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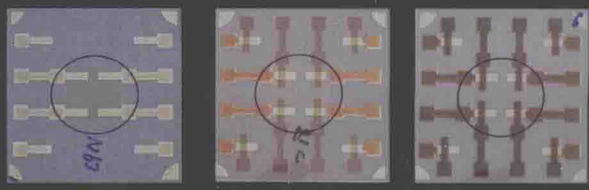

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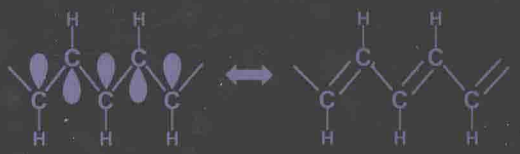
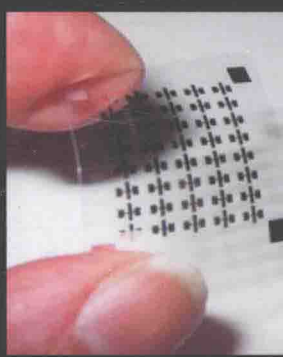


Organic Light-Emitting Materials and Devices



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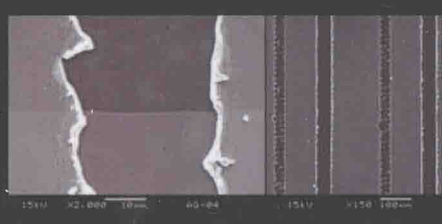

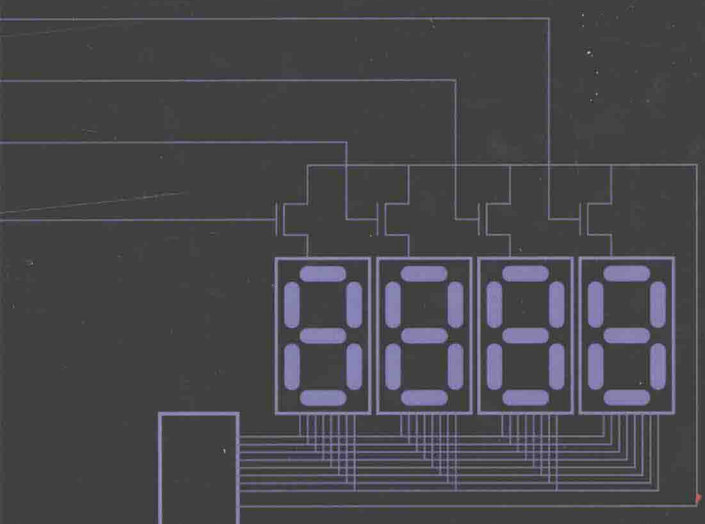

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Organic Light-Emitting Materials and Devices

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Preface

In my recent trans-Pacific flight, I had plenty of time to think about the evolution of our everyday display technology. After only eight short years since the first edition of this book was published, display technology has undergone enormous transformation, which is still continuing. Cathode ray tube (CRT) display technology, which dominated for several decades, suddenly disappeared in front of us. Superior organic light-emitting device (OLED) display has moved to center stage. During my trip, I even saw that my 85-year-old mother had started to play with a smartphone, communicating with her sons, grandsons, daughters, and granddaughters in other parts of the world. I could see the enormous joy in her face, brought forth by the new technology. Everywhere I went, I could see people using OLED smartphones. This is thanks to the discovery of organic semiconductors by Nobel laureates A. Heeger, A. MacDiarmid, and H. Shirakawa, and the invention of the first efficient OLED by C. W. Tang and S. VanSlyke. Indeed, OLEDs possess a number of advantages over conventional display devices, such as high brightness and contrast, high luminous efficiency, fast response time, wide viewing angle, low power consumption, and light weight. In addition, the new technologies offer the potential of low manufacturing cost. OLED displays can be fabricated on large-area substrates (including flexible substrates) and offer a virtually unlimited choice of colors. The technological promise of these unique characteristics places OLEDs at the forefront of research efforts of government agencies, industries, and universities. In fact, when in 2012 *Applied Physics Letter* listed the top 50 most cited papers in the journal for the past 50 years, OLED-related publications were ranked as numbers 1, 9, 15, 16, 30 and 35. Many major industrial electronics giants and newcomers have invested heavily in OLED research and development. As a result, a stream of new OLED products has reached the marketplace and a number of large-scale manufacturing facilities are now under construction. Although the field is growing rapidly and its impact is both pervasive and far-reaching, major challenges still remain. Overcoming these drawbacks will require further multidisciplinary studies and breakthroughs.

Until today, several books on related topics have provided the readers with essential information in the field of organic electroluminescence. However, none of these could serve as a comprehensive guide. Our aim is to provide readers with a single source of information covering all aspects of OLEDs, including the systematic investigation of organic light-emitting materials, device physics and engineering, and so on. In this spirit, we titled this book *Organic Light-Emitting Materials and Devices* (second edition)—a compilation of the progress made in recent years and of the challenges facing the future development of OLED technology.

Ten chapters by internationally recognized academic and industrial experts in their respective fields offer a broad perspective of interdisciplinary topics uniting organic materials synthesis with device physics and engineering. Chapter 1 introduces the history, fundamental physics, and potential applications of OLEDs. OLEDs can be divided into two categories: small-molecule and polymer-based light-emitting diodes (SMOLEDs and PLEDs). From the basic structure point of view, both devices employ multilayered architectures with the anode; hole-transporting, emissive, and electron-transporting layers; and the cathode. Developing high-efficiency OLEDs poses a great challenge for material scientists, requiring an understanding of the physics beyond device operation, and of structure–property relationships to allow for new material design. From this perspective,

Chapter 2 through Chapter 6 provide a comprehensive review of the synthesis, properties, and device performance of electroluminescent materials used in OLEDs. Chapter 2 deals with polymer light-emitting materials, subdivided into its most important classes: poly(*p*-phenylenevinylene)s (PPVs), polyfluorenes (PFs), polythiophenes (PTs), and other conjugated and nonconjugated electroluminescent polymers. It describes the progress and the current state of understanding of molecular design in the field, exemplifying >600 light-emitting polymers, and highlighting the most efficient materials and devices. Chapter 3 reviews small molecules–based OLEDs, specifically describing hole- and electron-injection and electron-transport materials, electron- and hole-blocking materials, sensitizers, and fluorescent and phosphorescent light emitters. Solution-processable phosphorescent polymer LEDs are described in Chapter 4, which starts with a brief discussion of the energy transfer processes. Chapter 5 depicts the progress of polarized OLEDs. Chapter 6 is dedicated to anode materials and focuses on novel transparent anode materials with a brief review of other actively investigated anode materials used in transparent OLED devices. Chapter 7 provides readers with well-structured information on vapor deposition manufacturing techniques employed in OLED fabrication. Chapter 8 and part of Chapter 6 focus on flexible display, a unique property of OLED-based display. Chapter 9 describes the backplane circuit technology for organic light-emitting displays. Chapter 10 describes microstructural characterization and performance measurement techniques currently used in the OLED field. The book includes abundant diagrams, device configurations, and molecular structures clearly illustrating the described ideas. Within space limitations, this book provides a comprehensive overview of the field and can serve as a primary reference source to those needing additional information in any particular subarea in organic electroluminescence. Furthermore, the described materials and principles of device physics have broad applications in other areas of organic electronics. A balance between the academic and industrial points of view is presented, enhanced by the diverse backgrounds of the contributing authors. This book should attract the attention of multidisciplinary researchers (e.g., materials scientists, synthetic chemists, solid-state physicists, and electronic device engineers), as well as industrial managers and patent lawyers engaged in OLED-related business areas.

The successful birth of this book is attributed to the hard work of our author teams. I take this opportunity to thank all contributors for their excellent work, from the bottom of my heart. I would like to thank Prof. Y. Cao (South China University and Technology) and Dr. J. Burroughes (CTO, CDT/Sumitomo, UK) for their discussion, first edition coeditor Prof. Meng (Beijing University at Shenzhen) for his contribution, and A. Gasque and J. Jurgensen at CRC Press/Taylor & Francis Group for their valuable support and help during the editing of this book. Finally, my love goes to my wife, daughter, mother, brothers, and sisters for their continuous support and encouragement—now I will have more time to be with you in person or through an OLED display from thousands of kilometers away.

Editors

Dr. Zhigang Rick Li, second edition editor and first edition coeditor, is a researcher at DuPont Central Research and Development, Wilmington, Delaware. He earned a BS degree in optics from Beijing Institute of Technology, Beijing, China, and a PhD degree in applied physics from the Laboratoire d'Optique Electronique du CNRS/Universite de Paul Sabatier, Toulouse, France. Dr. Li is a recipient of the Sino-France Abroad Study Awards.

For more than 20 years, he has worked in the field of optoelectronics, including OLED, magneto-optical recordings, and solar cells. He is the author or coauthor of more than 70 professional publications and a book chapter, and the editor or coeditor of two books. He is the organizer/co-organizer/session chair of many national and international conferences and gave numerous invited talks at the national/international meeting. He and his colleagues proposed the "nano-Ag colloids assisted tunneling" current conduction model of front-side metallization contact of p- and n-type crystalline silicon solar cells.

Dr. Hong Meng, first edition coeditor, was a research chemist at DuPont Central Research and Development, Wilmington, Delaware. His research interests are design and synthesis of conjugated organic materials and their applications in organic electronics, particularly organic thin film transistors and organic light-emitting diodes. He has contributed over 40 peer-reviewed journal articles, 25 conference papers, and 4 book chapters, and has filed several patents.

Dr. Meng received his PhD degree from the University of California, Los Angeles, under the supervision of Prof. Fred Wudl in 2002. Before joining DuPont Company, he pursued internship training at Lucent Technologies, Bell Laboratories, under Prof. Zhenan Bao (now at Stanford University) in the field of organic electronics. He is currently a professor at Beijing University at Shenzhen, China.

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Organic Light-Emitting Devices and Their Applications for Flat-Panel Displays

Qing Wang, Gang Yu, and Jian Wang

CONTENTS

1.1 Introduction

The electroluminescence (EL) phenomenon was first discovered in a piece of carborundum (SiC) crystal, by H.J. Round in 1907.[1] Commercial research into light-emitting diode (LED) technology started in the early 1960s, when Nick Holonyak, Jr., created the first inorganic LED in 1962.[2,3] Work on gallium arsenide phosphide (GaAsP) led to the introduction of the first mass-produced commercial 655-nm red LEDs in 1968, by Hewlett-Packard and Monsanto. In the 1950s, Bernanose first observed EL in organic material by applying a high-voltage alternating-current field to crystalline thin films of acridine orange and quinacrine.[4,5] The direct current–driven EL cell using single crystals of anthracene was first demonstrated by Pope and his coworkers after the discovery of LEDs made with III–V

compound semiconductors.[6] In 1975, the first organic EL devices made with a polymer, polyvinyl carbazole (PVK), were demonstrated.[7]

In early attempts to develop organic EL devices, the driving voltage of such devices was on the order of 100 V or above to achieve a significant light output.[8–10] Vincett et al. achieved an operation voltage of <30 V by using a thermally deposited thin film of anthracene.[11] The research had been mainly in the academic field until Dr. C.W. Tang and his coworkers at Kodak Chemical showed, for the first time, efficient organic light-emitting devices (OLEDs) in multilayer configuration with significant performance improvement.[12] Nowadays, small-molecule OLEDs (SMOLEDs) made by means of a thermal deposition process have been used for commercial display products. Pioneer Corporation has commercialized organic EL (OEL) display panels since 1999 for consumer electronics use, such as in car audio, CD/MP3 player, A/V receiver, etc. Kodak and Sanyo Electric Co. Ltd. demonstrated the first full-color (FC) 2.4-inch (2.4″) active matrix (AM) SMOLED display in 1999. Their joint manufacturing venture, SK Display Corp., produced the world's first AM SMOLED displays for Kodak's EasyShare LS633 camera.[13] The world's first commercially available OLED TV is SONLY XEL-1 with an 11″ size, released by SONY Corporation in 2007.[14] Nowadays, AM SMOLED displays have become ubiquitous in smartphones. In early 2013, LG started selling 55″ OLED TVs worldwide.[15]

Another type of organic semiconductor, conjugated polymer, was discovered in 1977 by Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa.[16,17] In addition to the focus on its novel physical and chemical properties in heavily doped states, great attention was paid to its intrinsic properties in undoped semiconducting phase, its nonlinear optical properties under photoexcitation,[18,19] and its interfacial behaviors with metal contacts. Schottky diodes made with polyacetylene film were demonstrated in a metal–semiconductor polymer–metal configuration.[20,21] Their optoelectric and electro-optical properties were studied. Although significant photosensitivity was demonstrated, the EL property of this system was intrinsically weak because of its electronic structure. Considerable works in the early and middle 1980s in the field of conjugated polymer were done on searching and developing new materials with solution processability. A popular, well-studied system consisted of polythiophene derivatives, one of which was poly(3-alkyl) thiophene (P3AT) (Figure 1.1). Solution-processed metal/P3AT/metal thin-film devices were demonstrated at the University of California at Santa Barbara in 1987.[22] Following the first demonstration of a light-emitting device with unsubstituted poly(*para*-phenylene vinylene) (PPV) (Figure 1.1) by Burroughes et al. at Cambridge University,[23] a highly efficient polymer LED (PLED) device was made with a solution-processable polymer, poly(2-methoxy-5-(2′-ethylhexyloxy)–1,4-phenylene vinylene), MEH–PPV (Figure 1.1), by Alan J. Heeger's group in Santa Barbara, California.[24] As will be discussed in later chapters, the commercialized soluble PPV derivatives nowadays are based on a synthesis approach originally developed by Fred Wudl's group in Santa Barbara in 1988,[25,26] and later modified by UNIAX Corporation (now DuPont Displays) in the middle 1990s and Aventis Research & Technologies GmbH (which later became Covion Organic Semiconductors GmbH, and now is part of Merck) in the late 1990s. Soluble PPV derivatives synthesized following this approach not only have high molecular weight but also show excellent solubility in common organic solvents. Most importantly, these materials have intrinsically low charged impurity, typically $<10^{14}$ cm^{-3}, and high photoluminescent efficiency (typically in the range of 20–60%).[25–28] PLEDs made with such PPV films show high EL efficiency, low operation voltage, and long device lifetime.[29–31] Displays made with PPV emitters were commercialized in 2002 by Philips (Norelco electric razor: Spectra 8894XL).

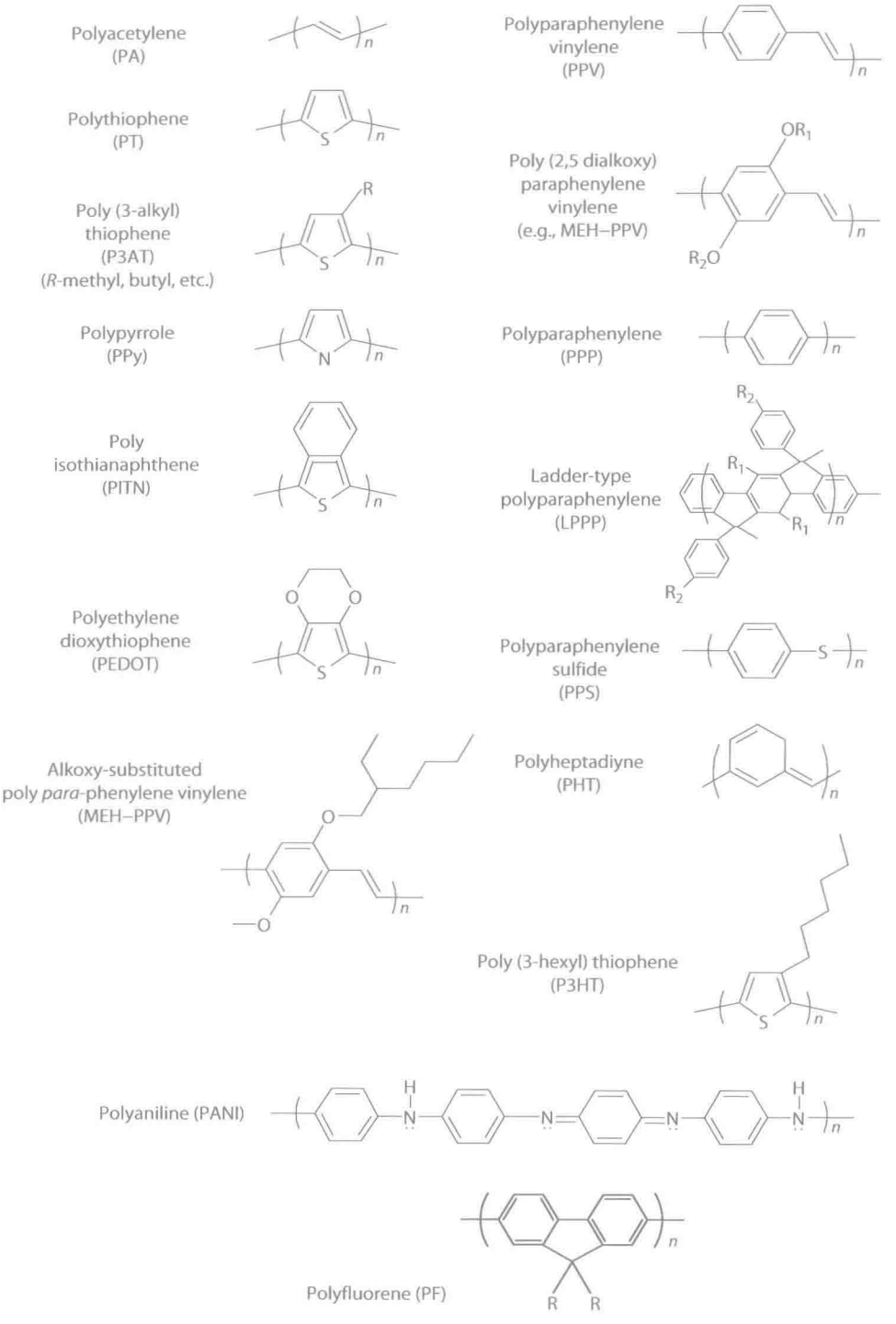

FIGURE 1.1
Chemical structures of popular conjugated polymers.

Although the energy gap in a PPV derivative can be enlarged by reducing the conjugation and planarization between the phenyl group and the vinyl group (as observed in PPVs with phenyl groups attaching at 2- or 5- or both sites),[27,32,33] it is not large enough to produce the saturated blue color needed for FC displays. Conjugated polymers with an optical energy gap of >2.9 eV are needed for PLEDs with blue emission. Significant effort has been made on searching and developing wide-energy-gap polymers (such as poly (*p*-phenyl) and its functional derivatives).[34–46] In addition to being used for making blue emitters, the same building blocks can also be used for making red and green emitters (as the host) by copolymerizing them with a proper emitter group (as the guest).[47–49] The red, green, and blue material sets developed by several companies (including Covion and Dow Chemical) are all soluble in common organic solvents with high optoelectric performance and good film-forming properties.[49,50]

PLED-based displays are attractive owing to their processing advantages in device manufacture. The organic materials used are soluble in common organic solvents or in water. Large-size, uniform, and pinhole-free thin films can be cast from solutions at room temperature by means of spin coating or other coating techniques commonly seen in the printing and painting industries. Because of the characteristic large elongation at rupture of polymers, they are flexible and easily fabricated onto rigid or flexible substrates in flat or curved shapes. Solution processing is also promising for forming patterned color pixels in FC displays. Different EL polymers can be deposited onto predefined locations by means of printing techniques such as ink-jet printing,[51,52] screen printing,[53,54] or by photolithographic patterning.[55] FC PLED displays made with an ink-jet process or with a laser-induced thermal transfer process have been demonstrated to have excellent image qualities.[56,57]

In Section 1.2, a brief review of conjugated polymers in semiconducting phase and metallic phase is given. Section 1.3 discusses device architectures and their corresponding processes. In Section 1.4, we discuss some novel devices and novel functions in thin-film polymer devices. Section 1.5 is devoted to the technical merits of SMOLEDs/PLEDs for use as emitter elements in flat-panel displays.

1.2 Conjugated Polymers in PLEDs

Conjugated polymers are a novel class of semiconductors that combine the optical and electronic properties of semiconductors with the processing advantages and mechanical properties of polymers. The molecular structures of several popular conjugated polymers are shown in Figure 1.1. Before the revolutionary discovery of conjugated polymers, polymer science and technology had focused on "saturated" polymers, i.e., conventionally nonconductive polymers (a term for macromolecules with repeat structure units). In "saturated" polymers, the valence electrons of the carbon atoms in the main chain are hybridized in sp^3 configuration, and each carbon atom is bonded to four other atoms. As a result, the electronic orbitals are fully saturated. Owing to their electronic structures, saturated polymers have wide energy gaps and are electrically insulating.

The fundamental difference between saturated polymers and conjugated polymers is their electronic configuration. Figure 1.2 compares the molecular and electronic structures of saturated (nonconjugated) polyethylene and conjugated polyacetylene. In a conjugated polymer, the carbon orbitals are in the sp^2p_z configuration, which leads to one unpaired

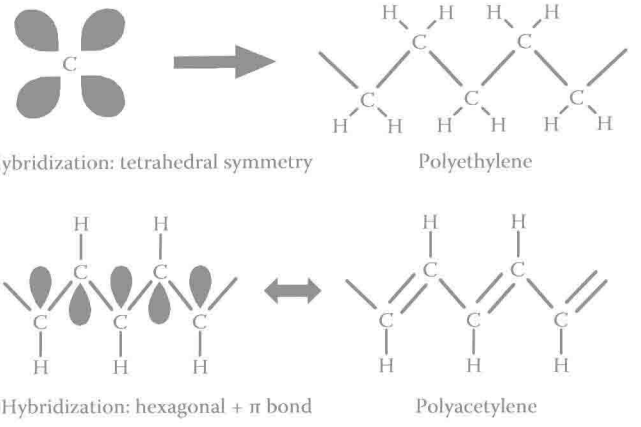

FIGURE 1.2
Electronic and molecular structures of (a) polyethylene and (b) polyacetylene.

electron (the π electron) per carbon atom. Since each carbon atom is covalently bonded to only three other atoms, and p_z orbitals of successive carbon atoms along the backbone overlap, delocalized π bands are therefore formed. As a result, conjugated polymers exhibit semiconducting or metallic properties depending on whether the bands are filled or partially filled. The number of π bands is determined by the number of atoms within the repeat unit. In the case of PPV, since the repeat unit contains eight carbons, the π band is split into eight subbands. Because each subband can hold two electrons per atom, the four π subbands with the lowest energy are filled and the four π* subbands with the highest energy are empty. The energy difference between the highest occupied π subband and the lowest unoccupied π* subband defines the π–π* energy gap, E_g.

One of the advantages of organic semiconductors is that one can modify their mechanical and processing properties while retaining their electric/optical properties. For example, PPV is a semiconductor with E_g ~2.5 eV. It is insoluble in any organic solvent after conversion from its precursor form into its conjugated form.[23,58] However, by attaching alkyl groups to the 2, 5 sites of its benzyl group, alkyl-PPV derivatives are formed. The alkyl-PPV derivatives possess similar energy band gap and luminescent emission profile to those of PPV, whereas they become soluble in most nonpolar organic solvents (such as xylene or toluene) and processable in conjugated form.[59] Another advantage of organic semiconductors is that one can tune the energy band gap of a given system while retaining its processing capability. For example, by replacing the alkyl groups of PPV derivatives with alkoxy groups at the 2- and 5- positions (e.g., poly(2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylene vinylene), MEH–PPV; Figure 1.1), one can reduce the energy band gap from 2.5 to 2.1 eV. Figure 1.3 shows the absorption and EL spectra of a series of PPV derivatives. The energy gaps are in the range of 2.5–1.9 eV, covering an ~0.6 eV range. These engineering flexibilities are especially promising for optoelectric and electro-optic device applications. Along with the change of the energy band gap is the change of luminescent profile and emission color, as shown in Figure 1.3b.

Photonic devices are often classified into three categories: light sources (LEDs, diode lasers, etc.), photodetectors (photoconductors, photodiodes, etc.), and energy conversion devices (photovoltaic devices, solar cells, etc.).[60] Most of the photonic phenomena known in conventional inorganic semiconductors have been observed in these semiconductor

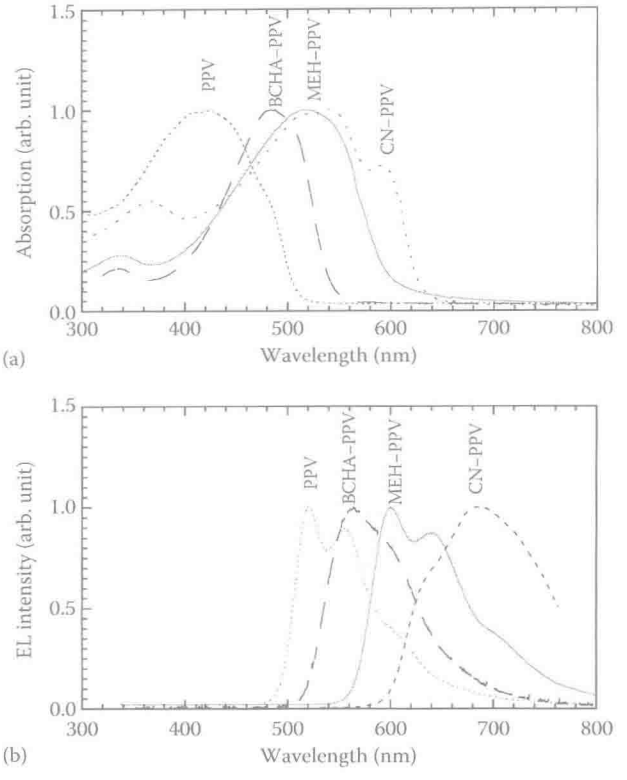

FIGURE 1.3
Absorption (a) and electroluminescence (b) of PPV derivatives. Energy band gap ranges from 2.5 eV (~500 nm) to 1.9 eV (640 nm).

polymers,[29,61] including luminescence and photosensitivity. Photoluminescence describes the phenomenon of light generation under optical radiation. An incoming photon with energy larger than the band gap excites an electron from the filled π band to the unoccupied π^* band to form an electron–hole pair (exciton), which subsequently recombines to emit a photon. In semiconductor polymers used for light emission applications, the photoluminescent quantum efficiency is typically in the 10–60% range. Photoconductivity describes the process of photogeneration of electric current. The electron–hole pairs generated by light illumination can migrate under electric field and be collected at the electrodes. Opposite to the light-emitting process, photoconductivity offers promise for large-area photovoltaic and photosensing applications.[62–64] In the applications of light emission and photoconduction, the carrier mobility of the polymer plays an important role. Depending on the detailed molecular structures, the morphology, and the electric field strength applied, carrier mobility in typical organic semiconductors is in the range of 10^{-7} to 10^{-2} $cm^2/V{\cdot}s$.

In EL applications, electrons and holes are injected from opposite electrodes into the conjugated polymers to form excitons. Owing to the spin-symmetry, only the antisymmetric excitons known as singlets could induce fluorescent emission. The spin-symmetric excitons known as triplets could not decay radiatively to the ground state in most organic molecules.[65] Spin statistics predict that the maximum internal quantum efficiency for EL

cannot exceed 25% of the photoluminescence efficiency, since the ratio of triplets to singlets is 3:1. This was confirmed by the performance data obtained from OLEDs made with fluorescent organic small molecules such as tris(8-hydroxyquinoline) aluminum (Alq_3). In PLEDs made with semiconducting MEH–PPV films, an EL-to-PL efficiency ratio of ~50% was detected by Y. Cao and his coworkers.[66] Since then, this phenomenon has been observed by other groups worldwide and in other polymer systems.[67] It was suggested that, in conjugated polymers, the singlet cross section could be considerably larger than that of triplets by a factor of 3 to 4.[68,69] The finding has triggered considerable interest in further enhancing the singlet recombination cross section and singlet populations in EL polymers. For instance, an EL-to-PL ratio of >75% was reported lately by introducing perturbation of ferromagnetic exchange interaction near the EL polymer chain.[70] Triplet excitons can also emissively recombine, a phenomenon known as phosphorescence. The lifetime of triplet excitons is much longer, typically in the range of 10^{-7} to 10^{-3} s,[71–74] than that of singlet excitons, typically 10^{-10} to 10^{-9} s.[75–78] There have been considerable activities of making SMOLED/PLED devices with the triplet excitons for their potential high quantum efficiency.[72,73,79–83] A challenge in this approach is to prevent the long-life triplet excitons from interacting with impurities in the organic layers. More rigorous requirements on material purity, charge blocking, and device encapsulation are anticipated.

The color of the EL from PLED devices can be selected by modifying the chemical structure of the polymer, either through the main-chain molecular structures or through the side-chain structures, as in the example of PPV derivatives.[23,24,31,34,37,84,85] The EL color can also be tuned by doping the host polymer with luminescent emitters. The emitters could be fluorescent dyes,[86–89] phosphorescent emitters,[79,80,83] or other luminescent polymers.[46,90–93] In such blend systems, the host polymer has a wider energy gap while the dopant has a smaller energy gap. The excitation energy of the host was transferred to the guest molecules through the dipole–dipole interaction (Förster energy transfer), or the direct quantum mechanical electrons transfer (Dexter energy transfer). By selecting appropriate host and guest materials, and adjusting the weight ratio of the guests to the host, white LEDs have also been successfully demonstrated.[87,89,94] To make a PLED-based FC display through the host/guest approach, a stable wide band-gap polymer with high efficiency is a must. Therefore, blue EL materials and devices have received considerable attention and become a focus in the field. In addition to formation of the red and green emitters with host/guest polymer blends, the red and green emitters can also be made by copolymerizing a wider band-gap host molecular unit with one or more guest units with desired emission profiles.[47–50,95] Blue emitters being studied include poly(*para*-phenylene) (PPP),[37–39] ladder-type poly(*para*-phenylene) (LPPP),[40–44] polyfluorene (PF)[34–36,48,95–97], and their stereotype variations.[50] Their molecular structures are provided in Figure 1.1.

Chemical doping and electrochemical doping applied to these semiconducting conjugated polymers lead to a wide variety of interesting and important phenomena. For example, by doping polyaniline (PANI) with phorsulfonic acid (CSA), one can achieve a conducting polymer with a bulk conductivity of 100–300 S/cm.[98] The thin film of the PANI:CSA complex in polyblends with poly(methyl methacrylate) shows optical absorption in the infrared range (due to free-carrier absorption and polaron absorption) and in the UV region (due to interband optical transition), while it is optically transparent in most of visible spectroscopic region.[99] Similar phenomena have also been observed in poly(ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) blends commercialized by Bayer Chemical (Batron-P),[100] and in polypyrrole (PPY).[101] Figure 1.4 shows the optical transmission spectra of PANI:CSA and PEDOT:PSS. The infrared electric conductivities of PANI are shown in Figure 1.5.[102,103] These data can be well described by heavily doped

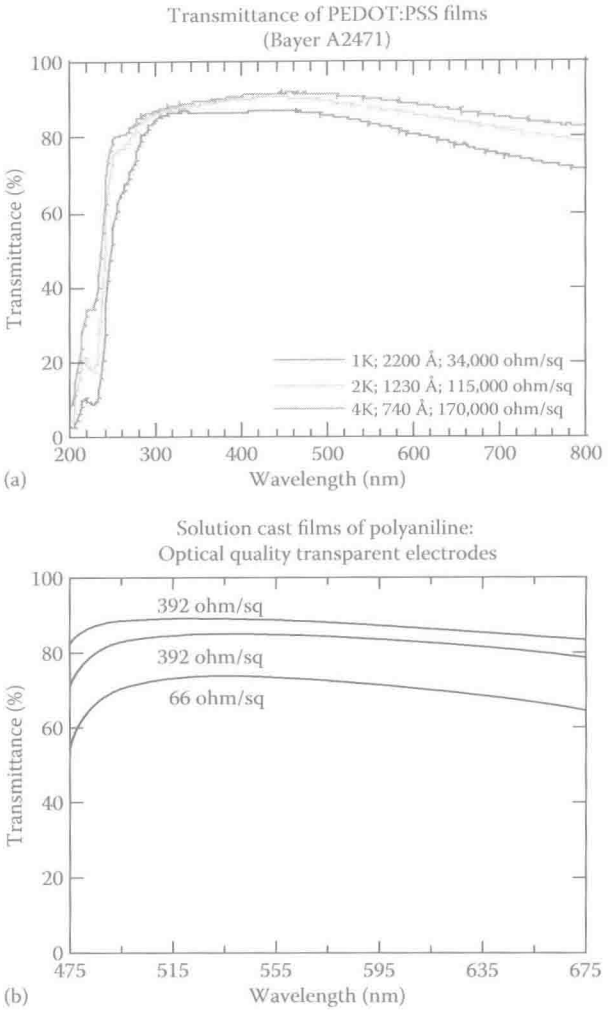

FIGURE 1.4
Optical transmission spectra of (a) PEDOT:PSS and (b) PANI:CSA.

semiconductors in disordered or amorphous systems. Such doped conjugated polymers are a novel class of thin, transparent conducting films that can be cast on rigid or flexible substrates through a solution process. These films have been widely used in PLED devices in single-layer anode form,[99] or as a buffer layer between the indium–tin oxide (ITO) electrode and the EL layer.[104] In addition to optimizing the hole injection, this buffer layer also serves as a planarization layer to eliminate pin holes in the EL layer caused by the rough ITO surface. It also serves as a chemical buffer preventing chemical impurities in the substrate and the transparent ITO electrode from reaching EL polymers, therefore significantly improving the PLED operation lifetime.[30]

The processable organic conductors, semiconductors, and insulators (not discussed in this chapter but well known historically for saturated polymers with sp^3 electronic configuration) form fundamental material sets for device applications. In the following sections, we discuss how to construct a PLED with such material sets.

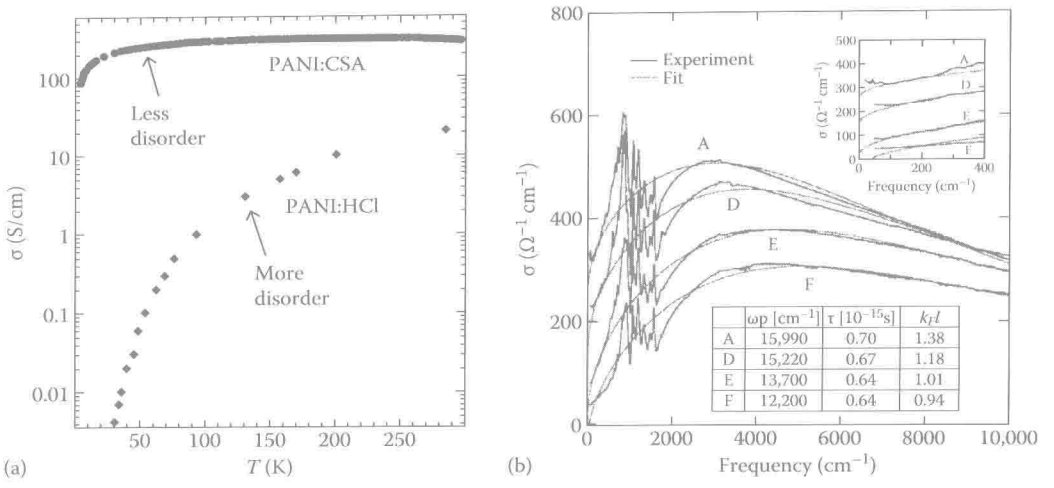

FIGURE 1.5
(a) Temperature dependence of electric conductivity; (b) infrared electrical conductivity of PANI:CSA.

1.3 PLED Structures, Processes, and Performance

The solution-processed PLED is typically prepared with a thin layer of semiconducting polymer film sandwiched between two charge injection contact electrodes, as shown in Figure 1.6. The device is generally made on a glass substrate or a thin plastic film with partially coated transparent electrode (such as ITO). A thin, semiconducting, luminescent polymer film with thickness typically in 50–200 nm range is then coated. Finally, the device is completed by depositing a low-work-function metal (such as calcium)[24] as the cathode electrode. While PLED is a typical single-layer device, the small-molecule OLEDs have a bilayer structure consisting of a hole transport layer and an emissive electron transport layer (ETL), sandwiched between a low-work-function cathode and a transparent anode.[12] To improve the brightness and efficiency of the basic bilayer devices, extra layers are often introduced. A popular multilayer structure used in phosphorescent OLED includes a hole

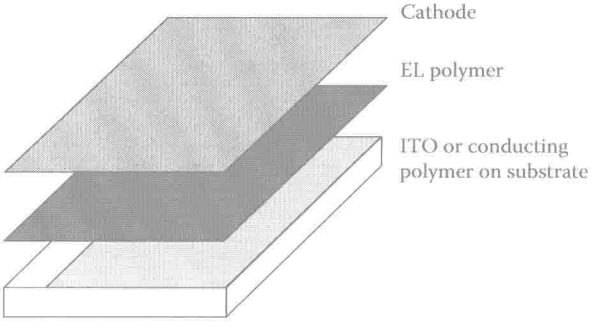

FIGURE 1.6
PLED in sandwich configuration.