

Chapter 1

Introduction

1.1 Background

Inorganic semiconductors and metal have long been well known for their excellent conductive, optical, and mechanical properties. At present, however, the potential of these conventional inorganic materials seems almost fully exploited. The ongoing miniaturization of integrated circuits is facing the physical limit as the device size approach the de Broglies's wavelength that will lead to the widening of the band gap of semiconductor [1, 2]. This demonstrates the demand for new functional materials with improved and novel properties. Since the discovery of metallic conduction in doped polyacetylenes in 1977 [3], the properties of organic semiconductors have attracted an increasing industrial interest. Numerous investigations of bulk properties such as photoconductivity [4], carrier transport [5] and electroluminescence [6] have led to their rapid development in light emitting devices [7], field effect transistors [8] and solar cells [9]. Moreover, the more flexible van der Waals bonding of organic molecules, as compared with the rigid covalent bonding of inorganic material, allows the possibility to develop flexible devices [10-12].

Instead of using conjugated polymers, one can also take advantage of the self-assembling ability of small organic molecules to form perfect molecular crystal, which provides a channel for charge carrier to transport along [13, 14]. The structures of molecular crystals are conveniently classified into three groups depending on the number of different intermolecular forces operating. The simplest group is composed of non-polar molecules where only dispersion and repulsion forces operate. The second group is composed of molecules with polar substituents where dipole-dipole and

dipole-induced dipole forces operate. Hydrogen-bonded molecular crystals form a special case within this group. Finally, in the third group are crystals in which charge-transfer interactions occur between different molecules forming electron donor-acceptor complexes or charge-transfer salts [15]. These molecular crystals are very fascinating for that some of them may self-assemble to form a columnar stack due to the π - π interactions between the aromatic cores. Consequently, a one-dimensional (1D) pathway for electronic charge to transport was formed. Figure 1-1 demonstrates planar molecules stacking into columnar aggregates under the force of π - π interactions. These materials exhibit a strong anisotropy in their optical and carrier transport properties, as indicated by the arrow in Figure 1-1. The one-dimensional conducting pathways play as potential charge transport media in molecular electronic devices. In order to achieve rapid migration of electronic charge in these organic semiconducting materials, well-ordered domains that extend over large distances, preferably into the micrometer range, are required.

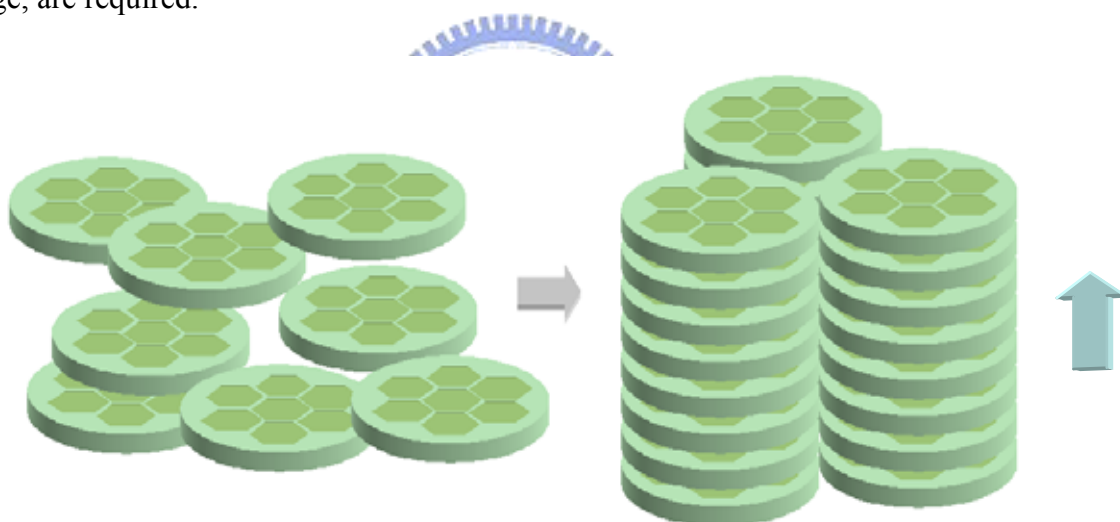


Figure 1-1 Self-assembly of planar molecules resulted in π -stacked columnar aggregates. The vertical arrow indicated the one-dimensional charge transport pathway along the columnar stacks.

1.1.1 Planar organic materials

Planar organic materials consist of molecules with a flat aromatic core, which is due to the fact that the orbital overlap between the p-orbitals of adjacent core atoms is optimal for a planar conformation [16]. This results in extensive molecular π -orbitals, above and below the plane of the disk, in which the p-electrons are delocalised. These delocalised

p-electrons result in the π - π interactions between the aromatic cores, and that makes these flat organic molecules form the columnar aggregates in a milder condition. There are many examples for the self-assembled molecular crystal [17], in this thesis I focus on three kind of small molecules, which are coronene and perylene tetracarboxylic dianhydride (PTCDA), molecules possess an all carbon-based aromatic core, and Copper phthalocyanine (CuPc), a different heterocyclic core structure with the incorporation of nitrogen and copper atoms in the aromatic system. The three different planar organic materials studied in this thesis are depicted in Figure 1-2.

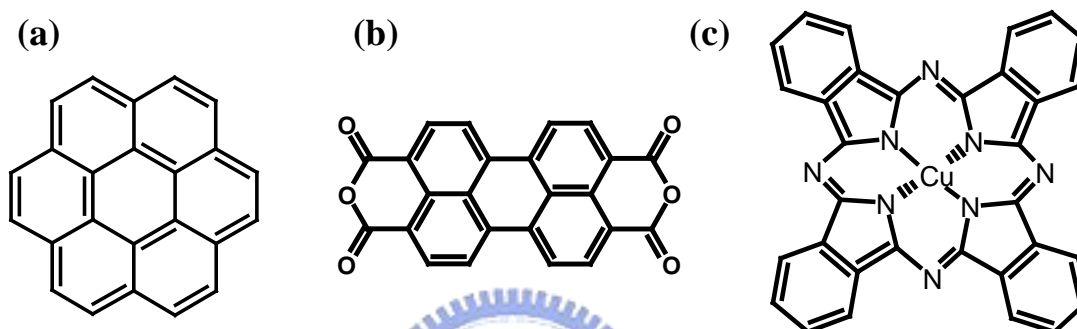


Figure 1-2 Planar molecule studied in this thesis: (a) coronene, (b) perylene tetracarboxylic dianhydride, and (c) copper phthalocyanine.

1.1.1.1 Coronene

The oligocenes have recently attracted considerable attention, since their charge transport properties were reported to be excellent [18, 19]. An important feature of oligocene seems to be that it can be grown in well-ordered thin films. The most famous one of oligocenes is the pence, which possesses the highest charge mobility and have been well studied for the organic thin film transistor device [20, 21]. Coronene, one of oligocenes, has similar delocalised p-electrons system but with a two-dimensional structure, a planar structure, which makes it easier to form a well-stacked molecular crystal.

1.1.1.2 Copper phthalocyanine (CuPc)

Phthalocyanines (Pc's) are rather popular [22 – 25], they exhibit a certain degree of “specific tenability”, due to the possible central metal ion, which can be changed within a broad range, and due to the choice of the sidegroup(s) [26, 27]. CuPc is particularly attractive, since it is considered a good candidate as a p-type conducting organic material

[28], and after fluorinating the sidegroups, $F_{16}CuPc$ can play as an n-type conducting organic material [29]. Moreover, it is the most stable n-type conducting organic material that can operate in air without serious degradation reported so far. As a blue dye it is also interesting for optoelectronic applications [30, 31].

1.1.1.3 Perylene tetracarboxylic dianhydride (PTCDA)

The perylene-derivative PTCDA (3,4,9,10-perylene-tetracarboxylic dianhydride, $C_{24}H_8O_6$, a red dye) has long been regarded as a model system for organic molecular beam deposition (OMBD) [32-34]. Its bulk structure (actually α and β phase) exhibits layered molecular planes, and it was expected that the regular stacking of these planes (along the [102] direction in a phase notation) is favourable for well-behaved film growth. The optical properties [35, 36] as well as the vibrational properties [37, 38] have been thoroughly studied.

1.1.2 Molecular Electronic Devices

Aromatic planar compounds, such as perylenes and phthalocyanines, are commercially exploited as pigments and dyes because of their strong absorption of visible light to give bright colours. The only application where the remarkable conductive properties of these materials is implemented is in the area of photocopiers and laser printers. However, the highly one-dimensional, coaxial nature of conduction with the possibility of controlling the alignment of the columnar stacks by mechanical or magnetic means justifies more electronic applications. It is mainly the combination of good processability and the semiconductive properties that offers multiple viable possibilities in the field of molecular electronics. The potential electronic devices in which planar organic materials may serve as active components comprise organic field-effect transistors, light-emitting diodes, and photovoltaic cells.

1.1.2.1 Organic Thin Film Transistors (OTFTs)

Organic, flexible components are possible candidates for cheap data storage, such as chip cards and identification tags. For these particular applications the present crystalline silicon technology is inappropriate and too expensive. It is here that the organic semiconductive materials may find a niche.

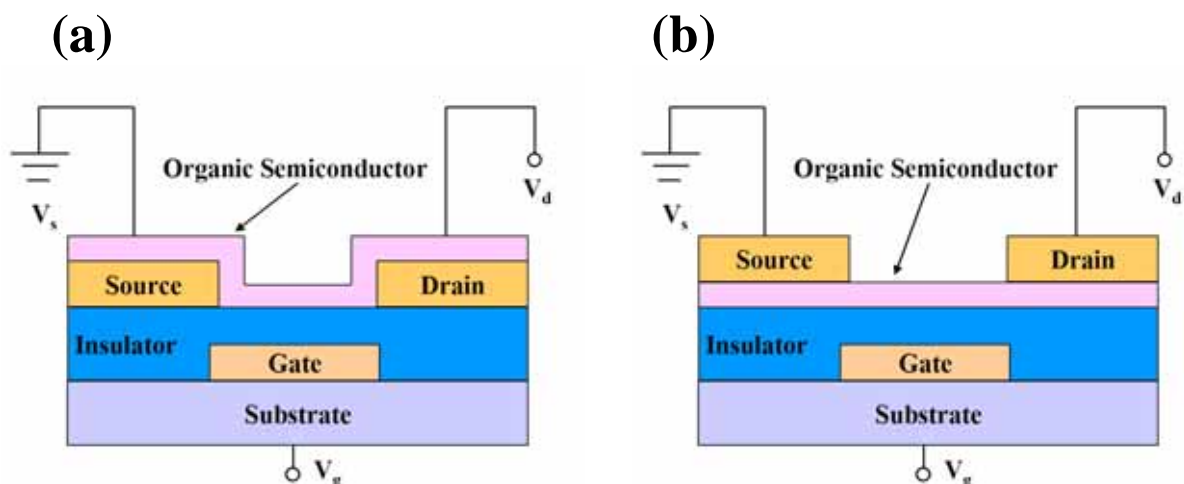


Figure 1-3 Two kinds of scheme of organic thin film transistor: (a) bottom contact mode, and (b) top contact mode.

Since the first observation of the field-effect in thin film devices of conjugated molecules [3], investigations have been extended with well-defined smaller organic oligomeric compounds [39, 40]. For devices based on pentacene [20, 41] performances have been steadily improved resulting in the extremely high FET mobility of $1.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ reported by Nelson and co-workers [42]. Most organic semiconductors display p-type semiconductivity. However, for some aromatic complexes such as a derivative of perylene [43, 44] and a phthalocyanine complex [29, 45], electron-transporting character has been demonstrated.

There are two kinds of structure that OTFTs are fabricated. One is the bottom-contact scheme, in which source and drain electrodes are beneath the organic semiconductor layer, the other is top-contact scheme, in which source and drain electrodes are above the organic semiconductor layer, as shown in Figures 1-3. Since the organic film deposited on insulator and electrode possesses different domain boundaries, and that will affect the carrier transporting ability [21]. To have a better charge carrier mobility, the top-contact scheme is the better way to fabricate the OTFT device. However, this approach is much complicated and incompatible with the traditional silicon process.

The most promising device characteristics combined with flexibility and ease of process ability, have been realized for thiophene derivatives [46-48], and particularly for the regioregular poly(3-hexylthiophene), P₃HT. One of the most remarkable development

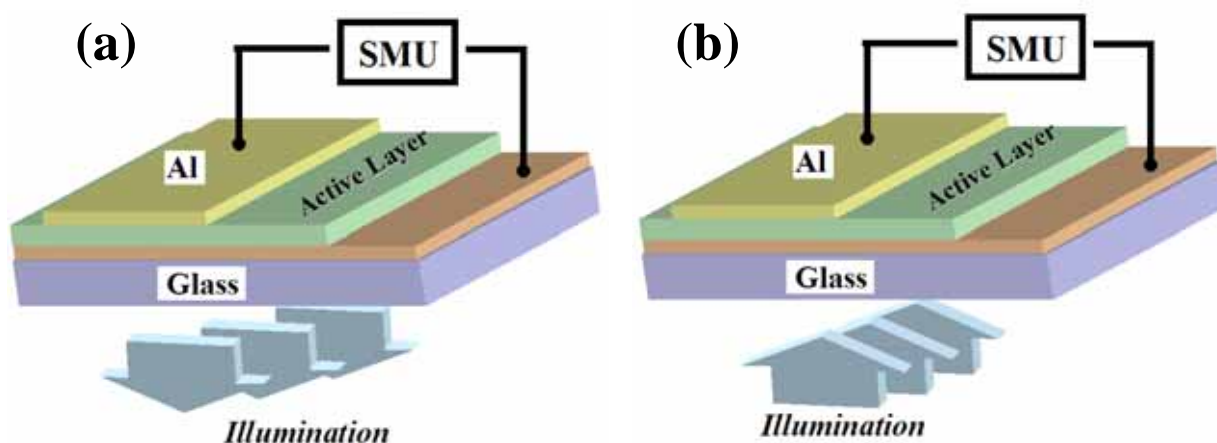


Figure 1-4 The scheme of (a) organic light emitting diode, and (b) photovoltaic device.

is the FET-LED device, in which a P₃HT-based thin-film transistor is used to drive a polymer light-emitting diode to produce light [49].

1.1.2.2 Organic Light Emitting Diodes (OLEDs)

The generation of light by applying an electric field –electroluminescence– has been demonstrated to be highly efficient for the conjugated polymer polyphenylenevinylene (PPV) [50]. This property can be exploited in a thin layer device or light-emitting diode, LED. Compared to conventional inorganic LEDs, the organic devices offer specific advantages and are expected to yield new applications, such as large-area flexible displays.

A simple LED device is shown in Figure 1-4 (a). Electrons and holes are injected at opposite sides of a thin semiconductive film and migrate towards each other under the influence of the applied electrical field. If the charges of opposite sign are close to each other, charge recombination may occur and an exciton can result. This excited state can decay to the ground state with the emission of light.

Organic planar molecules have only been used as the hole-transporting layer in organic LEDs [51, 52]. The beneficial self-organising nature of planar molecules into large, well-organised domains has been shown to improve the device characteristics. Unfortunately, most self-assembling aromatic systems cannot be used as the active, emissive layer in organic LEDs because of the low luminescence efficiency. This is

mainly owing to the high symmetry of molecules that forbid certain energy transfer; consequently most of planar molecules cannot relax the exciton in the way of light emitting.

1.1.2.3 Photovoltaic Devices

The reverse process of that implied in a LED is active in a photovoltaic device. Here an electric potential is induced when the material is illuminated. A simple photovoltaic device is shown in Figure 1-4 (b). This photovoltaic effect shows some similarity with the photosynthesis in plants where visible light is converted into electrical energy. Numerous attentions have been given to the incorporation of organic materials in photovoltaic cells with the aim of fabricating cheap and easily processable devices [53, 54]. Crucial prerequisites of these organic solar cells, which have not yet been achieved completely, are high conversion efficiencies and long lifetimes. However, if all requirements can be realized, organic solar cells might eventually form a useful alternative to the fossil fuels without environmental pollution problems.

Porphyrin and phthalocyanine compounds have drawn considerable attention since they have high absorption coefficients in the visible. However, the use of one type of planar macrocycle covers only a limited region of the available solar energy spectrum, which limits the device performance. Therefore, the possibility of combining different aromatic materials is an approach to solve the issue [55, 56].

1.1.3 One Dimensional Nanostructures

Recently, nanostructures such as thin films, wires, rods, belts, tubes, and dots have become the focus of intensive research owing to their peculiar and fascinating properties in mesoscopic physics [57-59]. Finding a way to fabricate such minuscule structures is important for modern science and technology. There are many ways to produce new types of nanostructures; the most successful example is provided by microelectronics, where “smaller” has meant greater performance, i.e. more components per chip provide faster operation, lower cost, and less power consumption [60]. It is also known that a lot of interesting phenomena are associated with nanostructures, e.g. size-dependent excitation or emission [61], quantized (or ballistic) conductance [62], and Coulomb blockade (or single-electron tunneling, SET [63]). It is generally accepted that quantum confinement

of electrons by the potential wells of nanometer-sized structures may provide the most powerful mean to control the electrical, optical, magnetic, and thermoelectric properties of a solid-state functional material.

Among these nanostructures, one-dimensional (1D) nanostructures are the most interesting topic due to that it provide a good system to investigate the dependence of electrical and thermal transport of mechanical properties on dimensionality and size reduction (or quantum confinement). They are also expected to play an important role as both interconnects and functional units in fabricating electronic, optoelectronic, electrochemical, and electromechanical devices with nanoscale dimensions. In comparison with quantum dots and wells, the development of 1D nanostructures has been slow until very recently, as hindered by the difficulties associated with the synthesis and fabrication of these nanostructures with well-controlled dimensions, morphology phase purity, and chemical composition. Although 1D nanostructures can now be fabricated using a number of advanced nanolithographic techniques [64], such as electron-beam or focused-ion-beam (FIB) writing [65], and X-ray or extreme-UV lithography [66], further development of these techniques into practical routes still requires great ingenuity. In contrast, unconventional methods base on chemical synthesis might provide an alternative strategy for producing 1D nanostructures in terms of material diversity, cost throughput and the potential for great-amount production [67].

To date, the most representative 1D nanostructure is the carbon nanotubes (CNTs), which can be produced in a great quantity by chemical vapor depositeon (CVD). However, the lowest process temperature to fabricate CNTs through the catalytic decomposition method was about 400 °C on the assistance of plasma enhanced chemical vapor deposition (PECVD) with Ni alloy as catalyst [68]. To fabricate similar 1D nanostructures in a lower temperature still lefts a plenty of space to explore.

1.2 Aims of this Thesis

It will be demonstrated in this thesis that several planar organic materials can self-assemble to form one-dimensional nanostructures, which provide efficient anisotropic charge transport pathways and can be utilized as electron emitters when biased in vacuum.

In the present work I will investigate how film growth conditions can influence the ultimate film morphology. Furthermore, I will characterize these 1D nanostructures with Grazing incident X-ray diffraction, Raman spectrometer and high-resolution transmission electron microscope (HRTEM) to identify their crystallinity. Besides, since thermal stability is a crucial property to evaluate feasibility for applying a new material, TDS-APIMS was used to monitor thermal desorption behavior. The ultimate goal is to evaluate electron-emitting ability of these organic fibers in order to develop a new application in organic electronic devices.

The objectives of this thesis are as follows:

- To study and review relevant literature on organic field emission materials.
- To synthesis 1D nanostructure with all carbon-based polycyclic aromatic hydrocarbon, i.e. coronene.
- To synthesis 1D nanostructure with phthalocyanine molecules, which are consisted with aromatic hydrocarbon, nitrogen and metal atoms, i.e. CuPc.
- To synthesis 1D nanostructure with perylene derivatives, which are consisted with carbon-based aromatic core and two symmetrical anhydride groups, i.e. PTCDA.
- To investigate the effect of various substrate on film morphology.
- To investigate the effect of various substrate temperature on film morphology.
- To characterize the obtained organic fibers with regard to their physical, thermal and electrical properties.

1.3 Outline of this Thesis

The synthesis of 1D organic nanobibers have been investigated in an attempt to discover the factors that dominate the film morphology. All of the planar molecules investigated display π -stacked columnar structures in which charge can migrate within and emit electrons from the fiber tip when biased in vacuum and in a high electric field.

In addition to this introductory chapter, the thesis includes 5 chapters. In Chapter 2 the literature review and some theory quoted in this thesis are presented. Owing to the surface energy and intermolecular forces are crucial factors that influence the film morphology; I took a lengthy paragraph to explain how these force affect the result.

Chapter 3 deals with the discussion of various factors that influence the morphology of coronene thin film. After finding an optimized way to synthesis 1D nanofibers, further characterization of HRTEM, TDS-APIMS and field emission were discussed. In Chapter 4 CuPc molecule, a heterocyclic planar molecule was used to form 1D nanostructure. In this study, substrate temperature that can alter the surface energy plays a crucial role to form the desired nanofiber structure. The resulting CuPc nanofibers were characterized with regard to their physical and electrical properties. The recently synthesized high-aspect-ratios PTCDA nanofibers are introduced in Chapter 5. Although this molecule has been studied thoroughly in molecular epitaxy by other researchers, the film morphology normally shows an island or facet structure, few were reported to form an out-of-plane nanofibers. In this study, by the assistance of pillar-structure topography and reactive sites on substrate, I synthesized PTCDA nanofibers on Ti metal substrate firstly. The field emission characterization also reveals a remarkably good result.

The dissertation is concluded with a chapter, which summarizes the results obtained on organic nanofibers. In this chapter an overview of the most important conclusions is given and some general remarks relevant to applications in molecular electronic devices are made.

