electronics materials, devices, and their applications. The book focuses primarily on the fundamental principles and theories behind organic electronics materials and devices, but also highlights state-of-the-art technologies, applications, and future prospects. For example, physics for organic transistors, structure control technologies of polymer semiconductors, nanotube electronics, organic solar cells, organic electroluminescence, and many other topics are included. In the first three chapters, the fundamental principles and sciences of organic electronics materials and devices are discussed. These include the physics and chemistry of organic electronics materials, organic light-emitting diodes, and organic solar cells. The following six chapters focus on practical knowledge essential for research and development and commercialization.

I am profoundly grateful to the members of the JOEM Academy committee who are also coeditors of this book: Prof. Jun Mizuno at Waseda University, Prof. Toshiyuki Watanabe at the Tokyo University of Agriculture and Technology, Mr. Satoru Toguchi at the NEC Corporation, and Dr. Kazuaki Furukawa at the NTT Basic Research Laboratories of the NTT Corporation. The production of this book would not have been possible without their enthusiasm for publication and stimulating discussion. I am also thankful to Emeritus Prof. Yoshio Taniguchi of Shinshu University, who is the emeritus chairman of JOEM; Dr. Hiroyuki Suzuki, who is the president of JOEM; and the executive directors Mr. Kei Fujinami and Dr. Ryuichi Nakamura for their help and encouragement. I am particularly indebted to Ms. Miyuki Kitamura, a secretary at JOEM, for her long hours of office work in communication with the authors and formatting manuscripts. I am also thankful to Dr. Shin'ichi Koizumi and Ms. Mihoko Kumazawa at Springer Japan, the publisher, for their help.

Some mistakes certainly remain because of my inability to amend and correct them. Nevertheless, I hope that this book will give a reasonable picture of what organic electronics materials and devices are and that readers will understand the

importance of organic electronics in creating a new future. I also hope that some readers will become researchers and engineers who lead the field of organic electronics and make a significant contribution to our society.

Fuji, Shizuoka, Japan   Shuichiro Ogawa
Spring, 2015

Contents

Chapter 1
Physics of Organic Field-Effect Transistors and the Materials

Tatsuo Hasegawa

Abstract Organic semiconductors that were discovered more than half century ago in Japan (H. Inokuchi, Org. Electron. **7**, 62 (2006)) are now transfigured into the practicable electronic materials by the recent concentrated studies of the materials, thin-film processing, and device fabrication technologies. In this chapter, we first present and discuss fundamental aspects of electronic phenomena in organic semiconductors as the bases to understand and study the organic electronics technologies. Then we discuss how to understand the charge-carrier transport in organic field-effect transistors (or more frequently refferd as organic thin-film transistors, or OTFTs). Finally we introduce recent studies to fabricate OTFTs by print production technologies.

Keywords Organic thin-film transistor • Organic semiconductor • π-electron • Carrier dynamics • Printed electronics

1.1 Fundamentals for Crystalline Organic Semiconductors

1.1.1 Semiconductors with Hierarchical Structure

Organic semiconductors are a class of semiconducting organic materials composed mainly of carbon elements. The rigorous definition of semiconductors – i.e., the filled electronic states and the empty electronic states are divided energetically by a moderate width of forbidden band or energy gap – is naturally satisfied by all the organic semiconductors, as is similar to other inorganic semiconducting materials. In fact, the most basic (or crude) characteristics of the materials and the devices based on the organic semiconductors are typical of semiconductors, whereas they exhibit specific characteristics unique to this whole class of the materials.

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The organic semiconductors may be defined, for a rather practical reason, as the semiconductors composed of organic molecules that are synthesized by the techniques of organic synthetic chemistry. Along with this feature, however, the organic semiconductors are quite unique in that the whole solid-state properties are ascribed to a hierarchical nature of [atom–molecule–solid], where the molecules are composed of atoms held together by covalent bonds, and the solids are formed by discrete molecules held together by van der Waals interactions. The key player to bridge this hierarchy is the π-electrons that are the source for all the functional electronic properties of the organic semiconductors. In this section, we outline the electronic structure and the origin of fundamental and specific characteristics of the organic semiconductors, with specially focusing on the roles of the π-electrons. Then we briefly outline the basic architecture of the organic field-effect transistors.

1.1.2   π-Electrons as Source of Mobile Carriers

A major source for an enormous number of organic materials is the unique nature of carbon that can form chains, rings, or branches by stable covalent σ- or π-bonds. The σ-bonds are formed by the 2s–2p hybrid orbitals (sp^1, sp^2, or sp^3) between the adjacent atoms, whereas the π-bonds are formed by the overlap between 2p orbitals of adjacent atoms that do not participate in the formation of σ-bonds (Fig. 1.1). The terms of σ and π are originally associated with the symmetry of the bonds with respect to the rotation along the inter-atomic axes, although the term of π is now frequently utilized to refer to the electrons in the π-bonds. The σ-bonds are relatively strong and the electrons in the σ-bonds are likely to be localized. In contrast, the π-electrons are widely delocalized when the 2p orbitals of respective atoms along the connected linear chains or rings are all aligned in parallel, as presented in Fig. 1.1.

The effect of the delocalized π-electrons most obviously appears in the color of the materials. The usual organic or plastic materials that are formed only by the σ-bonds do not have colors or are transparent. This is because the σ-bonds are so strong that the electronic excitation energy becomes high and the optical gap energy is much larger than the visible photon energy range (1.6–3.3 eV). In contrast, when the π-electrons are delocalized over the molecule, the electronic excitation energy considerably decreases, and the materials become colored. Figure 1.2 presents the optical gap energies of polyacenes (and polyenes), plotted as a function of the number of fused benzene rings and double bonds. When the molecules become larger and the

Fig. 1.1 Schematic for a linear chain of carbon connected with σ and π bonds
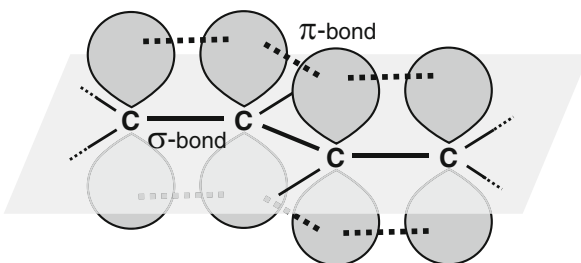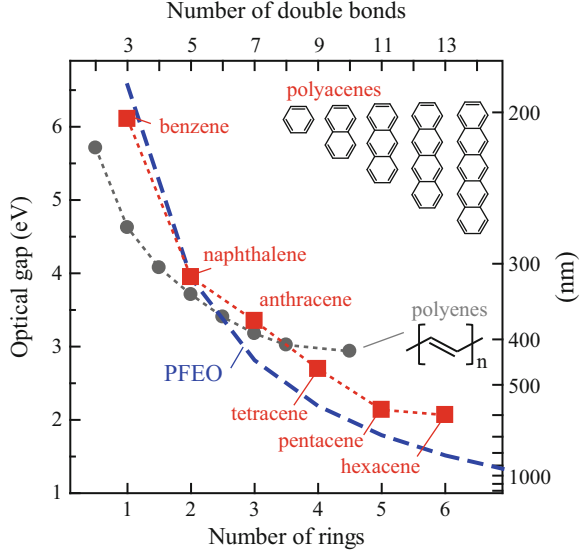
Fig. 1.2 Optical gap energy of polyacenes as a function of number of fused rings or double bonds (*red squares*); Values calculated by PFEO model (*blue dashed line*); Optical gap energy in polyenes as a function of double bonds (*gray circles*)

delocalized π-electrons are more extended, the excitation energy becomes considerably lowered and becomes colored due to the absorption of visible light.

In both the polyenes and polyacenes, each carbon has one π-electron along the alternating sequence of single and double bonds in the chemical notation. Actually, however, these π-electrons do not belong to each double bond but rather to a group of atoms along the alternating sequence of single and double bonds. The sequence is often called as conjugated double bonds, which allow a delocalization of π-electrons across all the adjacent aligned p-orbitals.

Here we present the most intuitive picture for the delocalized π electrons of polyacene by a perimeter-free electron orbital (PFEO) model [1]. We assume naphthalene, composed of two fused benzene rings as an example, that has 10 delocalized π-electrons along the circle, as presented in Fig. 1.3. For the simplicity, it is considered that the 10 π-electrons can move freely ($V = 0$) along the circle with a length L but infinite potential ($V = \infty$) outside the circle. The wave function ϕ^{PFEO} is the simple plane wave as a free electron, and the energy E can be written as a solution of the Schrödinger equation by the following form:

$$\phi_q^{PFEO} = \frac{1}{\sqrt{L}} \exp\left[-i\left(\frac{E_q}{\hbar}t - \frac{2\pi q}{L}x\right)\right], \tag{1.1}$$

$$E_q = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 q^2. \tag{1.2}$$

Here, $\hbar$ is the Planck constant, k is the wave number, and $q(=0, \pm 1, \pm 2)$ is the quantum number. The energy depends on the number of nodes in the wave
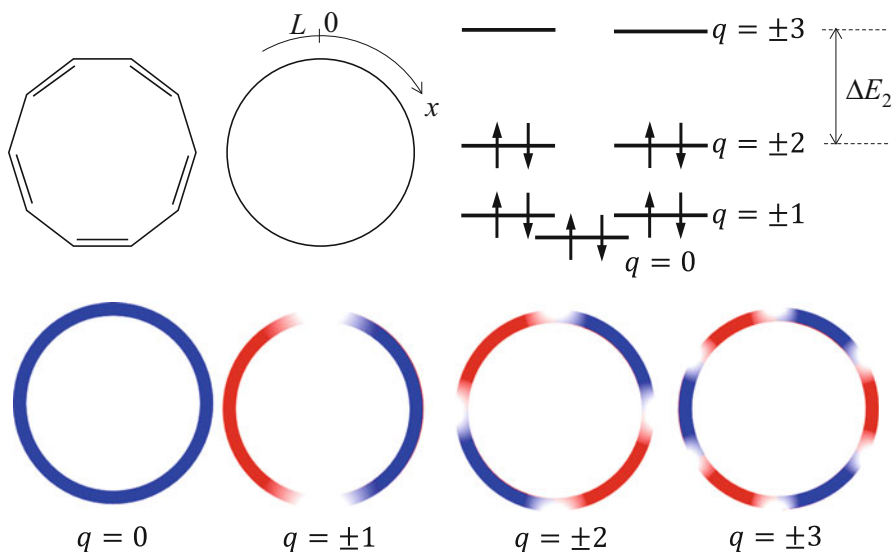
Fig. 1.3 Energy levels and wave functions in perimeter-free electron orbital (PFEO) model

functions, which is equal to $2q$. The energy diagram of the systems is depicted in Fig. 1.3. The circle length can be represented as: $L = Na = (4n + 2)a$, where N is the number of atoms ($N = 10$ in the case of naphthalene), a is the inter-atom distance, and n is the ring number ($n = 2$ in the case of naphthalene). As two electrons are filled at each level, the highest filled level will have $q = n$, and the lowest unfilled level have $q = n + 1$, so that the energy difference between the levels can be written (with using typical interatomic distance value of $a = 0.138$ nm) as

$$\Delta E_n = \frac{\pi^2 \hbar^2}{2ma^2} \frac{1}{2n + 1} = \frac{19.7 \text{ eV}}{2n + 1}. \tag{1.3}$$

The dashed line in Fig. 1.2 presents the result of the calculation. In spite of such simplicity, it is surprising to find the overall consistency as to the trend and rough values. Another important result is also obtained in terms of the stability of the molecules. As the electrons are filled from the lower levels, these ringlike molecules become stable, if there are $(4n + 2)$ π-electrons per molecule (one from each carbon atom). This is the origin of the stability of aromatic compounds and is often called as Hückel's rule. These features demonstrate that the delocalized nature of the π-electrons where the weak linkage between the 2p orbitals can form the nearly free electrons within the molecules. The unique nature of organic molecular materials is the designability of materials in terms of the shape and size of such free electron system within the molecules.

1.1.3 Molecular Orbitals

The molecular orbital (MO) theory is used to determine the π-electronic states in the molecules [2]. The MO theory is based on the concept that the electrons are not assigned to the individual bonds between atoms but to the molecular orbital that is extended to the whole molecule. This concept is in contrast to the valence bond (VB) or Heitler–London theory. The simplest model is based on linear combinations of atomic orbitals (LCAO) to present the molecular orbital ϕ^m as follows:

$$\phi^m = \frac{1}{\sqrt{N}} \sum_{n=1}^{N} c_n^a \chi_n^a, \tag{1.4}$$

where N is the number of atoms and c_n^a and χ_n^a are the coefficient and atomic orbitals of the nth atom, respectively. The linear combination should compose the eigenfunction of one-electron molecular Hamiltonian h with eigen energy ε as

$$h\phi^m = \varepsilon\phi^m. \tag{1.5}$$

By multiplying $\chi_{n'}^a{}^*$ (complex conjugate of $\chi_{n'}^a$) and integrating both sides as $\int \chi_{n'}^a{}^* h\phi^m \mathrm{d}\tau = \varepsilon \int \chi_{n'}^a{}^* \phi^m \mathrm{d}\tau$, and by substituting (1.4) into (1.5), simultaneous equations for coefficients c_n^a are obtained. In the Hückel theory for π-electrons, the following simplifications are assumed:

$$h_{nn'} = \int \chi_{n'}^a{}^* h\chi_n^a \mathrm{d}\tau = \begin{cases} \alpha \ (n' = n) \\ \beta \ (n' = n+1) \\ 0 \ (n' \neq n,\ n+1) \end{cases}, \tag{1.6}$$

$$s_{ij} = \int \chi_i^a{}^* \chi_j^a \mathrm{d}\tau = \begin{cases} 1 \ (i = j) \\ 0 \ (i \neq j) \end{cases}. \tag{1.7}$$

Here α and β are called as Coulomb integral and resonance integral, respectively. The s_{ij} is called as overlap integral. For example, the simultaneous equations in the case of benzene ($i = 1, 2, \ldots, 6$) can be simply represented by the matrix formula as

$$\begin{pmatrix} \alpha - \epsilon & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha - \epsilon & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha - \epsilon & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha - \epsilon & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha - \epsilon & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha - \epsilon \end{pmatrix} \begin{pmatrix} c_1^a \\ c_2^a \\ c_3^a \\ c_4^a \\ c_5^a \\ c_6^a \end{pmatrix} = 0. \tag{1.8}$$

By solving the equation, eigen energy and eigenfunction can be obtained. The eigen energy is obtained as $\epsilon = \alpha - 2\beta, \alpha - \beta, \alpha + \beta, \alpha + 2\beta$, as presented in Fig. 1.4.

Fig. 1.4 Molecular orbital and energy diagram of benzene

$\phi_{j=3}$

$\alpha + 2\beta$

$\phi_{j=\pm2}$

$\alpha + \beta$

$\phi_{j=\pm1}$

$\alpha - \beta$

$\phi_{j=0}$

$\alpha - 2\beta$
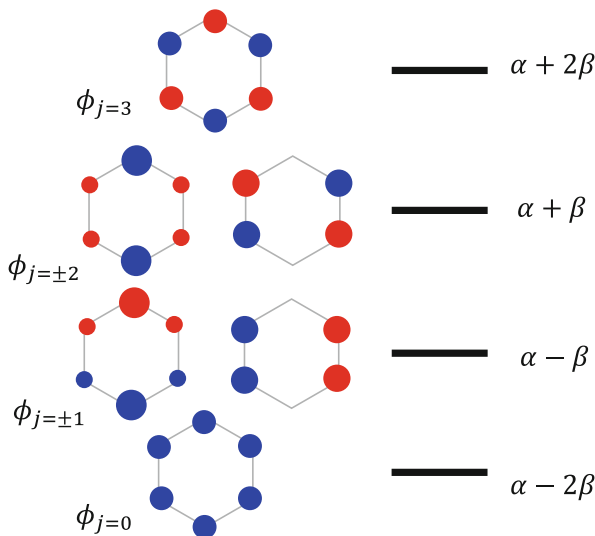
It is also important to understand, for solving the equation, that the coefficients c_n^a obey some relations due to the molecular symmetry. In the case of benzene, the $\pi/3$ rotation of the eigenfunction as to the axis perpendicular to the molecular plane at the center of the molecule still affords the eigenfunction with the same eigen energy. It means that the $\phi^m = c\phi^{m'}$, where c is complex number with absolute value 1 and $\phi^{m'}$ is the molecular orbital after the rotation. Furthermore, the 6 times repetition of the $\pi/3$ rotation should give it back to the original eigenfunction. Therefore, the eigenfunction of benzene can be represented as

$$\phi^m = \frac{1}{\sqrt{6}} \sum_{n=1}^{6} e^{i\frac{2\pi n}{6}j} \chi_n^a \ (j = 0, \pm 1, \pm 2, \pm 3). \tag{1.9}$$

The wave functions of molecular orbitals of benzene are depicted in Fig. 1.4.

The cyclic compounds can also include non-carbon elements within the cycles (which are called as heteroatoms). For example, 5-membered ring becomes stable due to the Hückel's rule ($N = 4n + 2$), in case that one sulfur atom is included, because two electrons in the lone pair of 3p orbitals contribute to the molecular orbitals. In particular, the thiophene ring is known to be an extremely important unit to obtain high-performance organic semiconductors. This is associated with the characteristics of the 3p orbitals of sulfur, which is more extended outside the molecules than 2p orbitals of carbon, and is effective to increase the intermolecular interactions when the semiconducting molecular crystals are formed.

In the simplest MO calculations, empirical values are used for α and β to describe the one electronic states in the molecules. Electrons in the molecules fill the states from lower levels with satisfying the Pauli principle. Ground states of the molecules that are formed by many electrons are approximated by using the Slater
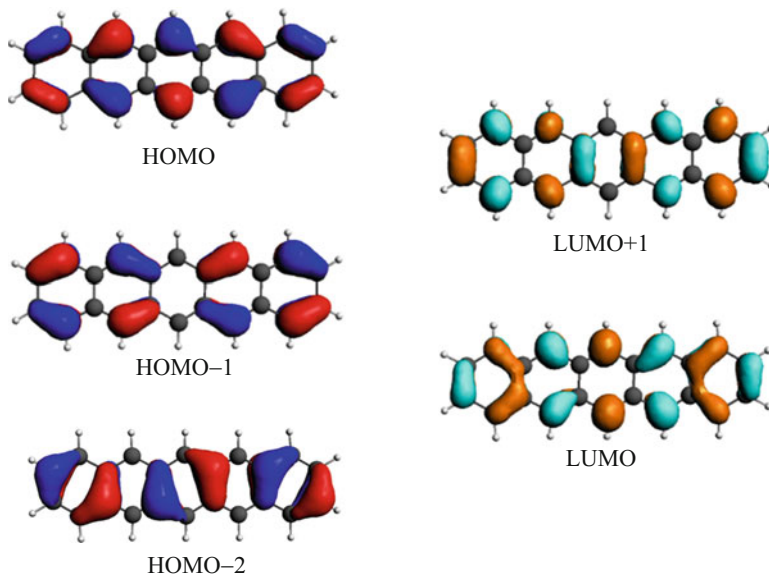
Fig. 1.5 Wave functions of molecular orbitals in a pentacene molecule calculated by ADF program [5]

determinant, the treatment of which is called as the Hartree–Fock approximation. The detailed calculations for the many-electron system are conducted by ab initio (or first principles) calculations. In the states of many electrons, Coulomb and exchange interactions between electrons should be considered and are treated by configuration interactions that hybridize many excited electronic states to minimize the total energy and to obtain the more reasonable ground states of the molecule.

Recently, calculations using density functional theory (DFT) is more frequently used to calculate ground states of many-electron system; the method is based on the calculation of distribution function of electron density, $n(r)$, and the effective potential. These methods are now familiarized, owing to the rapid development of programs and calculation speed of the computers. Today, DFT applications such as B3LYP (Becke, Lee, Yang, and Parr) [3] or ADF (Amsterdam density function) [4] calculations are commercially available and are used by using laptop computers with standard configuration. Figure 1.5 illustrates the wave function of molecular orbitals of pentacene as obtained by the ADF calculations [5].

1.1.4 Electronic Band Formation

When same kinds of organic molecules are gathered, they are self-organized to form crystals, if the molecular shapes have relatively high symmetry and the molecules can be packed densely without opening within the molecular

arrangement that holds the translational symmetry. In the crystals composed of densely packed molecules, molecular orbitals of π-electrons, composed of such as spatially extended carbon 2p orbitals, are overlapped and interacted with those of the adjacent molecules. Thus, the electronic states of the π-electrons are extended widely over the crystals. In the crystals, the intermolecular interactions between the combination of adjacent molecules should become equivalent with others between a crystallographically equivalent combinations. Such a formation of crystals that have translational symmetry is essentially important for the (translational) charge-carrier motion in the semiconductors.

Here we discuss the electronic wave function in the crystals with certain intermolecular interactions. In the case of organic semiconductors in which the molecules are bound by relatively weak van der Waals interactions, it is quite effective, as a first approximation, to use the tight-binding model in which the wave function is formulated by linear combination of molecular orbitals for obtaining wave functions in solids. This is analogous to the LCAO for the formation of molecular orbitals by the linear combination of atomic orbitals. The wave function is represented by the following form [6]:

$$\varphi^s(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{n=1}^{N} c_n^m \phi_n^m(\mathbf{r} - \mathbf{R}_n). \tag{1.10}$$

where N is the number of molecules and c_n^m and $\phi_n^m(\mathbf{r} - \mathbf{R}_n)$ are the coefficient and molecular orbitals of the nth molecule at the position $\mathbf{R}_n$, respectively. Because of the translational symmetry of the crystals, the wave function can be represented by the following form (by obtaining the same procedure as (1.9)):

$$\varphi_{\mathbf{k}}^s = \frac{1}{\sqrt{N}} \sum_{n=1}^{N} \exp(i\mathbf{k} \cdot \mathbf{R}_n) \phi_n^m(\mathbf{r} - \mathbf{R}_n). \tag{1.11}$$

This kind of formula is called as the Bloch function and satisfies the Bloch's theorem.

Electronic energy, $E(k)$, which is plotted as a function of wave number k is the electronic band structure. The tight-binding method affords the trigonometric function (or called as "cosine" band). Because the intermolecular interaction is relatively weak in organic semiconductors, the highest occupied valence band (HOVB) is mainly composed of HOMOs of the molecules, and the lowest unoccupied conduction band (LUCB) is mainly composed of LUMOs of the molecules. Therefore, the solids composed of closed-shell molecules should be the semiconductors (each band is filled) and are divided by the energy gap. Effective mass of each band is approximated by the following equations:

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{\partial^2 E(k)}{\partial k^2}. \tag{1.12}$$

Thus the effective mass m^* is inversely proportional to the intermolecular transfer integrals. Band transport usually means the free-carrier motion with the effective mass as is determined by the band curvature. Under an electric field, free carriers are not infinitely accelerated but are frequently scattered such as by phonons in the crystals at finite temperature, so that they have average velocity. In other words, the mean free path of free carriers is finite at room temperature in the crystals, so that the transport of charge carriers becomes "diffusive" motion. In the diffusive motion, the average velocity of diffusive drift motion under an electric field carrier is proportional to the applied electric field, whose proportional coefficient is defined as the drift mobility (or simply mobility) μ of carriers as

$$v = \mu E. \tag{1.13}$$

By using the mobility, the electrical conductivity σ is described by the following equation:

$$\sigma = ne\mu. \tag{1.14}$$

Here n is number of carriers per unit volume and e is the elementary charge. In the diffusive motions of carriers, the following Einstein relation generally holds with assuming the diffusion constant D (defined as the coefficient in diffusion equation):

$$D = \frac{\mu k_B T}{e}. \tag{1.15}$$

Intrinsic mobility in the semiconductor single crystals should be determined by such a mechanism.

For achieving efficient carrier transport in organic semiconductors, it is necessary to design organic molecules which can form highly crystalline solids with large intermolecular interactions and translational symmetry. The molecular orbital calculations using the DFT are also utilized to calculate intermolecular interactions between the molecules by using the atomic coordinates as is obtained by the crystal structure analysis. Figure 1.6 shows a result of the intermolecular interactions in pentacene calculated by the ADF method. The pentacene is known to crystallize layered-crystal structures where the molecules packed by herringbone-type motif, as presented in Fig. 1.7. It is empirically known that a number of materials with this type of packing motif afford high-performance OTFTs.

Crystal structure analysis [7] is an indispensable tool for investigating the molecular packing. The structure analysis is done by irradiating monochromatic x-ray beam on single crystals and collecting data of a number of Bragg reflections of respective indexes. By the Fourier transformation of the intensity distributions of each index, distribution of electron density in the unit cells can be obtained. As is different from inorganic materials, it is difficult to conduct the crystal structure analysis of organic semiconductors by means of x-ray analysis for polycrystalline films or powders, because the materials are composed of many atoms in the unit cell. So it is indispensable to use the full x-ray single-crystal structure analysis to obtain the reliable crystal structures.
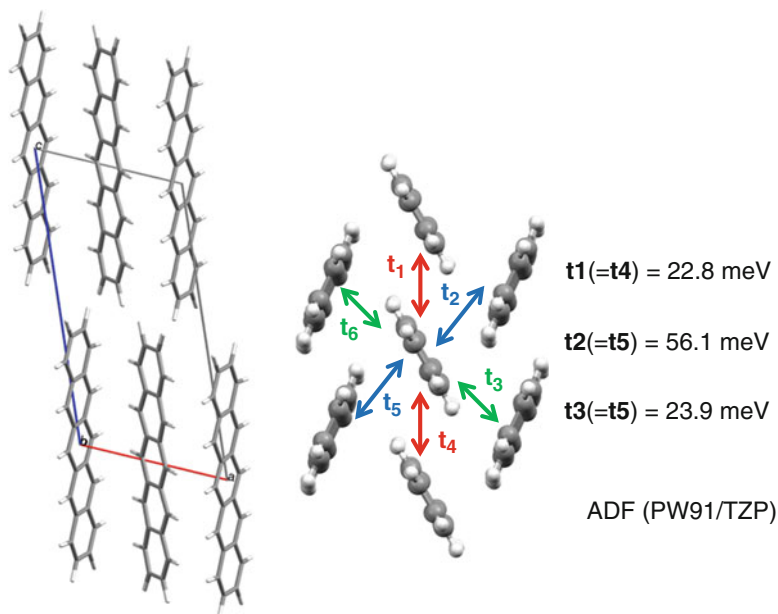
t1(=t4) = 22.8 meV

t2(=t5) = 56.1 meV

t3(=t5) = 23.9 meV

ADF (PW91/TZP)

Fig. 1.6 Crystal structure and intra-layer transfer integrals of thin-film pentacene [5]

Fig. 1.7 Herringbone-type
molecular packing and
atomic contacts in
pentacene crystals

So far it is actually difficult to predict what kind of crystal structure can be
formed by a molecule before it is synthesized and crystallized. For the development
of materials, it is actually necessary to obtain the materials and to conduct the
crystal structure analyses. Probably from many actual examples, we could empir-
ically predict what kind of crystal structures can be obtained in the designed
molecules. Nonetheless, the stability of molecular packing in the crystals are also

studied, based on molecular dynamics (MD) simulations that can simulate the motion of respective atoms and molecules classically with assuming an inter-atomic potential. By the technique, the stability and origin of actual crystal structures are confirmed by the MD calculations for some typical organic semiconductors [8].

1.1.5 Architecture of Organic Field-Effect Transistors

Figure 1.8 shows typical device structure of OTFTs. The device is composed of semiconductor layer, gate dielectric, and gate/source/drain electrodes. In the device, drain current flows between source and drain electrodes, by applying drain voltage between the source and the drain electrodes. The drain current can be controlled by the gate voltage which is applied between the source and the gate electrodes. Nominally, there should be no current through the gate dielectric layer. Carriers are accumulated both at the gate electrode and semiconductor layer as like a capacitor. These accumulated charges contribute to the drain current as a drift current.

The channel semiconductors are usually composed of intrinsic organic semiconductors without intentional doping. This feature of the device is much different from that of conventional field-effect transistors composed of inorganic semiconductors like covalent-bonded crystals of silicon [9]. The first reason of this feature is that the intentional doping in organic semiconductors is difficult, because the crystal lattice in which molecules are densely packed without opening and are bound by weak intermolecular interaction is very easily broken by the introduction of molecular dopants with different shapes. The second is a rather positive reason that the surface states due to dangling bonds in covalent-bonded crystals are not formed in organic semiconductors, so that the carrier injection is possible without intentional doping.

Due to the feature of the OTFTs as presented above, a type of the device is rather close to the enhancement-type Si-MOSFET. Carriers are injected into the organic semiconductor layer, if the Fermi level of metal for source/drain electrode coincides with the band energy of semiconductors. Therefore, the organic semiconductors with higher HOVB energy (i.e., lower work function) usually show p-type

Fig. 1.8 Schematic for organic thin-film transistors
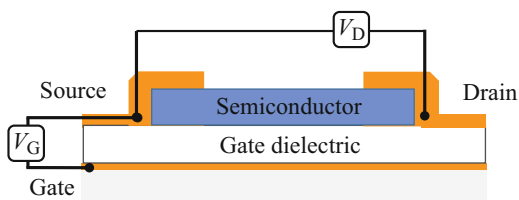
operation, while those with lower LUCB energy (i.e., higher work function) usually show *n*-type operation. Indeed, even if the small number of charge carriers with different types (hole for *n*-type operation or electron for *p*-type operation) could be injected into the semiconductor layer by the direct semiconductor-metal junctions, they are usually trapped in some trap agents within the semiconductor layers and do not contribute to the drain current. We note that if the carriers are not accumulated under the application of the gate voltage, gate electric field should be penetrated into the channel semiconductor layers.

We give the expression for the drain current I_D as a function of gate voltage V_G and drain voltage V_D [10]. When V_D is smaller than V_G, the charge accumulation covers the whole channel region between the source and drain electrodes. In this case, I_D is proportional to $(V_G - V_T)$ (V_T is the threshold voltage), which is called as the linear regime and can be described by the following equation:

$$I_D \cong \frac{Z}{L}\mu C_0 (V_G - V_T) V_D, \qquad (1.16)$$

where Z is channel widith, L is channel length, and C_0 is capacitance of the gate dielectric layer per unit area. The threshold voltage is associated with the number of traps within the semiconductor layer. When V_D is larger than V_G, the charge accumulation does not cover the whole channel region but is limited in the region close to the source electrodes. The location where the charge accumulation is depleted is called as the pinch-off point. In this case, I_D is proportional to $(V_G - V_T)^2$, and becomes independent of V_D. This is called as the saturation regime and can be described by the following equation:

$$I_D^{\text{sat}} \cong \left(\frac{Z\mu C_0}{2L} \right) (V_G - V_T)^2. \qquad (1.17)$$

These equations are used to evaluate the mobility of the semiconductor layers in the experiment.

From the architecture of the field-effect transistors, layered-crystalline organic semiconductors are quite suitable to afford high-performance OTFTs. It has been demonstrated that a high degree of layered crystallinity is essential for the production of single-crystalline or uniaxially oriented polycrystalline thin films in which high-mobility carrier transport occurs along the film planes. We give some typical examples of materials that show high-performance OTFTs in Fig. 1.9.
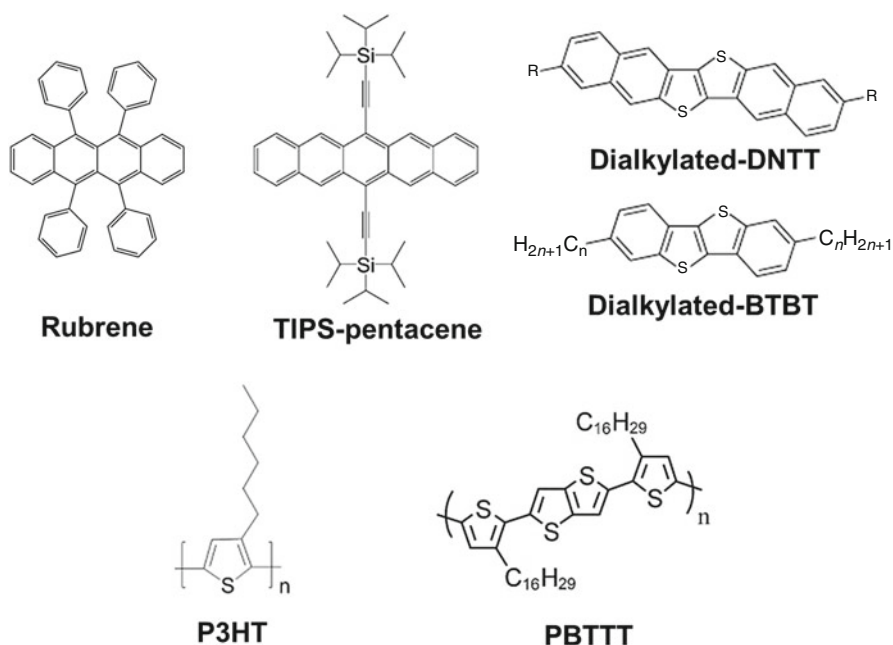
Fig. 1.9 Some important materials for high-performance organic semiconductors

1.2 Charge-Carrier Dynamics in Organic Field-Effect Transistors

1.2.1 Overview

In the Sect. 1.1, we discussed that the electronic band structures with relatively narrow bandwidths are formed in crystalline organic semiconductors that feature periodic crystal lattices. This picture provides a primary fundamental basis for understanding the charge-carrier transport in organic semiconductor thin films of OTFTs. However, we also have to know that the charge-carrier dynamics in actual OTFTs is not that simple as is determined by the "free motion" of charge carrier with an effective mass that is prescribed by the electronic band structure. As a clue to address this issue, temperature dependence of carrier mobility (or conductivity) is frequently utilized to characterize the carrier transport in real devices as either "metallic type" or "activation type." Figure 1.10 presents an example of current–voltage characteristics of a pentacene OTFT at various temperatures (gate voltage is fixed). When assuming free-carrier (i.e., metallic-type) transport, the mobility is expected to gradually increase by lowering the temperature due to the reduction of phonon scattering. In reality, however, almost all the OTFTs including single-crystalline organic field-effect transistors present activation-type characteristics at least at low temperature, even if the "metallic-type" behavior is observed at relatively high temperature [11–13]. In this

Fig. 1.10 Transfer
characteristics of pentacene
OTFT at various
temperatures
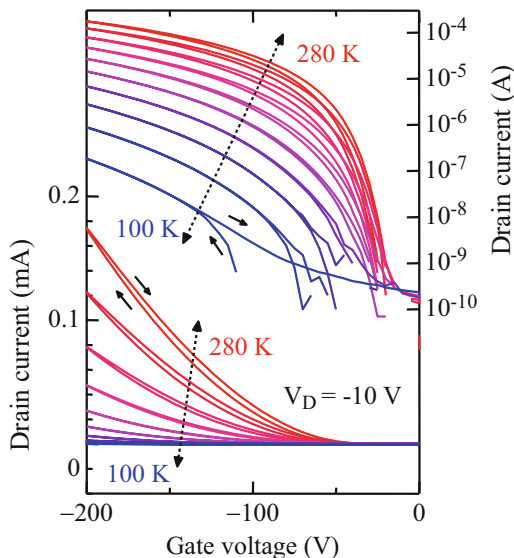
respect, the charge transport has an intermediate character between the band transport
and the charge localization at finite temperature.

Here we have to comment that the use of the "hopping" theory should not be
justified in crystalline organic semiconductors that show relatively high carrier
mobility, even if the activation-type characteristics are observed. In the hopping
model, it is assumed that the charge transport is based on a hopping process
between diabatic molecular states, where the molecules are energetically relaxed
to localize the hopped charge on the respective molecule. The hopping frequency,
k_{hopping}, is simply given by [14–16]

$$k_{\text{hopping}} = \frac{t^2}{\hbar} \left(\frac{\pi}{\lambda k_B T} \right)^{1/2} \exp\left(-\frac{\lambda}{4k_B T} \right), \qquad (1.18)$$

where t is transfer integral, $\hbar$ is Planck constant, λ is reorganization energy, k_B is
Boltzmann constant, and T is temperature. The hopping model makes a basic
assumption that the nuclear motion that "reorganizes" the molecular structure via
ionization is much faster than the charge hopping rate between molecules. How-
ever, it is difficult to apply this picture into the crystalline organic semiconductors
that involve strong intermolecular interactions in the range of 0.01–0.1 eV; the
energy is comparable to the calculated reorganization energy for isolated molecules
which is limited by a fast intramolecular vibrational mode, such as C=C bond
stretching, and is less than 0.2 eV at most. Thus, the hopping picture may be only
applicable to the disordered amorphous organic semiconductors whose
intermolecular hopping rate is very small due to the small intermolecular electronic
coupling less than 1 meV. It was also pointed out that the hopping transport