1.1 Introduction

Crystals have been attracting mankind in the past due to their aesthetic beauty and it ranges from the most valuable diamond to artificial stones like American diamond. Before 20th century the crystals are extensively utilized for patterned purpose. Their roles in scientific approach were understood only after application of the material in various fields by earlier scientists. Single crystal growth has prominent role to play in the present era of rapid technical and scientific advancement, where the application of crystals has unbounded limits. Many of the useful applications of crystals arise not only from their close approach to perfection but also from the ability to control and manipulate their defects. The mission of crystal grower is to adopt suitable technique for a particular material to produce high quality crystal with reasonable size from its polycrystalline form. However production of most of the single crystals is a difficult process and is requiring significant technical skills in the synthesis of materials, growth, processing and characterization [1].

1.2 Significance of single crystal growth

The growth of single crystals is both scientifically and technologically important and the applications of such crystals today range from electronics to thermal management to synthetic gemstones. Single crystals reveal the fundamental properties of materials, especially properties with directional dependencies, which make crystals unique in technological applications. Crystal growth technology is largely dependent on crystals such as Nonlinear Optical (NLO) crystals, piezoelectric crystals, ferro-electric crystals, sensitive crystals and crystalline films. The thirst for the crystals in these applications has resulted in the demand for the preparation of large size single crystals. The preparation of single crystals is mainly based on the availability and nature of the starting materials and their physico-chemical properties. Fields as diverse as physics, chemistry, chemical engineering, mineralogy and biology have contributed much to the field of
crystal growth, also these fields benefited from crystal growth. Crystal growth concept has been fundamental to many areas of science and technology.

Crystals can be grown in any of the following four transformations [2]
1. Solid-state reaction involving solid-solid phase transition.
2. Solution growth process involving liquid-solid phase transition.
3. Vapour growth process involving vapour-solid phase transition

The general condition for all the above mentioned process is that the growing crystals must have lower free energy than the initial state of the system.

1.3 Crystal Growth Technique

A number of crystal growth techniques are developed to grow bulk size single crystals. The low and high temperature solution growth and melt growth methods come under liquid-solid transformations. In the following section, fundamentals of low temperature solution growth are described.

1.4 Crystallization from Low Temperature Solution

A large amount of crystals produced for many basic research and technological applications are from low temperature solution growth. The method involves seeded growth from a previously saturated solution, where the necessary supersaturation is generated. Growth of crystals from solution at low temperature has many advantages over the other growth methods though the rate of crystallization is slow. Since the growth is carried out at room temperature, structural imperfections in low temperature solution grown crystals are relatively low [3]. Rate of growth from solution falls in the range 0.1–10 mm per day, which is much smaller than the rates of growth from melt method.

1.5 Solution, Solubility and Supersolubility

Solution is a homogeneous mixture of a solute in a solvent. Solute is the component, which is present in a smaller quantity. Solubility of the material in a solvent decides the amount of the material, often used which is available for the
growth and hence defines the total size limit. Solubility gradient is another important parameter, which dictates the growth procedure. Growth of crystals from solution is mainly a diffusion-controlled process; the medium must be viscous to enable faster transference of the growth units from the bulk solution by diffusion. Hence, a solvent with less viscosity is preferable. Supervsaturation is an important parameter for the solution growth process. The solubility data at various temperatures are essential to determine the level of supersaturation. Hence, the solubility of the solute in the chosen solvent must be determined before starting the growth process. The solubility diagram is divided into three zones, which are termed as region I, region II and region III (Fig. 1.1). Region I corresponds to the undersaturated zone, where crystallization is not possible. This region is thermodynamically stable. The region II between the supersolubility curve and the solubility curve is termed as metastable zone where spontaneous crystallization is improbable. Seeded crystal growth can be achieved in this region. The unstable or labile zone (region III) where the spontaneous nucleation is more probable.

![Solubility diagram](image)

**Fig. 1.1 Miers solubility curve**

In order to grow crystals, the solution must be supersaturated; the concentration of the solute in the solvent should be more than the equilibrium concentration. Supersaturation is the driving force, which governs the rate of crystal
growth. The supersaturation of a system may be expressed in number of ways. The degree of supersaturation of a solution is defined using the concept of absolute supersaturation ($\alpha$)

\[
\alpha = C - C_0
\]

where $C$ is the concentration of the dissolved substance at a given moment and $C_0$ is its solubility limit. The degree of supersaturation can also be defined as the relative supersaturation given by

\[
\beta = \frac{C - C_0}{C_0} = \frac{\alpha}{C_0}
\]

or as the coefficient of supersaturation. The quantities, $\alpha$ and $\beta$ are obviously inter related [4, 5].

1.6 Nucleation

Crystallization kinetics is an essential part in crystal growth that is governed by the level of supersaturation. In a supersaturated solution the process of crystal growth proceeds in two stages. The first step (primary process) involves the formation of a microscopic nucleus. The second step (secondary process) involves the successive growth of this nucleus to yield the crystal and its habit. The simplest theory involves the consideration of the energy reduction on compound solidification. So the comprehensive study on the growth of crystals should start from an understanding of nucleation process [6].

1.7 Methods of Crystallization

Low temperature solution growth method can be subdivided as

(i) Slow cooling method

(ii) Slow evaporation method

(iii) Temperature gradient method
1.8 Crystallization by slow cooling method

This is one of the best methods to grow bulk single crystals. In this method, supersaturation is produced by a change in temperature usually throughout the whole crystallizer. The crystallization process is carried out in such a way that the point on the temperature dependence of the concentration moves into the metastable region along the saturation curve in the direction of lower solubility. Since the volume of the crystallizer is finite and the amount of substance placed in it is limited, the supersaturation requires systematic cooling. It is achieved by using a thermo stated crystallizer and volume of the crystallizer is selected based on the desired size of the crystals and the temperature dependence of the solubility of the substance. The temperature at which such crystallization can begin is usually within the range from 45 to 75 °C and the lower limit of cooling is the room temperature.

1.9 Crystallization by slow evaporation method

In this method, an excess of a given solute is established by utilizing the difference between rates of evaporation of the solvent and the solute. In contrast to the cooling method, in which the total mass of the system remains constant, in the solvent evaporation method the solution loses particles which are weakly bound to other components, and therefore, the volume of the solution decreases. In almost all cases, the vapour pressure of the solvent above the solution is higher than the vapour pressure of the solute and therefore, the solvent evaporates more rapidly and the solution becomes supersaturated [3]. Usually, it is sufficient to allow the vapour formed above the solution to escape freely into the atmosphere. This is the oldest method of crystal growth and technically, it is very simple. Typical growth conditions involve temperature stabilization to about ± 0.05 °C and the rate of evaporation of a few mm³/hr.

1.10 Temperature gradient method

This method involves the transport of the materials from a hot region containing the source material to be grown to a cooler region where the solution is supersaturated and supplied to the growing crystal. The main advantages of this method are given below
(i) Crystal grows at a fixed temperature
(ii) Insensitive to change in temperature provided both the source and the
    growing crystal undergo the same change
(iii) Economy of solvent and solute

The principal factors in determining a satisfactory crystal are

(i) Nature of the seed
(ii) The temperature lowering (or evaporation) rate
(iii) The agitation of the crystal/solution

1.11 Application of Crystals
1.11.1 Nonlinear Optics

Nonlinear optical process is useful in optical communications, signal processing, laser surgery, parallel image processing and integrated optics. Nonlinear optics (NLO) has gained importance with the advent of lasers followed by a demonstration of harmonic generation in quartz by Franken et al. [7]. It deals with the interaction of intense electromagnetic field in a suitable medium, producing magnified fields that are different from the input field in frequency, phase or amplitude. NLO is essentially a material phenomenon and the usual nonlinear optical medium is a crystal. Hence, the search for new nonlinear optical materials with superior properties acquired importance in recent years.

Frequency conversion is an important and popular technique for extending the useful wavelength range of laboratory lasers. Despite considerable efforts over the last 25 years only single crystal of a handful of materials, Lithium niobate (LiNbO3), Potassium Dihydrogen Phosphate (KDP), Ammonium Dihydorgen Phosphate (ADP), Triglycine sulfate (TGS), barium borate and urea are available. While each one of these crystals is attractive for certain particular uses, they all have limitations other than their nonlinear and phase matching properties.

A crystal which exhibits the following properties is required for nonlinear device fabrication,
\begin{itemize}
\item High effective nonlinear optical coefficient
\item Good optical quality
\item Wide transparency region
\item Good mechanical and chemical stability
\item Low absorption
\item Easy device fabrication
\end{itemize}

\subsection{1.11.2 Nonlinear optical effects}

The dependence of the material properties on the field strengths is the origin of the nonlinear optical responses. In nonlinear optics, the polarization can be described by a power series in $E$ by

$$P = \varepsilon_0 (\chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \ldots)$$

(1.3)

$$P = P^{(1)} + P^{(2)} + P^{(3)} + \ldots$$

(1.4)

where $\varepsilon_0$ is the permittivity of the vacuum, $E$ is the electric field component of the electromagnetic wave, and $\chi^{(2)}$ and $\chi^{(3)}$ are known as the second- and third-order nonlinear optical susceptibility respectively. These susceptibilities depend on the frequencies of the applied fields. $P^{(2)}$ and $P^{(3)}$ are the second and third order polarization respectively. The second order nonlinear optical interactions occur only in noncentrosymmetric crystals and vanish in materials that possess inversion symmetry. The third order nonlinear optical interactions occur in both centrosymmetric and noncentrosymmetric crystals [8].

\subsection{1.11.3 Second order nonlinear effect}

Different nonlinear processes involving second order susceptibility $\chi^{(2)}$ can be understood by considering the second order polarization $P^{(2)}$. The optical field incident on the nonlinear optical medium consists of two distinct frequency components represented by

$$P^{(2)} = \varepsilon_0 \chi^{(2)} E^2$$

(1.5)

$$E(t) = E_1 e^{-i\omega t} + E_2 e^{-i\omega t} + \ldots$$

(1.6)
1.11.4 Third order nonlinear effect

Different nonlinear processes involving third order susceptibility $\chi^{(3)}$ can be understood by considering the third order polarization $P^{(3)}$. The optical field incident upon the nonlinear optical medium consists of three distinct frequency components represented by

$$P^{(3)} = \varepsilon_0 \chi^{(3)} E^3$$

$$(1.7)$$

$$E(t) = E_1 e^{-i\omega_1 t} + E_2 e^{-i\omega_2 t} + E_3 e^{-i\omega_3 t} + ...$$

The first systematic investigation of third-order nonlinearity on conjugated systems was conducted by Hermann [9] in 1973, in which the author measured the $\gamma$ of trans $\beta$-carotene using Third Harmonic Generation (THG). Soon after, a theoretical analysis by Rustagi and Ducuing [10] recognized the importance of $\pi$-electron conjugation in determining third order NLO properties. Following the path of second-order nonlinear materials, third order nonlinear materials also have been shown to be affected by donor-acceptor groups, symmetry, the nature of the $\pi$-electron bonding sequence, the dimensionality, and the substitution of alternate atoms into the conjugated structure; however, no clear structure property relationship has been forged. Third-order materials are not constrained to be acentric and thus do not require any bulk order. Therefore, all materials including random media such as liquids and amorphous structures such as glass, exhibit $\chi^{(3)}$. Using polyenes, Helflin and Garito [11] have shown that similar to second-order materials, trans conformations seem to generate larger third-order NLO response than cis conformations. Garito et al. [12] also used a series of one and two dimensional $\pi$-conjugated molecules to show, that higher dimensionality will decrease the third-order optical nonlinearity. Furthermore, Ducuing [13] suggested that the $\gamma$ value should decrease as the square root of the dimensionality. Also, charge-transfer complex formation seems to be an effective means of enlarging third-order optical nonlinearity, as shown by Kakuta [14] in tetrathiofulvalene and tetracyanoquinodimethane. Inorganics such as Beta Barium Borate (BBO) and Lithium niobate (LNB) have been widely used in device applications; however, organic materials, due to their versatility and ease of modification, hold much promise.
for the future. To have the potential to be used in a practical NLO device, in addition to exhibiting a strong NLO response, a material should possess a combination of photophysical properties such as high laser damage threshold, fast optical response time, wide phase matchable angle, structural flexibility and adaptability, optical transparency, ease of fabrication, nontoxicity, high mechanical strength, and environmental and thermal stability [15]. Compared to inorganic materials, organic material fulfills many of these requirements. However, organic material typically has short comings in environmental and mechanical strength, performance at high and low temperatures, and linear transparency [15,16].

1.12 Measurement Techniques of NLO Response

Quantum mechanical calculation of molecular susceptibilities is a very useful tool for forming a relationship between molecular structure and NLO response; however to truly test the theory, measurements on the material must be made. The most common techniques for measuring $\chi^{(3)}$ are the Kurtz powder technique [17,18], the Maker fringe [15, 19, 20] and phase-matching methods [15, 21], Electric Field Induced Second Harmonic generation (EFISH) [9,15,17] and the Hyper-Rayleigh scattering [15, 22] technique. The most common methods for measuring $\chi^{(3)}$ are Third Harmonic Generation (THG) [15, 17, 23, 24] Degenerate Four-Wave Mixing (DFWM) [25-28, 15, 17]. EFISH, the optical Kerr gate [14, 29, 30] method, the optical power limiting [15, 31, 32] technique and the Z-scan [17, 19, 33-35] method. $\chi^{(3)}$ is a fourth-rank tensor that is the lowest optical nonlinearity that does not disappear in isotropic media such as liquids, solutions and amorphous polymers. In an isotropic medium, there remain three independent nonzero components of the third-order susceptibility [16].

1.13 Z-scan

A good complement for DFWM is the Z-scan technique, in that it can simultaneously measure the nonlinear absorption (NLA) and nonlinear refraction (NLR), which are related to the imaginary and real parts of $\chi^{(3)}$ respectively. Z-scan is a self-focusing technique developed by Sheik-bahae et al. [33] in 1990 that involves focusing a laser beam through a thin sample and then detecting the light transmitted
by a small aperture in the far field, in which the nonlinear medium acts like an intensity-dependent lens. The goal of a Z-scan measurement is to obtain the aperture transmission as a function of sample position (Z) on the Z-axis. From the transmission curves, the magnitude, sign and real and imaginary parts of $\chi^{(3)}$ are then extracted [16]. Not only does the Z-scan have the advantage of being a simple technique, it is extremely sensitive and provides fast and clear results. However, Z-scan cannot measure off-diagonal elements of the susceptibility tensor and is greatly affected by beam shape, beam quality, sample distortions, and thermal effects. Furthermore, the beam often comes to a focus inside the sample, there is a significant possibility of damage to the sample or sample holder at high light intensities.

The sample causes an additional focusing and defocusing, depending on whether nonlinear refraction is positive or negative. The sensitivity to nonlinear refraction is entirely due to the aperture and the removal of aperture completely eliminates the effect. The enhanced transmission near the focus is suggestive of the saturation of the absorption at a high intensity. Absorption saturation in the sample enhances the peak and decreases the valley in the closed aperture Z scan. However, instead of analyzing the entire transmission curve, it is possible to quickly get the sign and magnitude of the nonlinearity for some special cases by analyzing the shape of the curve. For a material with cubic nonlinearity ($\Delta n=n_2$) and negligible NLA ($\Delta \alpha=0$). The nonlinear refractive index ($n_2$) of the crystal was calculated using the relations [36-38]

$$\Delta T_{p-v} = 0.406(1-S)^{0.25}|\Delta \Phi_0|$$  \hspace{1cm} (1.8)

where $\Delta T_{p-v}$ is the difference between the normalized peak and valley transmittance, $\Delta T_{p-v}/\Delta \Phi_0$ is the on-axis phase shift at the focus, $S$ is the linear transmittance aperture and is calculated using the relation

$$S = 1 - \exp\left(-\frac{-2r_a^2}{\omega_a^2}\right)$$  \hspace{1cm} (1.9)

where $r_a$ is the radius of aperture and $\omega_a$ is the beam radius at the aperture. The nonlinear refractive index ($n_2$) is given by
\[ n_2 = \frac{\Delta \phi}{k I_0 L_{\text{eff}}} \]  

(1.10)

where \( k \) is the wavenumber \( (k = 2\pi/\lambda) \), \( I_0 \) is the intensity of the laser beam at the focus \((Z=0)\) and \( L_{\text{eff}} = [1-\exp(-\alpha L)]/\alpha \) is the effective thickness of the sample, \( \alpha \) is the linear absorption and \( L \) is the thickness of the sample.

From the open aperture Z-scan data, the nonlinear absorption coefficient \( (\beta) \) is estimated from the relation [36]

\[ \beta = \frac{2\sqrt{2} \Delta T}{I_0 L_{\text{eff}}} \]  

(1.11)

From Z-scan calculation we determine the nonlinear refractive index \( (n_2) \) and nonlinear absorption coefficient \( (\beta) \) of the crystal.

1.14 Nonlinear optical material

Nonlinear optical (NLO) materials play a vital role in nonlinear optics and in particular they have a great impact on information technology and industrial applications. In the last decade, however this effort has also brought its fruits in applied aspects of nonlinear optics. This can be essentially traced to the improvement of the performances of the NLO materials. The understanding of the nonlinear polarization mechanisms and their relation to the structural characteristics of the materials has been considerably improved. In the present work focus is made on the Schiff base derivative materials for NLO applications.

1.14.1 Schiff bases

In 1864, German chemist Hugo Schiff developed a new class of organic compound [39, 40]. These groups of compounds called imines are often referred to as Schiff bases in his honor. The Schiff base is synonymous with an azomethine [40] and their one of the derivative is Benzylidene aniline (Imine) compounds. The general structure of the benzylidene aniline [41] is shown in Fig. 1.2.

Fig. 1.2 General Structure of Benzylidene aniline
The preparation of these compounds is simple and elegant. They are prepared by condensing a carbonyl compound with an amine, generally refluxing in alcohol. Schiff bases are often used as ligands in inorganic chemistry.

1.14.2 Importance of the Schiff base materials

Organic photochromic compounds have received considerable attention due to their potential applications such as optical data storage, electronic display system, optical switching devices, ophthalmic glasses and so on [42]. Investigators are interested in the combinatorial synthesis procedure for the rapid formation of large libraries of polar compounds (a focused library) which can be used for preparation of nonlinear optical (NLO) materials [42, 43]. Because of the structural characteristics of the Schiff base products (i.e. electron donor and acceptor groups connected to a $\pi$ conjugated chain, will be potential NLO or electro-optical materials). Bond length alternation is observed in the central $\pi$-conjugated chain of the molecules. There is considerable research interest in exploring materials having large nonlinearities. The Z-scan method has gained rapid acceptance by the nonlinear optics community as a standard technique for separately determining the nonlinear changes in refractive index and absorption. The present investigation aimed to synthesize some of the Schiff base materials and to characterize them for their structural, spectral, linear and nonlinear optical, dielectric, mechanical and thermal properties.

1.15 Organic Field-Effect Transistors (OFETs)

Many impressive advances in the field of organic electronics have proved capable of performing a wide variety of functions. The practical advantages primarily root from the following: (1) large-area electronics in which the active devices are distributed and embedded over a large area; (2) low-cost or large volume electronics (cheap and disposable electronics are increasingly used as the replacement for bar codes and various forms of personal identification); (3) flexible construction and electronics where ruggedness is necessary; (4) new advances in fabrication methods that may impact the manufacturing of organic electronics and conventional electronics; (5) novel functionality.
A field-effect transistor is a three-terminal device (source, drain and gate electrodes) configured like a parallel-plate capacitor. By controlling the voltage on one plate (the gate), a charge can be induced on the other. These charges are injected from the source electrode and collected across the conducting channel at the drain by applying a voltage between the two [44]. A special type of transistor called the Metal Oxide Semiconductor Field-Effect Transistor (MOSFET) has become particularly important in modern electronic devices. Traditionally, silicon has been the most widely used semiconductor material. In addition to the great quality of Si-SiO₂ interface in MOSFETs devices exhibit fast switching speeds and are therefore suitable for use in modern processors [44]. There are however, many applications for field-effect devices where fast switching speed is not a requirement. These include [45] large-area coverage, mechanical flexibility and low cost integrated circuits. For example, amorphous Si FETs nowadays constitute the active matrix of liquid crystal displays [46] with the mobility in these devices being two orders of magnitude lower than their single crystal counterparts. With the successful synthesis of the first organic transistor in 1986 based on electrochemically grown poly-thiophene films [47], the prospect of replacing costly and labor-intensive inorganic devices with cheaper and more flexible organic electronic materials entered a new era. Over the past 25 years, we have seen dramatic improvements in growth, fabrication and processing of organic electronic materials and devices, placing them as good candidates for use in applications [45] such as electronic displays, smart cards and identification tags. A good example of this progress is a five -order of magnitude increase in the field-effect mobility from 1986 to present [48], making the organic electronic devices a viable replacement for amorphous Si devices. However, despite the considerable improvements in the fabrication and characterization of thin-film organic field-effect transistors these devices are still not fully understood and therefore still in the research stage. In the following the design and the functionality of an OFET is presented.

An OFET is very similar with an MOSFET in what concerns the design and the functionality. It also consists of three electrodes namely source (S), drain (D) and gate (G). However, additionally to the traditional MOSFET (where the current flow is
due to the minority carriers of the formed inversion layer (under an imposed gate voltage) the OFETs have an organic material which forms the active layer. In the case of OFETs the inversion layer does not exist and the current will be given by the majority carriers formed at the interface between the organic material and the gate dielectric. OFETs can be generally designed in two configurations: bottom-contact and top-contact. In the bottom-contact configuration the source and drain electrodes are underneath the organic material whereas in the top-contact configuration (Fig.1.3) the electrodes are on top of the organic semiconductor.

![Schematic representation of a top-contact OFET](image1)

**Fig.1.3** Schematic representation of a top-contact OFET

### 1.16 Operating Principle

In the following the device operation and its characteristics will be discussed.

![Graphs showing output and transfer characteristics](image2)

**Fig 1.4** The output (a) and transfer (b) characteristics of an OFET

In Fig. 1.4 (a) and Fig.1.4 (b) the two characteristics of OFETs namely output and transfer characteristics are plotted. The output characteristic is displayed (Fig.1.4 (a)) by a plot of the drain-source current $I_{DS}$ as a function of the drain-source voltage $V_{DS}$. 

In contrast, the transfer characteristic (Fig.1.4 (b)) shows the dependence of the drain current $I_{DS}$ on the gate-source voltage $V_{GS}$ with the drain-source voltage $V_{DS}$ held constant.
at fixed gate-source voltages $V_{GS}$ and it is divided in two regions: the linear and the saturation regions. The transfer characteristic can be plotted in two ways: $I_{DS}$ vs. $V_{GS}$ at a fixed $V_{DS}$ or the square root of $I_{DS}$ vs. $V_{GS}$ at a fixed $V_{DS}$ as shown in Fig. 1.4 (b). The first way shows how effectively the gate voltage can switch the device ON or OFF. If a p-type transistor switches ON at $V_{GS} > 0$, this could mean among other things that a significant density of impurity dopants is present in the semiconductor, constituting a bulk current, even when a gate voltage is not present [49]. From the $\sqrt{I_{DS}}$ vs $V_{GS}$ plot at fixed $V_{DS}$ the threshold voltage $V_{Th}$ can be determined from the extrapolation of the straight line to the $V_{GS}$ axis at zero current. $V_{Th}$ is traditionally defined as the voltage below which the transistor is OFF.

In the following the two regions of the output characteristic will be explained. At a fixed $V_{GS}$, $V_{DS}$ initially increases linearly with $I_{DS}$ and the conducting channel acts like a resistance. This is the linear region and is described by the equation 1.18 [44].

$$I_{DS} = \mu_{lin} (W/L)C_i[(V_{GS} - V_{Th})]V_{DS} \quad \text{for } V_{DS} < V_{GS} - V_{Th} \quad (1.18)$$

where $W$ is the channel width, $L$ is the channel length, $C_i$ the capacitance per unit area of the gate insulator, $\mu$ is the charge carriers mobility. When the value of the drain-source voltage becomes comparable to the gate-source voltage (assuming $V_{Th}$ is small), $I_{DS}$ increases to increase and the transistor enters the saturation regime. In the saturation, the channel is pinched off at the drain and the current levels off (see Fig. 1.4 (a)). The field-effect mobility in the saturation regime ($\mu_{sat}$) can be calculated from the following expression:

$$I_{DS} = (1/2)\mu_{sat}(W/L)C_i(V_{GS} - V_{Th})^2 \quad \text{for } V_{DS} > V_{GS} - V_{Th} \quad (1.19)$$

Although it is expected that the linear regime and the saturation regime $\mu$ values to be similar for a device, this is not always the case [45]. Source and drain contact resistances or high electric fields often affect the linear regime mobilities.

1.17 Organic Polymers and small molecules

Organic materials used in the manufacture of OFETs can be classified into two groups: small molecules and polymers. The family of the small molecules includes the organic compounds made up of a small number of monomers whose
total molecular mass does not exceed 1000 amu (atomic mass unit). A monomer is either an atom or a small molecule that has the potential of chemically binding to other monomers of the same species to form a polymer. Consequently, the main difference between small molecules and polymers is the amount of monomers they contain. As small molecule p-type, for example pentacene or phthalocyanine and for the n-type fullerene (C60), Perfluoropentacene, PTCDI-C13 (N,N'-ditridecy1-3,4,9,10-perylenejetcarboxylic diimide) or PTCDA (3,4,9,10-perylenejetcarboxylic Dianhydrid). Regarding polymers, for example, PQT-12 (3,3'-dialkylquarterthiophene), P3HT (3-hexylthiophene) or F8T2 (dioctylfluorene cobithiophene). A second difference lies in the technological processes used to deposit a thin film. Polymers can be deposited from solution by spin-coating or printing, the small molecule in turn is deposited from thermal evaporation under vacuum, because almost all the small molecules used in OFET are insoluble. Despite these differences, the physics is behind the small molecules and polymers are very similar.

The OFET studied in this thesis are small molecules, specifically, the samples are composed of semiconductors with p-type pentacene and with their derivatives. The pentacene is an aromatic compound composed of 5 rings of benzene, it has been extensively studied as a semiconductor for its relatively good stability and its remarkable results in terms of conductivity. Pentacene, oligothiophenes (nT, where n stands for the number of thiophene units) and phthalocyanines (Pcs) are the most representative p-type semiconductor materials based on small molecules. Vacuum deposition is the normal process for producing thin films of these materials. However, some compounds can be processed by solution-based methods using a soluble precursor molecule that may afford certain advantages in device fabrication [49].
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