有机光电子

双语教程

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内容简介

本书阐述了有机光电材料中电子结构及其相关电子和光子的相关过程，解释了有机分子及其固体凝聚态的各种性质，并详细介绍了有机材料光电及热稳定性质的测试表征方法，最后对有机光电材料相关光电器件的结构、工作原理及应用进行了讨论。有机光电子学是一门发展中的交叉科学，本书融合了该领域的理论基础和前沿进展，注重深入浅出，并在每章末尾附有思考题。全书以英文为主，并对重点和难点内容辅以中文翻译。

本书可作为材料科学与工程专业或者光电信息专业的研究生、本科生、专科生的专业课教材，也可以作为从事有机光电材料及器件领域相关工作的科技工作者的参考书。

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前　言

“有机光电子学”是一门与电子元器件相关的交叉、前沿学科，目前处于蓬勃发展阶段，国内尚未有相应的教材出版。南京邮电大学自2006年成立材料科学与工程学院以来，有机电子学就作为特色专业课程，成为本科生及研究生的重点教学内容之一，目的在于培养学生掌握有机光电材料在光电器件中应用的基础知识。

全书采取双语编排，有助于学生在掌握专业知识的同时，熟悉英文形式的科学术语，方便知识拓展及文献调研。每个章节都包括：①正文（英语，局部中文翻译），②本章小结（中文），③专业词汇（双语），④思考题（英文）。文字深入浅出，非常适合学生作为教材使用，为学生今后从事与有机光电材料相关的工作奠定基础。书中的英文大部分来自原汁原味的英文原版书籍，通过作者的二次创作及编辑加工而成，英文纯正，逻辑清晰，易于理解，有利于读者专业英语水平的提高。另外，书中含有英文重点、难点句子的中文翻译，可帮助英文相对薄弱的学生理解专业知识、提高英文水平。特别地，本书有相应配套的慕课视频及文字内容，已经在江苏省的在线开放课程平台上线。

本课程的教学时数建议为32～48学时，视学生的培养方案而定。各章的参考教学课时见如下学时分配表。

学时分配表

章　节	课程内容	学　时
Chapter 1	Introduction to organic optoelectronics	2～3
Chapter 2	Bonding and electronic structures in organic materials	2～4
Chapter 3	Energy related processes in organic materials	8～12
Chapter 4	Electrical properties and related processes in organic materials	6～9
Chapter 5	Property characterization for organic materials	3～4
Chapter 6	Organic field effect transistors	3～4
Chapter 7	Solar cells containing organic materials	3～4
Chapter 8	Organic light-emitting diodes	3～4
Chapter 9	Organic sensors	2～4
课时总计		32～48

本书的编写参考了多本中文和英文文献（见参考文献部分），在此对这些参考文献的作者表示感谢。同时，感谢以下基金的支持：有机电子与信息显示国家重点实验室定向项目、江苏省高校优势学科建设工程（PAPD：YX03002，YX03003）、南京邮电大学卓越教师培育计划（ZYJH201402）、有机电子学慕课建设项目（2014MOOCA1）。

由于作者能力所限，加之双语，疏漏和不妥之处在所难免。恳请广大读者在使用过程中给予批评指正，以利于再版之际的修改和完善。与本书相关的讨论与交流，也十分欢迎。

密保秀、高志强

2023劳动节前于南京

目　录

CHAPTER 1　INTRODUCTION TO ORGANIC OPTOELECTRONICS ……………………… 1

CHAPTER 1 INTRODUCTION TO ORGANIC OPTOELECTRONICS

Starting from historical remarks about optoelectronics，this chapter gives a brief introduction to organic optoelectronics，including history，concept，development and types/characteristics of organic materials，as well as their main optoelectronic processes and corresponding device applications.

1.1 Optoelectronics

Optoelectronics refers to the optoelectronic science and technology not only for devices and systems of electronic in nature，yet involving light（such as the photo voltaic device and the light-emitting diode），but also for closely related areas that are essentially optical in nature but involve electronics（such as crystal light modulators）. In a broad sense，pure electronic devices，such as field effect transistor，also belong to this category. In these devices，electrons and photons are used to generate，process，transmit，and store information at unprecedented rates and with ever-decreasing power requirements[1].

Optoelectronic devices have dramatically impacted the way humans live in the twentieth and twenty-first centuries. The development of classic and quantum mechanical theories，particularly the discovery and development of classic inorganic semiconductors and subsequent optoelectronic devices such as radios，telephones，televisions，integrated circuits，and computers，has given birth to the human society of an "information age" and a "global village，" where the information is processed and transferred at the level and speed of electrons and photons. In today's world，it is virtually impossible to find a piece of electrical equipment that does not employ optoelectronic devices as a basic necessity—from CD and DVD players to televisions，from automobiles and aircraft to medical diagnostic facilities in hospitals and telephones，from satellites and space-borne missions to under water exploration systems—the list is almost

[1] 光电子学指的是光电子方面的科学和技术，它不仅是本质上为电子却涉及光的器件和系统（如光伏器件和发光二极管），也包括本质上为光学，但是涉及电子学的紧密相关领域（如晶体光调制器）。广义上，纯电子器件，例如场效应晶体管，也属于这个分类。在这些器件中，电子和光子被用来产生、加工、传导以及存储信息，其速率前所未有，其功率需求不断降低。

endless. Optoelectronics is in virtually every home and business office in the developed modern world, in telephones, fax machines, photocopiers, computers, and lighting, etc[2].

2. 在发达的现代世界，光电子学实际上存在于每一个家庭和企业办公室：存在于电话、传真机、复印机、计算机以及照明，等等。

As one branch of optoelectronics, electronics refers to the science and technology of how to control electric energy, energy in which the electrons have a fundamental role. Electronics deals with electrical circuit comprising active components, inert components and connection technology, and has experienced development from vacuum, solid state, micro electronics, integrated circuit (IC) and super large IC, and now is heading for molecular electronics (Figure 1.1).

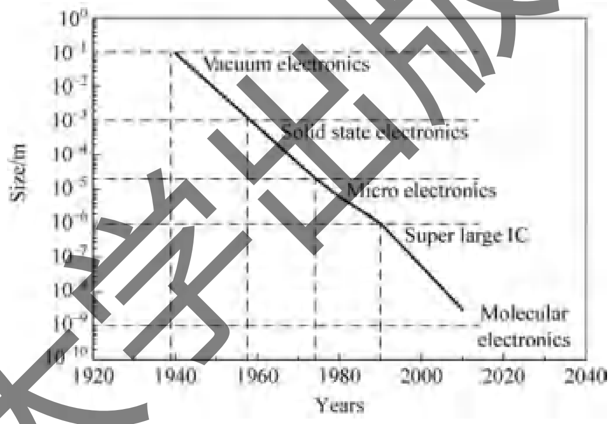

Figure 1.1　Development of electronics with times

Most of today's commercially available optoelectronic devices are inorganic material based ones, which are fabricated from inorganic semiconductors and conductors. The former includes elemental semiconductors (e.g., silicon and germanium) and compound semiconductor (e.g., gallium arsenide, zinc oxide, cadmium sulfide); Examples of latter are metals of Al, Au and Ag, and transparent oxide conductors (e.g., indium tin oxide). Inorganic materials based optoelectronics are well developed with features of fast and reliable. However, these devices bear the disadvantages of limited types and amounts in materials, consuming large amount of energy in fabrication, difficult in flexibility, incompatible to biosystem, often detrimental to environment, and hard/expensive to further miniturization, etc[3].

3. 基于无机材料的光电子学，高度发达，具有快速和可靠性好的特点。但是，这些器件存在如下缺点：材料的种类和数量少、制备时消耗大量能源、难于柔性、与生物系统不兼容、通常对环境有害，以及进一步小型化昂贵/困难，等等。

In the past several decades, research and development on organic/polymeric optoelectronic materials and devices have grown rapidly. These devices/systems have exhibited advantages such as flexibility, compatibility to biosystem, processability in solution process (e.g., spin coating, spray, roll to roll inkjet printing and doctor blade printing), and the potential for low-cost mass production, and thus being a very useful supplement to inorganic counterparts.

Devoted to organic electronics, this text book will discuss the basic science in the aspects of optoelectrical-active organic materials, and their device applications.

1.2 Organic Optoelectronics

1.2.1 Optoelectronic Organic Materials

1. Advent of Organic Materials

Materials are useful maters, which were initially divided into metals and non-metals. Later, it was found that there was a kind of non-metallic materials, which contained essential element of carbon and could only be obtained via a living organism, and hence this kind of materials were termed as organic materials. In 1828, by synthesis of small molecule urea (NH_2CONH_2), F. Wöhler demonstrated for the first time that an organic compound could be prepared in laboratory without a living organism, proving the capability for artificial synthesis of organic materials[4].

After the successful preparation of small molecules in laboratory, great progress has been made for polymer-type organic materials in 1920: German scientist H. Staudinger proposed that polymers were made of repeating molecule units regularly in long chains, forming polymer concept. Figure 1.2 schematically illustrates the formation of polymer from monomers. At that time, people thought that plastics are polymers, and unlike metals, they do not conduct electricity and can be used as insulation round the copper wires in ordinary electric cables.

[4] 材料是有用的物质，最初被划分为金属和非金属。后来人们发现，有这样一种非金属材料，含有碳元素并且只能通过有机生物体才能获得；因此，这类材料就被命名为有机材料。1828年，通过合成小分子尿素（NH_2CONH_2），F. Wöhler 首次展示了在脱离生物体的情况下，在实验室能够合成有机化合物，以此证明了人工合成有机材料的可能性。

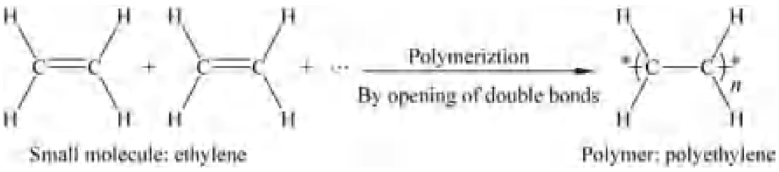

Figure 1.2 Formation of polymer from monomer

As time goes on, the concept of organic materials is evolved as such that organic materials refer to those containing carbon, hydrogen and other possible elements of oxygen, nitrogen, halogen, sulphur, phosphor, and even metal, etc, where the carbon atoms are bound to each other to form the carbon frameworks of small molecules or polymers[5]. The carbon atoms are bound together by either σ-bonds or π-bonds. Single bonds like C-H bonds are σ-bonds while double bonds consist of a hybrid orbital of a σ-bond with a π-bond. σ-bonds are strong while π-bonds are weak. Electrons involved in π-bonds are delocalized over the molecule and are responsible for most of the interesting optical properties of organic materials. On the other hand, the σ-bonds are more localized and hold the molecule together, but usually do not play a major role in optoelectronic properties.

5. 随着时间的推移，有机材料的定义演变为：有机材料包含碳和氢元素，也可能包含氧、氮、卤素、硫、磷、甚至金属等；其中的碳原子相互成键，形成了小分子或者聚合物的碳骨架。

2. Milestones in the Development of Organic Optoelectronic Materials

The photoconductive and semiconducting properties of organic materials were reported in 1906 and 1950, respectively. Since then, basic research has steadily continued, forming a series of important milestones. Examples are as following[6].

6. 有机材料的光导和半导体特性分别报道于 1906 年和 1950 年。自此，有机材料的基础研究稳步推进，形成了一系列重要的里程碑性历程，举例如下。

From 1950s, steady works on crystalline organics started, resulting in lots of crystalline organic materials with semiconductive/photoconductive properties. Figure 1.3 schematically shows some small-molecule based crystals (a), and polymer chain based crystalline and amorphous states (b). Then, after the appearance of organic non-linear optical materials in 1970s, the first conducting polymer was prepared by A. J. Heeger, A. G. Macdiarmid and H. Shirakawa in

1977 (the reaction is shown in Figure 1.4). Due to this revolutionary work, the Nobel Price of Chemistry 2000 was given to them for the discovery and development of conductive polymers. It was clear that for a polymer to be able to conduct electric current it must consist alternatively of single and double bounds between the carbon atoms. It must also be "doped", which means that electrons can move along the molecules — it becomes electrically conductive[7]. This was of great importance for chemists as well as physicists, because: ① industrially, conductive plastics can be used as anti-static substances for photographic film, shields for computer screen against electromagnetic radiation and for "smart" windows that can exclude sunlight; ② conductive plastics also can be applied in organic optoelectronic devices, such as organic light-emitting diodes and organic solar cells[8].

7. 已经很明确，要想使聚合物导电，它必须在碳原子之间含有交替的单双键结构，还必须“掺杂”，这样电子可以沿着分子移动，从而具有导电性。

8. ①工业上，导电塑料可以用作胶卷的防静电物质、计算机屏幕的电磁波辐射防护、能够去除太阳光的智能窗口。②导电塑料还可以被应用于有机光电器件中，如有机发光二极管和有机太阳能电池。

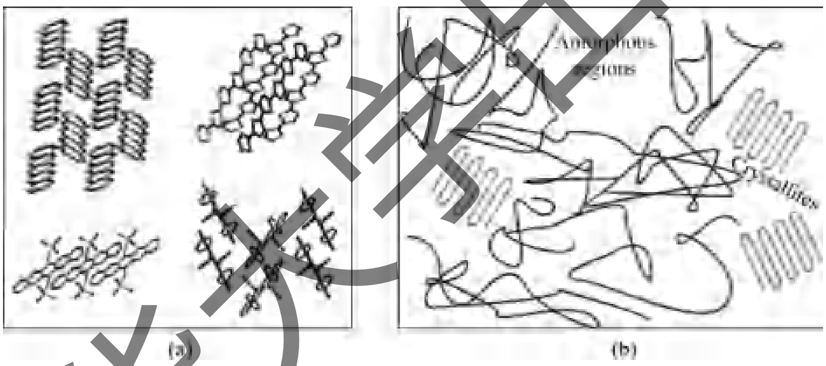

Figure 1.3 Small-molecule based crystals (a), polymer chain based crystalline and amorphous states (b)

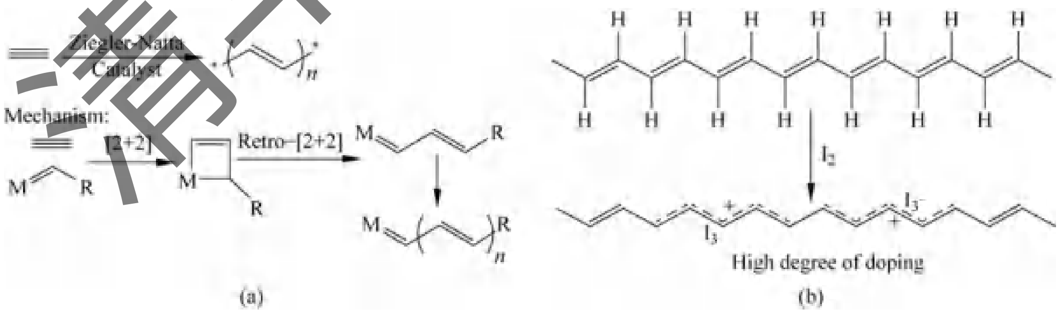

Figure 1.4 The Noble Price work of 2000 Chemistry: Ziegler-Natta polymerization for polyacetylene (a), and the conducting mechanism for doped polyacetylene (b)

In the afterward years of 1985, 1993 and 2004, semiconductor fullerene, conducting polymer PEDOT: PSS (Poly (3, 4-ethylenedioxythiophene): poly (styrenesulfonic acid)) and conductive/semiconductive graphene were reported, respectively (Figure 1.5 for their molecular structures).

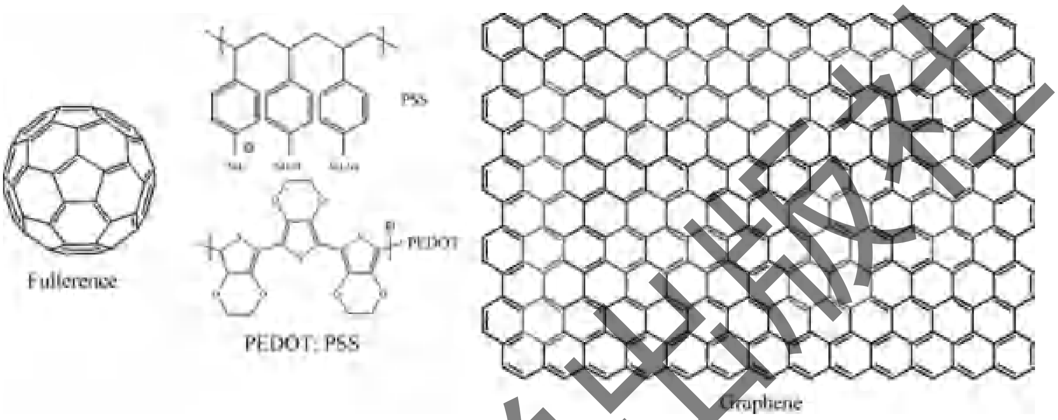

Figure 1.5 Molecular structures of fullerene, PEDOT: PSS and graphene

The earliest optoelectronic application of organic materials is the composite organic materials with hole transport organic molecules dispersed in insulating polymers, which were commercialized as photoreceptors for electrophotography in 1980. The manufacturing process for this organic photoreceptor was a coating process, which contributed to the low cost of the photoreceptor[9]. Organic field effect transistor, organic light-emitting diodes (OLEDs) and organic solar cells were appeared in1986, 1987, and 1986, respectively. These devices were highly efficient at that time and showed brilliant futures. OLEDs were commercialized as an automotive display in 1997, and are currently being used in high-definition OLED TVs and OLED lighting. In the future, it is expected that organic materials will be successfully applied to flexible displays, biosensors, and other devices that could not be realized with conventional inorganic semiconductors.

9. 最早的有机材料光电应用是 1980 年商业化的、作为光感器应用于电子复印机的复合有机材料，其组成是空穴传输小分子分散在绝缘体聚合物中。这个有机光感器的加工过程是涂覆，使得其成本很低。

Currently, organic materials contribute nearly 90% of all known materials, and can exhibit the following properties: photoconductivity, electroluminescence, triboelectricity, metallic conductivity, superconductivity, photovoltaic effects, or charge storage and release, etc[10].

10. 当前有机材料占所有已知材料的 90% 以上，可能具备如下性质：光导、电致发光、摩擦电、金属导电性、超导电性、光伏效应和电荷存储与释放等。

3. Structural and Property Features of Organic Materials

1) Bonding Characteristics

Different to other-type materials composing the smallest unit of atoms, the smallest units in organic materials are molecules that consist of atoms with covalent bondings only within a molecule. These discrete molecules are held together by weak van der Waals forces (Figure 1.6). For this reason, organic materials are also called molecular materials. Due to the weak nature of the bonding between molecules, the properties of the individual molecule are retained in the solid state to a far greater extent than would be found in solids exhibiting the other types of bonding[11].

11. 基于这个原因，有机材料也称为分子材料。由于分子间较弱的成键，相比于其他成键类型的固体，有机材料中个体分子的特性在固态时得到了极大程度的保留。

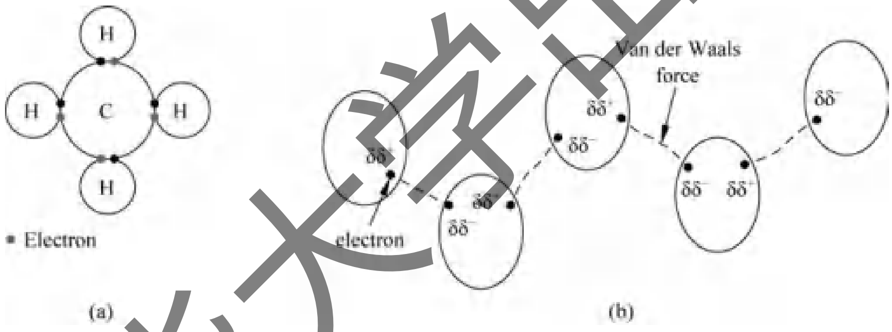

Figure 1.6 Covalent bonding within one organic molecule of methane (a), and van der Waals force between molecules (molecules are represented as circles) (b)

2) Conjugation

For use as active components in optoelectronic devices, the organic molecules must present structural feature of conjugation. The term conjugation refers to the alternating sequence of single and double bonds in between atoms (mostly are carbons) of organic molecules[12]. Figure 1.7 exemplifies four conjugated molecules and three non-conjugated molecules. As shown in Figure 1.7(b), although these molecules contain both single and double bonds, they do not have conjugation structure, and are not conjugated materials, because their double and single bonds don't present in an

12. 作为活性组分应用于光电器件，有机分子必须存在共轭结构。术语共轭指的是有机分子中的原子之间（多数情况下是碳原子）形成的单键与双键交替结构。

alternative single-double sequence. Conjugated organic materials are one important type of organic materials, which have interesting optoelectrical properties, and are the main concerned-materials in organic optoelectronics. Organic semiconductors belong to conjugated organic materials that exhibit semiconducting properties^{13}.

13. 共轭有机材料是一类非常重要的有机光电材料，因为它们表现出令人感兴趣的光电特性，是有机光电子学中主要考虑的有机材料。有机半导体就是共轭有机材料，表现出半导体特性。

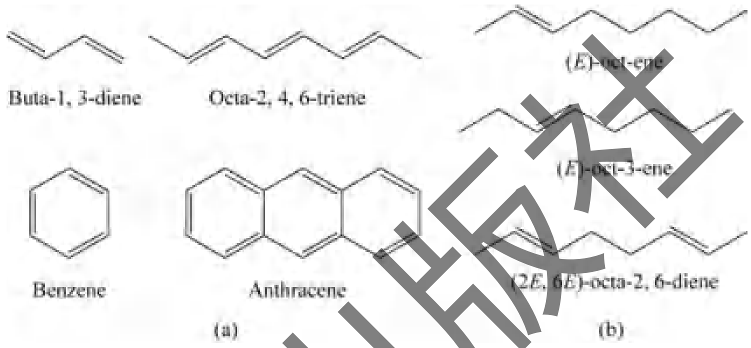

Figure 1.7 Molecules with conjugation structure (a), and without conjugation structure (b)

3) Large Amounts

The quantity of organic materials is large without limitation, because the molecular structures are much easier to modify compared to other type of materials. New materials can be produced just by a single modification. For example, as shown in the Figure 1.8, merely changing a linking mode from para- to meta- in the molecule results in different materials^{14}.

14. 有机材料的数量是无穷无尽的，非常巨大。因为相比于其他类型的材料，有机分子结构非常容易进行分子结构修饰。任何一点点的修饰都会产生新的材料。如图1.8所示，仅将分子的一个链接模式从对位改为间位，就形成了新材料。

4. Classification of Organic Materials

There are several classification methods for organic materials.

(1) According to molecular weight, organic materials can be classified into small molecule, macromolecule and polymer. Small molecule refers to compounds possessing definite molecular formula and molecular weight. The molecular weight of small molecules is usually smaller than several thousands. Macromolecule possesses definite molecular formula with molecular weight in the range of several thousands and ten thousands. Polymer is long-chain molecule consisting of an indeterminate number of molecular

repeat units，with molecular weight of several hundred thousands even several millions. Polymer is not a pure substance but a mixture[15].

15. 根据分子量，有机材料可以分为小分子，大分子和聚合物。小分子指的是具有确定分子式和分子量的化合物，其分子量通常小于几千。大分子也具有确定的分子式，其分子量在数千至数万之间。聚合物是由不确定数目的分子重复单元组成的长链分子，分子量为数十万甚至数百万。聚合物不是纯物质而是混合物。

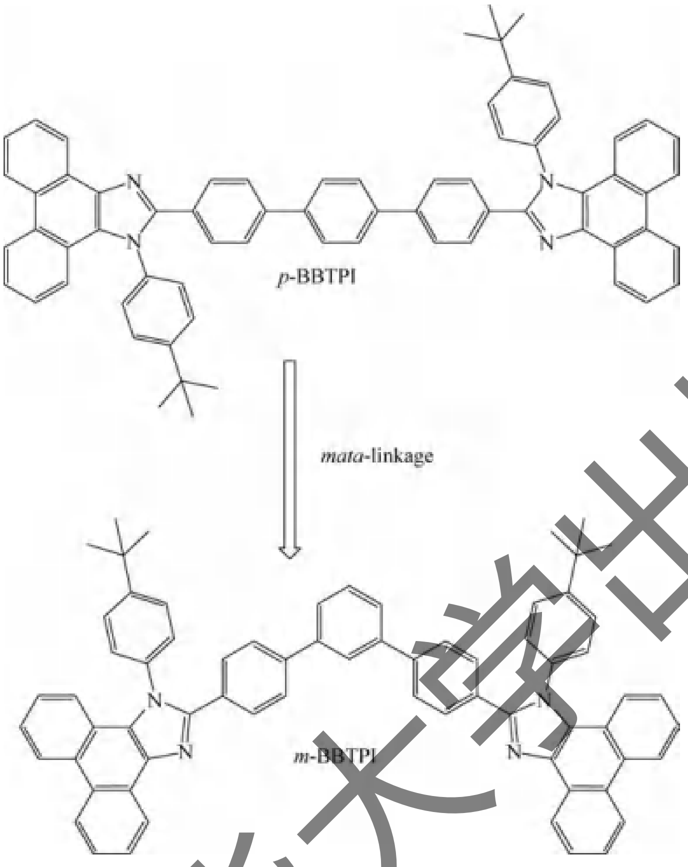

Figure 1. 8 Production of a new organic material by only changing the linking mode

(2) According to structure complexity，organic materials can be classified into small molecule，polymer and biomolecule (Figure 1. 9). Biomolecules are also organic molecules. Due to their less application in organic optoelectronics，they are beyond the discussion of this textbook[16].

16. 根据结构的复杂程度，有机材料可分为小分子、聚合物和生物分子(图 1.9)。生物分子也是有机分子。由于它们在有机光电子学中的应用较少，本书不作讨论。

(3) According to molecular shapes，there are disc，linear，starburst，and super branched molecules，etc (Figure 1.10).

5. Differences between Organic & Inorganic Semiconductors

Semiconductors are the key components in optoelectronic devices. The molecular nature of organic semiconductors leads to a number of significant physical differences with respect to inorganic counterpart. The most significant differences between them are summarized below[17].

17. 光电子器件中的关键组分是半导体。有机半导体的分子特性，导致了有机半导体和无机半导体之间的一些重要物理差异。下面总结最主要的差别。

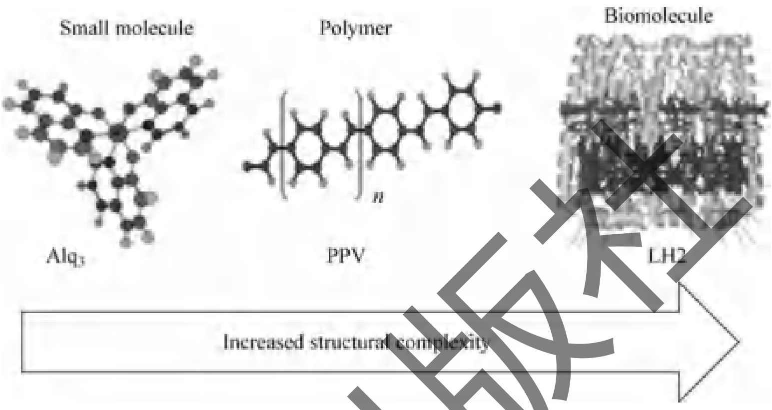

Figure 1.9　Three types of organic materials according to structure complexity

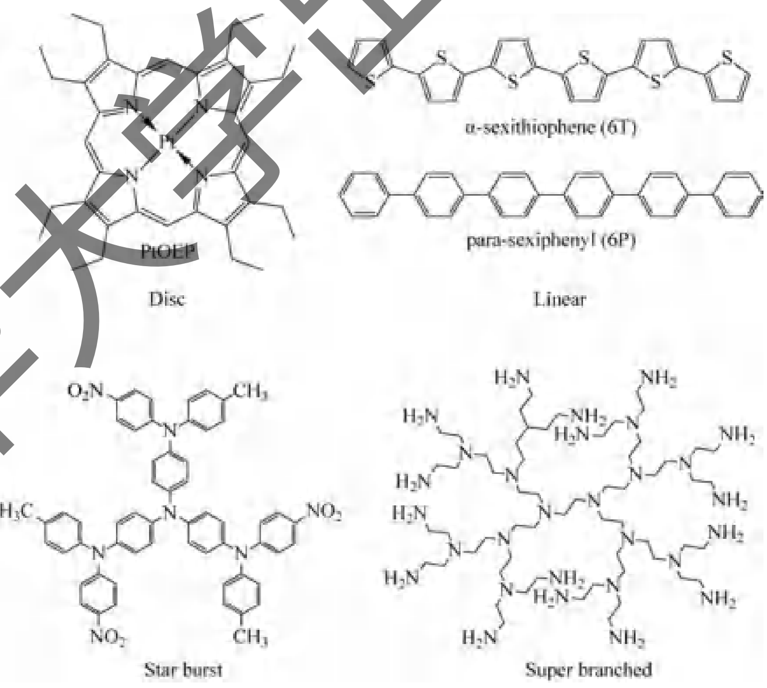

Figure 1.10　Organic materials classified according to molecular shapes

1) Structural Difference

Structurally, organic and inorganic semiconductors often compose of different elements. Besides, the bondings between atoms are not the same. Organic semiconductors are molecular solids which contain weak van der Waals bonding despite of the covalent bondings within molecules, while inorganic semiconductors are made of covalently bonded atoms[18].

Typical van der Waals force is smaller than 42 kJ · mol^{-1}, which is much smaller than that in inorganic semiconductors, e.g., the bond energy in silicon is 318 kJ · mol^{-1}. Moreover, the van der Waals force decreases with R^6, while the valence bond energy decreases proportionally to R^2. Figure 1.11 shows the crystal structures of silicon and a polycyclic aromatic hydrocarbon, demonstrating their differences in bonding and spacial stretching[19].

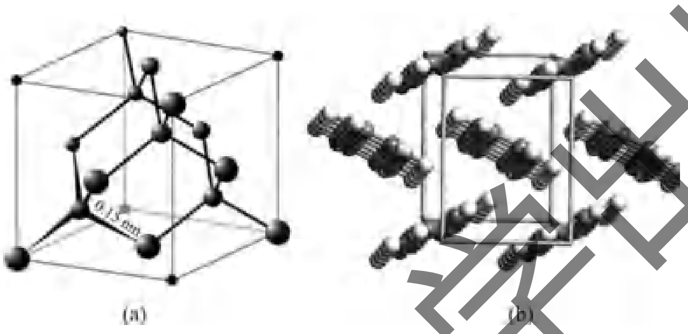

Figure 1.11 Structural differences between organic and inorganic materials: covalently bonded crystal of silicon (a), and crystal structure of a polycyclic aromatic hydrocarbon (b)

2) Exciton Difference

Excitons in inorganic semiconductors belong to weakly bound Wannier－Mott excitons. They have large Bohr radii and small binding energies. For example, in GaAs the exciton Bohr radius is 140 Å and its binding energy is 4.2 meV. This is in contrast to excitons in organic materials, which are referred to as tightly bound Frenkel excitons with small Bohr radii (5～10 Å) and large binding energies (0.5～1.0 eV). The exchange energies, i. e., the energetic difference between singlet- and triplet-excitons in organic materials are often 0.5～1.0 eV[20].

3) Optoelectronic Transition Difference

Electronic transitions in organic materials need to be considered together with vibrational states, as opposed to

18. 在结构上，有机半导体和无机半导体通常由不同元素组成。另外，原子之间的成键也不同。有机半导体是含有弱范德瓦耳斯力的分子固体，虽然其分子内是共价键；而无机半导体材料是由以共价键相结合的原子组成。

19. 典型的范德瓦耳斯力通常小于 42 kJ · mol^{-1}，远远小于无机半导体中的作用力。例如，硅的键能为 318 kJ · mol^{-1}。更进一步，有机材料中的范德瓦耳斯力随分子间距的六次方（R^6）降低，而无机半导体中的共价键键能随原子间距的平方（R^2）降低。图 1.11 给出了 Si 晶体和有机稠环芳香烃晶体的结构示意图，展示了有机半导体和无机半导体在成键和空间伸展的不同。

20. 无机半导体中的激子属于弱结合的万尼尔-莫特激子。它们的玻尔半径较大，结合能较小。例如，GaAs 中激子的玻尔半径是 140 Å，结合能是 4.2 meV。这与有机材料中紧密结合的弗仑克尔激子不同，其玻尔半径小（5～10 Å），结合能大（0.5～1 eV）。有机材料中的交换能，即单线态和三形态激子能量差异通常在 0.5～1.0 eV。

inorganic materials, where the electronic transitions and the vibrational states can be easily separated[21]. This is because the atoms in organics are often small, e. g., hydrogen has a small mass, whereas an inorganic solid, like NaCl, has atoms with much larger mass. The smaller mass makes the vibrational frequencies, $(f/m)^{1/2}$ (f: oscillator strength, m: atomic mass), much larger in organics. The vibrational states are then treated like simple harmonic oscillators with quantized energy levels, forming configurational coordinates[22]. Optical transitions become combined electronic and vibrational transitions. Electronic transitions occur between the ground state and excited state both with vibrational quantized energy levels. In such, compared to optical absorption, the fluorescence emitted on radiative decay to the ground state may display a relatively large Stokes shift and pronounced vibronic structure. In inorganic semiconductors, excitonic absorption usually manifests itself as a series of strong absorption peaks just below the energy band gap, generally without vibrational transitions. A photon may also be emitted as a result of bound electron - hole recombination, resulting in an excitonic emission with very small Stokes shift[23].

Furthermore, in contrast to the delocalized features of excitation in inorganic materials with band structures, the excitations in organic materials are generally localized, due to the localized electron wavefunctions. For instance, the wavefunction coherence in a conjugated polymer extends only about a few repeat units (i. e., the effectively conjugated segment, ECS), but not further. Localization leads to a strong coupling between excitations and local molecular geometry, hence often leading to electron clouds and bond lengths redistribution after excitation. In the case of charged excitations, these geometric relaxations can break the local symmetry, and thus activate vibronic bands in the infrared that are symmetry-forbidden (i. e., Raman-but not IR-active) in the ground state. Consequently, electronic transition moments are strong and highly directional, parallel to the chain or molecular axis. Charged excitations in organic materials are generally more akin to the concept of the

21. 有机材料中的电子跃迁需要同时考虑振动态，与无机材料中电子跃迁和振动态可以很容易地分离不同。

22. 较小的质量使得有机材料的振动频率，即$(f/m)^{1/2}$（f为谐振子强度，m为原子质量），非常大。振动态被视为量子化简谐振动的谐振子，形成构象坐标。

23. 在无机半导体中，激子型吸收通常表现为一系列在能带之下的较强吸收峰，通常没有振动跃迁。光子可以作为束缚的电子-空穴复合的结果被发射出来，导致非常小斯托克斯位移的激子型发射。

"radicalion", as familiar from solution-based chemistry, than the concept of a "polaron" in solid state physics (nevertheless, the term "hole" is commonly used for radical cations)[24].

4) Carrier and Mobility Difference

In contrast to inorganic solids where the allowed energy levels form valence and conduction bands (VB and CB), organic molecular materials are characterized by their HOMO, the highest occupied molecular orbital, and LUMO, the lowest unoccupied molecular orbital. Carrier transport occurs primarily by hopping in organics. For example, electrons and holes on polymer chains hop from one chain to another for transport. In inorganic crystalline solids, the dominant carrier transport mechanism is band-like transport, relying on the presence of a periodic crystalline structure and a well-defined density of states. As a result, the carrier mobility in organic and inorganic semiconductors is significantly different. In organic materials, the mobility of the carriers is $10^{-5} \sim 10^{-3}\ \mathrm{cm^2 \cdot V^{-1} \cdot s^{-1}}$. In inorganic materials, the carrier mobility is $10^{2} \sim 10^{4}\ \mathrm{cm^2 \cdot V^{-1} \cdot s^{-1}}$. Figure 1.12 schematically shows the comparison between the hopping transport in organics and the bandlike transport in inorganics[25].

24. 例如，在共轭聚合物中波函数的相干仅存在于几个重复单元（即有效共轭部分，ECS），不会再多。定域性导致了激发态与局部分子几何构型的强烈耦合，因此在激发之后，电子云和键长都会重新分布。对于带电的激发，这些几何弛豫可以打破局部对称性，因此激活了基态时对称性禁阻的（拉曼而不是红外活性）红外域振动能带。结果，电子跃迁矩很强并且具有很高的方向性，平行于分子链或者分子轴。有机材料中的带电激发，相比于固体物理中极化子的概念，通常更类似于溶液化学中熟悉的自由基离子（不管怎样，"空穴"是对自由基阳离子通常使用的术语）。

25. 这导致了有机和无机半导体中载流子迁移率的显著不同。在有机材料中，载流子迁移率为 $10^{-5} \sim 10^{-3}\ \mathrm{cm^2 \cdot V^{-1} \cdot s^{-1}}$。在无机材料中，载流子迁移率为 $10^{2} \sim 10^{4}\ \mathrm{cm^2 \cdot V^{-1} \cdot s^{-1}}$。图 1.12 给出了有机材料中跃进运输模式和无机材料中带状运输模式的比较。

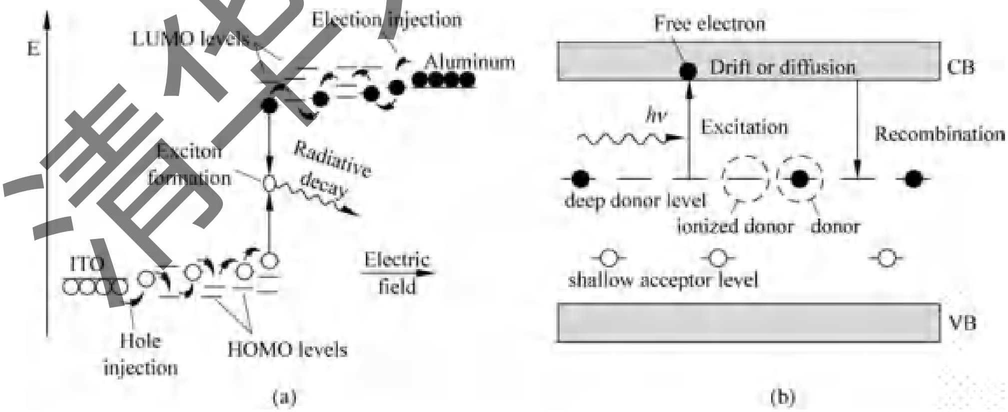

Figure 1.12 Carrier behavior difference between hopping in organic semiconductors (a) and bandlike transport in inorganic semiconductors (b)

5) Intrinsic Defect Difference

In amorphous or surface of crystalline inorganic semiconductor， e. g.， the vapor-deposited inorganic semiconductor films， the surface states and the defect-containing bulk states are not chemically saturated， hence “dangling bonds” and surface attachment of atoms， such as oxygen， exist (Figure 1.13)， leading to large intrinsic defects^{26}.

26. 在无定形无机半导体或者晶态无机半导体的表面，例如气相沉积的无机半导体薄膜，表面态以及含有缺陷的内部态不是化学键饱和的，存在悬挂键及原子(例如氧原子)在表面的结合(图 1.13)，这会导致大量的本征缺陷。

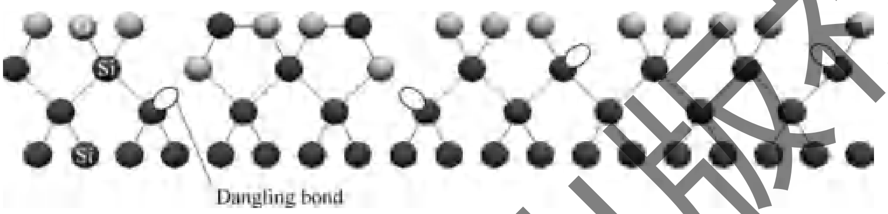

Figure 1.13 Dangling bonds in surface of crystalline inorganic semiconductor

Things are different in organic materials. Organic materials compose of molecules， whose frontier orbitals are saturated. Even a very thin organic film always consists of complete molecules， with the chemical coordination at the film surface equal to that in the bulk. The absent of “dangling bonds” in organic materials leads to far lower intrinsic defects^{27}.

27. 有机材料不是这样。有机材料由分子组成，其前沿轨道饱和。即使是非常薄的有机薄膜，也总是由完整的分子组成，其表面及材料内部的化学配位情况是相等的。有机材料中没有悬挂键，因而本征缺陷非常少。

These “dangling bonds” distort the band structure at the film surface from its bulk properties. In contrast， surface- and bulk-ionization potentials， and electron affinities of organic semiconductors are generally equal.

6) General Property Difference

Due to the weak van de Waals force between molecules， organic semiconductors generally possess low melting point， high compressibility， soft， combustible， soluble in organic solvents， simple and quick preparation/purification. While inorganic semiconductors are generally hard， brittle， and relatively stable in the environments of damp or corrosive. On the other hand， organic materials are compatible to biosystem， but inorganic materials are difficult to be implanted into biosystem^{28}.

28. 由于分子之间较弱的范德瓦耳斯力，有机半导体通常具有低熔点、高压缩系数、柔软、可燃烧、溶于有机溶剂、简单快速的制备/纯化。而无机半导体材料通常坚硬、易碎，当处于潮湿或者腐蚀环境时，相对稳定。另外，有机材料与生物系统兼容，而将无机材料移植到生物系统就比较困难。

In terms of material processing, lots of organic films can be obtained by solution process, which is not only compatible with flexible substrate, but also has the advantages of easy/cheap fabrication and large area. Figure 1.14 demonstrates two solution process methods: roll to roll injket printing and doctor blade printing[29].

29. 在材料加工方面，很多有机薄膜可以溶液法制备，这不仅仅与柔性基底兼容，还具有简便/廉价制备和大面积的优点。图 1.14 展示了 2 个溶液加工方法：卷对卷喷墨打印和刮涂打印。

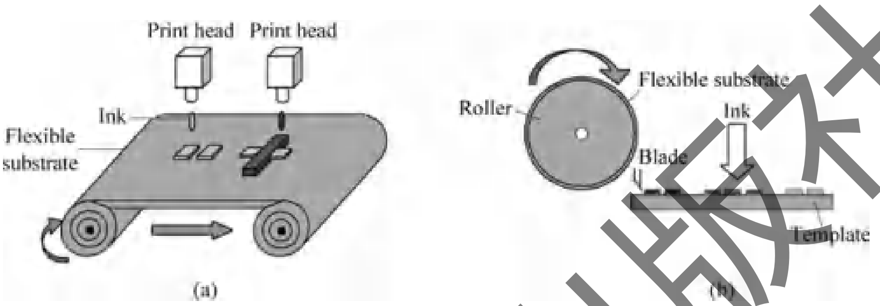

Figure 1.14 Solution processes based on roll to roll ink jet printing (a) and doctor blade printing (b)

1.2.2 Optoelectronic Processes and Device Applications of Organic Materials

Organic optoelectronics mainly deals with the optoelectronic properties of organic materials, which heavily depend on the optoelectronic processes occurring in frontier electronic levels of these materials. There are electron transition and transport, with the former generally relating to the electron transfer between low and high electronic levels, while the latter generally concerning with electron transfer among similar energy levels between molecules[30].

30. 有机光电子学主要针对有机材料的光电子性质，而这些性质强烈地依赖于材料中前沿电子能级中发生的光电过程。材料中存在电子跃迁和电子传输，前者通常与高低能级之间的电子转移有关，而后者通常考虑分子间的相似能级之间的电子转移。

Figure 1.15 shows an organic molecule with different energies. From low to high, there are molecular energy states of S_0, T_1/S_1, and T_2/S_2, representing molecules with energy of ground state, the first triplet/singlet excited state, and the second triplet/singlet excited state, respectively. Also shown in the figure, are many vibrational energy levels representing for the vibration energy of the molecules (short and fine lines) overriding on the pure electronic energy of molecules (long and coarse lines). Different energy state of molecules means that the frontier electrons of the molecule locate at different electronic levels. For example, the S_0 molecular means that electrons with the highest energy in the molecule locate at its HOMO level. The occurrence of all kinds of optoelectronic processes can be described according to Figure 1.15. As can be see, within a molecule, there are electronic transition of absorption, internal conversion, inter system crossing, fluorescence and phosphorescence. By electron moving from an electronic level of a molecule to that of another molecule, there can be electron transition processes of Förster energy transfer and Dexter energy transfer, as well as electron transport process by hopping/trapping/detrapping[31].

31. 图 1.15 表示的是具有不同能量的有机分子。由小到大，分子能量依次为 S_0、T_1/S_1 和 T_2/S_2，分别代表具有基态、第一激发态的三线态/单线态和第二激发态的三线态/单线态能量的分子。图上还包含了在分子纯电子能级上（粗长线）叠加的、许多代表分振动能量的振动能级（短细线）。分子的不同能量状态意味着分子内前沿电子处于不同的电子能级上。例如，S_0 分子代表分子内最高能量的电子处于 HOMO 位置。所有种类的光电子过程可以根据图 1.15 进行描述。如图所见，在分子内存在吸收、内转换、系间窜跃、荧光和磷光电子跃迁过程。通过电子从一个分子的电子能级到另外一个分子能级的运动，可能是 Förster 能量转移和 Dexter 能量转移过程，也可能是通过跃进/俘获/脱俘获过程的电子输运。

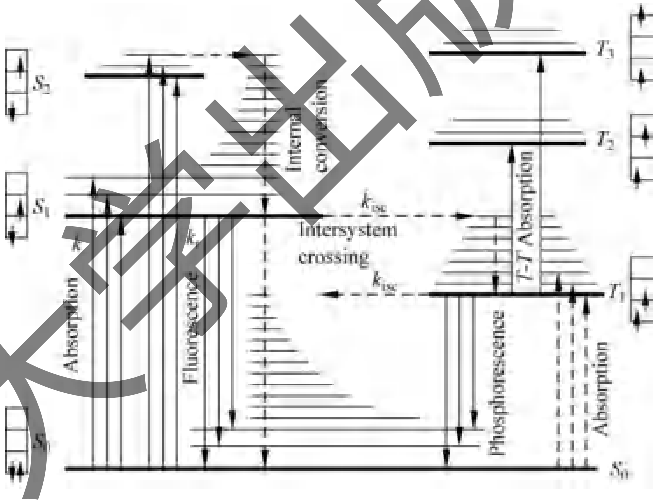

Figure 1.15　An organic molecule in different energy levels

In a common sense, the optoelectronic properties from organic materials exhibit the following features.

(1) Intensive Absorption: Organic materials exhibit good absorption in visible light region with very large extinction coefficient. Hence, when used as active components in photodetector or photovoltaic device, the active layer can be very thin[32].

32. 强吸收：有机材料在可见光范围内表现出良好的吸收现象，具有非常大的消光系数。因此，当在光电检测器或光伏器件中作为活性组分时，其厚度可以很薄。

(2) Large Stokes Shift: Many fluorescent organic dyes show very large spectra shift between absorption and emission, i.e., large Stokes shift. Therefore, organic light-emitting diodes have little reabsorption loss[33].

33. 大的斯托克斯位移：许多荧光有机染料在吸收和发射之间表现出非常大的光谱位移，即大的斯托克斯位移。因此，有机发光二极管光发射的再吸收损失很小。

（3）Strong Fluorescence/Phosphorescence Covering Visible Range：As shown in Figure 1. 16，fluorescence is a spin-allowed radiative decay from singlet excited state to ground state；while phosphorescence refers to the radiative decay from triplet excited state to the ground state. Phosphorescence is generally spin forbidden，which can be released by introducing heavy metal in organic molecules. By molecular design，strong fluorescence or phosphorescence can be obtained with organic materials. Additionally，tailoring molecular structure can tune the emission wavelength，realizing full coverage in the visible range：approximately from 390 nm to 780 nm. Figure 1. 17 is an example for emission color-tuning[34].

34. 覆盖可见光范围的强荧光/磷光：如图 1.16 所示，荧光是自旋允许的单线态激发态到基态的辐射衰变过程；而磷光指的是三线态到基态的辐射衰变。磷光通常是自旋禁阻的，通过在有机分子中引入重金属，可以缓解这个禁阻。通过分子设计，可以实现有机材料的强荧光或者强磷光发射；而且，分子结构的裁剪可以调控发射波长范围，实现可见光范围的全覆盖，大约从 390 nm 到 780 nm。图 1.17 是一个发射光调控的例子。

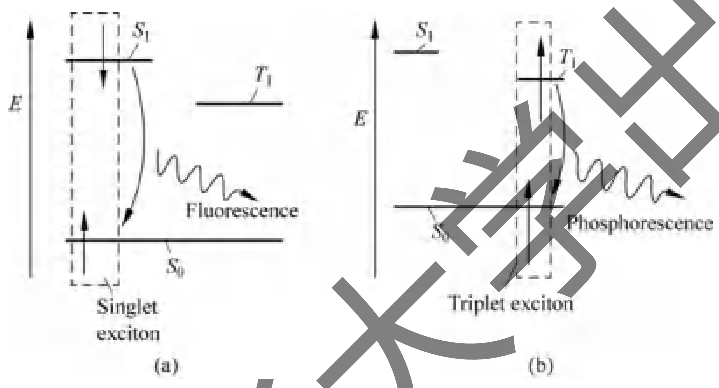

Figure 1. 16 Processes of fluorescence（a）and phosphorescence（b）

Utilizing the optoelectronic properties of organic materials，many organic optoelectronic devices can be realized，including organic field effect transistor（OFET），xerography，optical memory，liquid crystal display（LCD），organic solar cells，photo detector，organic light-emitting diodes（OLED）and organic memory. The main features of the optoelectronic devices are cheap，flexible，easy miniaturization and printable[35].

35. 应用有机材料的光电子特性，可以实现多种有机光电子器件，包括有机场效应晶体管（OFET）、静电复印、光学存储器、液晶显示器（LCD）、有机太阳能电池、光检测器、有机发光二极管（OLED）和有机存储器。有机光电子器件的主要特点是便宜、可柔性、便于小型化和可打印。

The above-mentioned optoelectronic processes/properties of organic materials，as well as their applications in devices will be discussed in detail in the later chapters.

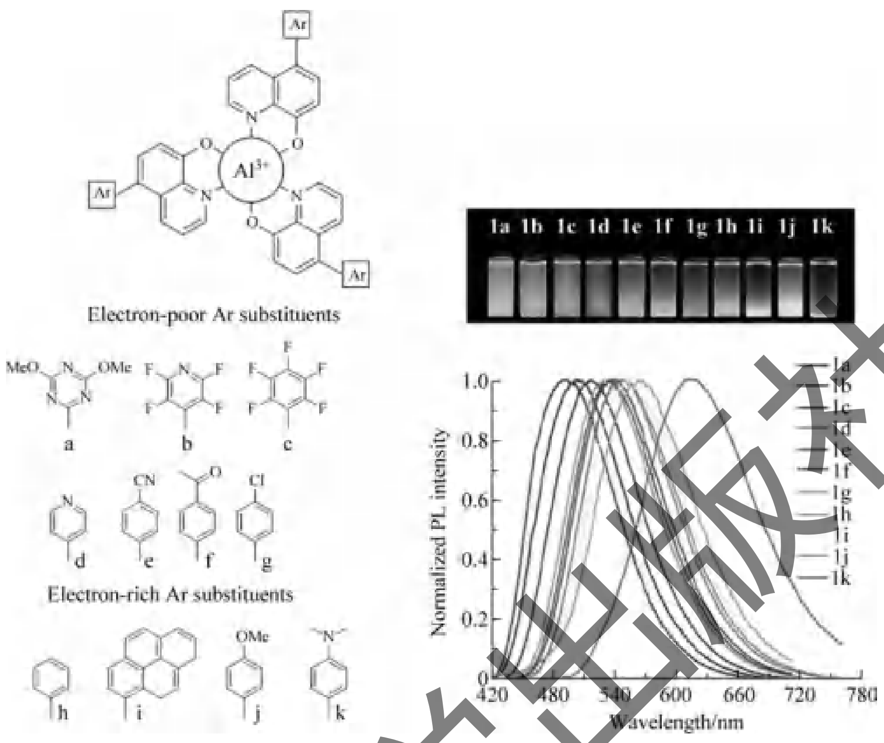

Figure 1.17　Emission color tuning by molecular design

本章小结

1. 内容概要：

本章首先从历史角度，对光电子学进行了评论，然后简明介绍了有机光电子学，包括有机材料的历史、定义、发展、类型/特征，以及它们的主要光电过程及其器件应用。

2. 基本概念： 光电子学、有机材料、有机半导体、小分子、大分子、聚合物、生物分子、光电过程、器件。

3. 主要公式： 无。

Appendix

1. Award Ceremony Speech (2000 Nobel Prize for Chemistry)

“for the discovery and development of conductive polymers”

Plastic that conducts electricity

We have been taught that plastics, unlike metals, do not conduct electricity. In fact plastic is used as insulation round the copper wires in ordinary electric cables. Yet this year’s Nobel Laureates in Chemistry are being rewarded for their revolutionary discovery that plastic can, after modifications, be made electrically conductive. Plastics are polymers, molecules that repeat their structure regularly in long chains. For a polymer to be able to conduct electric current it must consist alternatively of single and double bounds between the carbon atoms. It must also be "doped", which means that electrons can move along the molecule—it becomes electrically conductive. Heeger, Macdiarmid and Shirakawa made their seminal findings at the end of the 1970s and have subsequently developed conductive polymers into a research field of great importance for chemists as well as physicists. The area has also yielded important practical applications. Conductive plastics are used in, or being developed industrially for, e. g. anti-static substances for photographic film, shields for computer screen against electromagnetic radiation and for "smart" windows (that can exclude sunlight). In addition, semi-conductive polymers have recently been developed in light-emitting diodes, solar cells and as displays in mobile telephones and mini-format television screens. Research on conductive polymers is also closely related to the rapid development in molecular electronics. In the future we will be able to produce transistors and other electronic components consisting of individual molecules—which we now carry around in our bags would suddenly fit inside a watch.

2. Award Ceremony Speech (2010 Nobel Prize for Chemistry)

Your Majesties, Your Royal Highnesses, Ladies and Gentlemen. This year's Nobel Laureates in Chemistry are rewarded for a method to link carbon atoms together, and this method has provided chemists with an efficient tool to create new organic molecules. The Laureates have utilized the metal palladium to couple two carbons to one another under mild conditions and with high precision.

Organic molecules contain the element carbon, where carbon atoms are bound to each other to form long chains and rings. Carbon-carbon bonds are a prerequisite for all life on earth and they are found in proteins, carbohydrates and fats. Plants and animals mainly consist of organic molecules in which carbon atoms bind to each other, and we human beings, we who have gathered here today, are to a large extent built up by carbon-carbon bonds. In living organisms, bonds between carbon atoms are created via Natur's own pathways utilizing various enzyme systems.

To create new organic molecules in an artificial manner that can be used as medicines, plastics, and various other materials, we need new efficient methods for synthesizing carbon-carbon bonds in our laboratories.

Looking back in history we find that the German chemist Kolbe synthesized the first carbon-carbon bond in 1845. Since then a number of methods for the synthesis of bonds between carbon atoms have been developed of which several have been awarded with a Nobel Prize. This year's Nobel Prize in Chemistry is the fifth that rewards the synthesis of carbon-carbon bonds.

Richard Heck's pioneering work from 1968－1972 laid the foundation for palladium-catalysed formation of carbon-carbon bonds. He coupled two rather unreactive molecules to one another with the aid of palladium. One of these is a molecule with a handle，e.g. bromobenzene and the other has a double bond and is called an olefin. In 1977，Ei-ichi Negishi reported a mild method to couple one of Heck's unreactive molecules to a carbon bound to zinc with the aid of palladium. Two years later，in 1979，Akira Suzuki found that the corresponding palladium-catalyzed coupling of an unreactive molecule such as bromobenzene to a carbon bound to boron could be made under very mild conditions.

Carbon is stable and carbon atoms do not easily react with one another. Earlier methods used by chemists to bind carbon atoms together were therefore based upon various techniques for rendering carbon more reactive. Such methods worked when creating simple molecules，but when synthesizing more complex molecules chemists ended up with too many unwanted by-products in their test tubes. The palladium-catalyzed cross coupling solved that problem and provided chemists with a more precise and efficient tool to work with. In the Heck reaction，Negishi reaction，and Suzuki reaction，the carbon atoms meet on a palladium atom. When the carbon atoms meet on a palladium atom，chemists do not need to activate the carbon atom to the same extent. This entails fewer by-products and a more efficient reaction.

The palladium-catalyzed cross couplings have been used for large-scale industrial manufacturing of，for example，pharmaceuticals，agricultural chemicals，and organic compounds that are used by the electronic industry.

Professors Heck，Negishi and Suzuki：You are being awarded the Nobel Prize in Chemistry for palladium-catalyzed cross couplings in organic synthesis and with these achievements you have provided organic chemists with efficient and useful methods for synthesizing compounds that were previously difficult to obtain. On behalf of the Royal Swedish Academy of Sciences，I wish to convey to you our warmest congratulations and I now ask you to step forward to receive your Nobel Prizes from the hands of His Majesty the King.

3. Award Ceremony Speech（2010 Nobel Prize for Physics）

Your Majesties，Your Royal Highnesses，Ladies and Gentlemen. The 2010 Nobel Prize in Physics is awarded for research concerning a new ultra-thin material with exceptional properties. This material is called graphene and is the first of a new class of materials. Surprisingly，it can be produced in small quantities with the help of ordinary office materials such as pencils and adhesive tape.

Carbon is probably the most important element in nature. It is the basis of all life that we know of. The most common form of pure carbon is graphite，which we find in pencils，for example. If carbon is subjected to high pressure，it can also assume the form of a diamond，which is considerably more expensive and is undoubtedly found in some of