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

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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

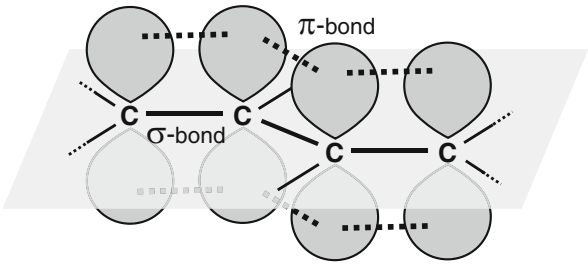

Fig. 1.1 Schematic for a linear chain of carbon connected with σ and π bonds

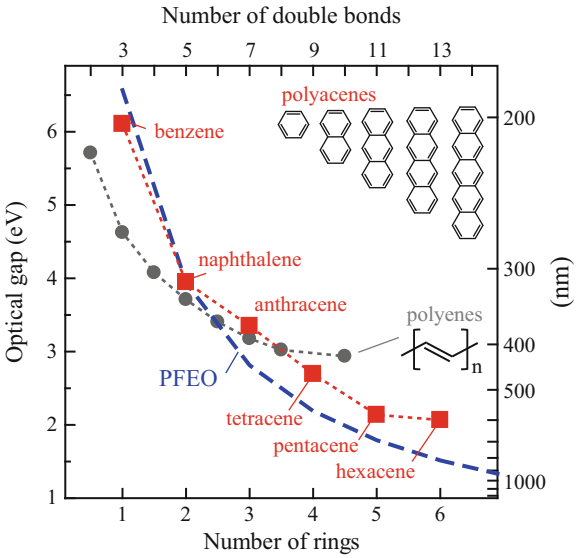

Fig. 1.2 Optical gap energy of polyacenes as a function of number of fused rings or double bonds (*red squares*); Values calculated by PFEO model (*blue dashed line*); Optical gap energy in polyenes as a function of double bonds (*gray circles*)

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:

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

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

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