Growth and physical properties of organic semiconducting single crystals

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NANYANG
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**GROWTH AND PHYSICAL PROPERTIES OF ORGANIC
SEMICONDUCTING SINGLE CRYSTALS**

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SCHOOL OF MATERIALS SCIENCE & ENGINEERING
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**GROWTH AND PHYSICAL PROPERTIES OF ORGANIC
SEMICONDUCTING SINGLE CRYSTALS**

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Supervised by
Prof Christian Kloc

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Abstract

Electronic instruments that operate using organic semiconductors are already available on the market. Organic light emitting diodes are in numerous displays of mobile phones or some TV sets. Organic solar cells with efficiency larger than 5% are produced by small start-up companies. Organic field effect transistors have achieved charge mobilities larger than that of amorphous silicon. Therefore it is justified to ask for the intrinsic limit of organic semiconductors and how to improve the physical properties of organic semiconductors. This study focuses on the most perfect form of solid state made from an organic semiconductor, on organic single crystals. High defect concentrations and grain boundaries cause hindrance to the charge carrier's transport. Relatively long radiative decay of excitons can be achieved in high quality Light Emitting Organic Field Effect Transistors (LEOFET) built from high charge carrier mobility materials. Therefore, using high quality molecular single crystals for fundamental research in organic electronics will be valuable in pushing forward the cutting edge of these technologies.

To study organic semiconductors, single crystals of numerous organic semiconductors have been produced. Furnaces with high precision temperature control were built for growing of high quality single crystals. The high quality of a single crystal was defined in terms of high crystallinity, high purity and molecularly smooth crystal surface. Numerous high quality mono-component and charge-transfer (CT) binary-component molecular single crystals have been grown using solution phase and gas phase methods. Powder X-ray diffraction (PXRD), single crystal X-ray diffraction (SCXRD) and cross-polarized light microscopy (CPLM) were done to characterize the crystallinity and the crystal phase of the single crystals. High performance liquid chromatography (HPLC), liquid

chromatography mass spectrometry (LCMS), Matrix-assisted laser absorption/desorption mass spectrometry (MALDI-ToF-MS), photoluminescence (PL) and attenuated reflection fourier transform infrared spectroscopy (ATR-FTIR) were used to study the purity of the single crystals. Atomic force microscopy (AFM) was used to investigate the surface roughness of the single crystals.

The bandgap of the molecular single crystals could be reduced by growing CT binary-component molecular single crystals. High conductivity molecular single crystals could be attained with peri-substituted dichalcogenide polycene, such as tetrathiotetracene (TTT).

The highest charge carrier mobilities of holes and electrons were measured for rubrene, tetracene, F16CuPc and few more single crystal FETs. Yet, the limit of the mobility of organic materials is still a mystery. It was found that the measured mobilities from the single crystal FETs do not represent the intrinsic mobility of the materials. The measured mobility highly depends on the surface states of the single crystals which are largely affected by the fabrication process of the single crystal FETs. The physical properties of these molecular single crystals are highly sensitive to impurities and defects in the single crystal whose impurities level is still far higher than its inorganic counterpart. For instance, oxides of rubrene and pentacene were detected in high mobility rubrene and pentacene single crystals. Current theoretical knowledge doesn't allow prediction and modeling of the structure-properties relation with precision sufficient for material selection. Therefore, experimental studies aids in finding parameters responsible for the physical properties of materials. This study describes numerous efficient organic semiconductors, structure of these materials and their physical properties useful for device preparation.

Chapter 1 - Introduction

An Organic material having a system of alternating single and double bonds, commonly called a π conjugated system, can have interesting electrical and optical properties resulting from delocalization of π electrons. Professors Alan Heeger, Alan MacDiarmid and Hideki Shirakawa have been awarded the Chemistry Nobel Prize in 2000 for their discovery of metallic “doped” polyacetylene. The metallic properties are caused by free electrons moving within the organic solid. Small organic molecules having the π conjugated system can have high charge carrier mobility in crystals. This is due to the delocalized electron wave functions within the molecule. Molecular orbital overlap plays an important role in the transport of charge carriers from one molecule to another. Single crystals are expected to have higher mobility than their polycrystalline or disordered counterpart. The increase in defects and grain boundaries in such structure would not favor the charge carrier’s transport. With good charge carrier mobility, relatively long radiative decay of excitons was achieved which can be observed in Light Emitting Organic Field Effect Transistors (LEOFET). Thus, applications such as fancy foldable colour displays consisting of large matrices of Organic Light Emitting Diode (OLED) have been on the market. Organic semiconductors used for device preparation are built from complex organic molecules. Examples of such different types of semiconducting molecular single crystals used in this study are included in Table 1 as shown below.

p-type semiconductor
Rubrene Single Crystal	CuPc Single Crystal	Perylene Single Crystal
Anthracene Single Crystal	Tetracene Single Crystal	Pentacene Single Crystal
n-type semiconductor
TCNQ Single Crystal	F16CuPc Single Crystal	

Table 1: Semiconducting Molecular Single Crystals grown in this study

Fig. 1: Research flow in the field of molecular single crystals. Organic chemists are interested in synthesizing new and novel molecules, and understanding how material properties change through molecular engineering. They will provide the new molecules to the single crystal growers for growing into high quality single crystals. Single crystal growers will provide high quality single crystals to the physicists where fundamental physics such as electrical and optical properties are of interest and will be investigated. Through the feedback from each role, the single crystal grower will learn and constantly improve the quality of the single crystals.

Research work on the fundamental science of organic electronics is a challenging task. The work requires multidisciplinary knowledge such as chemistry, physics and material sciences. And different research teams from different disciplines often come together, collaborate and work toward a common goal. The research flow in the molecular single crystal field works in the way as shown in Fig. 1.

Organic chemists are interested in understanding how material properties change through molecular engineering. Therefore they will synthesize new and novel molecules. They will provide the new molecules to the single crystal growers for growing into high quality single crystals. Single crystal growers will provide high quality single crystals to the physicists where fundamental physics such as electrical and optical properties are of interest and will be investigated. Through the feedback from each role, the single crystal grower will learn and constantly improve the quality of the single crystals. There will certainly be some overlap between the roles.

Many organic compounds are white or transparent insulators in the solid crystalline state. Millions of these compounds are used in every branch of industry. New organic compounds are continuously synthesized by chemists for pharmaceutical applications [1, 2] and in search of new physical properties [3]. Already in the previous century, it was noticed that some organic compounds may exhibit photoconductivity, like anthracene which shows significant conductivity after proper doping [4]. A number of molecular semiconductors; metals [5] and even superconductors have been discovered [6]. It was found that organic compounds need delocalized π electrons in the host molecules and charge transfer from part of the molecules or even from donor or acceptor molecules to be considered for microelectronic applications.

It was noticed that the properties of molecular semiconductors need to be studied in a similar manner as inorganic semiconductors like silicon or GaAs.

Therefore the following questions appear important during the exploration of molecular semiconductors:

- What is the relationship between the chemical formula and the physical properties of molecular semiconductors?
- What are the crystalline structures and their relations to the transport properties?
- Which parameters limit the performance of molecular single crystal field effect transistors (FETs)?
- Where is the limit of organic performance in electronic applications?

Most of these questions have been approached during study of organic devices based on thin films. However, once molecular semiconductors are embedded in devices it was very difficult to extract the intrinsic properties of the semiconductor from the device technological performance. Therefore a new direction has been developed in research laboratories: the study of molecular semiconductors of as high as possible purity and in the high quality form of single crystals.

The presented PhD thesis is devoted to this category. The following questions are formulated and explored in the course of this study:

- How can the purity of the starting materials be determined and how may it be improved to approach the material purity similar to inorganic semiconductors?
- How can the crystal growth be improved to eliminate the defect influence on measured properties?
- How can one produce materials with band gaps appropriately small for numerous applications including solar cells and OLED?

The following hypothesis has been formulated: **control of chemical and structural properties is achievable through growth of high purity and high quality single crystals. The band structure is controllable through binary compound formation and the study of physical properties of these compounds is the most efficient on single crystals of binary compounds.**

To answer the above formulated questions and resulting hypotheses following research steps have been accomplished.

- single crystal growth instruments for growth from the gas phase, fluxes and solutions have been designed and constructed (chapter 3)
- semiconducting single crystals of rubrene, pentacene, tetracene, anthracene, DPA, perylene, TCNQ, CuPc, F₁₆CuPc, C₆₀, C₇₀ and TTT have been successfully grown (chapter 3)
- purity of starting materials have been evaluated and impurity removed in growth processes (chapter 4)
- crystal structures have been determined (chapter 3)
- physical properties of single crystalline organic semiconductors have been measured (chapter 5)
- devices (FET) have been constructed and measured (chapter 5)
- Binary compounds have been synthesized, crystallized and measured (chapter 3 and 5).

Chapter 2 - Literature Review

2.1. Molecular Single Crystal Growth using Physical Vapor Transport (PVT)

Molecular single crystals could be grown by various methods. These methods could be easily view as three different categories: from solution phase, melt phase and gas phase.

Fig. 2: Crystal growth apparatus. The temperature is adjusted for each substance but the steepest temperature gradient is generally at the position shown [8]

C. Kloc et al. had used horizontal and vertical PVT to grow centimeter-sized crystals of α -hexathiophene (α -6T) [7, 8]. The PVT set up was shown in Fig. 2 above. The PVT method is a purification method and at the same time a separation method; it has the ability to grow high purity single crystals. Molecular single crystals grown from gas phase are widely believed to be much cleaner compared to those from solution-growth methods. High quality molecular single crystals could be obtained from this method. In this method, the purity of the carrier gas and starting source material is very crucial to obtain high quality single crystals. By minimizing the effects of grain boundaries, defects and impurities, study of molecular single crystal could provide a good platform for understanding the basic

science in organic electronics. Hence, crystals grown from this method such as anthracene, tetracene, pentacene, rubrene, oligothiophenes, tetracyanoquinodimethane (TCNQ), phthalocyanines, biphenylbithiophene (BP2T) and diphenylbenzodiselenophene were widely used for the research on the basic science in organic electronics [9].

2.2. Molecular Single Crystal Growth using Solution Methods

As compared to gas phase methods, molecular crystal growth using solution methods are not as popular for growth of semiconductors. This is because solvent molecules are believed to be incorporated into the single crystals as impurities during the growth process. However, it is important to note that lower temperature crystal growth could be performed using solution methods. Growing crystals at lower temperature could reduce the risk of organic molecule decomposition and good quality single crystals of low temperature phase could be obtained. The crystal growth is carried out by heating up the solution, defined as the mixture of solute and solvent molecules, and followed by slow cooling to the eutectic point. The solute-solvent interaction energy allows the solution to form at this lower temperature, thus crystals could be formed at lower temperature. Solution methods are also advantageous as the crystal formed is determined not by the component with the higher melting point but by the composition of the solution [10].

Solute concentration at the crystal surface is typically lower than the equilibrium concentration in the bulk solution. The difference between the solute concentration at the crystal surface and in the bulk solution leads to bulk diffusion to the crystal surface. Solute molecules or particles in the diffusion boundary layer could either diffuse onto the surface, cling at kinks or steps playing a part in the crystal growth or return to the bulk solution as shown in Fig. 3 [11].

Fig. 3: Different sites for particles to crystallize when the solution brings the solute to the crystal-solvent interface where they are adsorbed at kinks, steps and terraces [11].

2.3. Molecular Single Crystal Growth using Melt Methods

There are basically three different techniques of growing organic single crystals from melt. They are the Czochralski method, the Bridgeman-Stockbarger technique and the Floating Zone technique. The Czochralski method was successfully used by J. Bleay et al. to grow benzophenone and benzil single crystals [12] which were commonly grown by solution and vapor phase only. 9, 10 – Diphenylanthracene single crystal ingot was grown by the Bridgeman-Stockbarger technique, and the Time-of-Flight (ToF) measurement for the electron and hole mobilities were $13 \text{ cm}^2/\text{Vs}$ and $3.7 \text{ cm}^2/\text{Vs}$ respectively [13]. Growth and doping of anthracene single crystals with various organic electron acceptors had been done using the Bridgeman-Stockbarger technique too [14]. The

modified floating zone technique was used to grow 6mm diameter benzil and salol single crystals ingots [15].

2.4. Purity of Molecular Single Crystals

The use of molecular single crystals in FETs gives a good platform to investigate the effects of defects and impurities on FET performance [16]. As early as 1966, A. A. Arabidze tried to determine the purity of coronene and pentacene using luminescence spectra [17].

N. Kart et al. had purified naphthalene and perylene into ultrapure single crystals and demonstrated high charge-carrier mobility of several hundred cm^2/Vs at low temperature of around 10K. The purification procedures involved prepurification of the precursor by liquid chromatography, followed by vacuum sublimation and up to several hundred steps of zone melting. The mobility was measured by the “time-of-flight” technique. [18].

Nevertheless, N. Kart had compared different methods for detection of ppm impurities in organic molecular crystals [19]. He had discussed the chromatography, mass spectrometry and fluorescence methods as effective methods for detecting ppm impurities. He had mentioned in a book chapter [20] that doping of 1 ppm impurity tetracene in anthracene single crystals could drastically reduce the crystals’ electron and hole mobility [21]. K. Kamaras et al. also demonstrated the impurity effects in the organic charge transfer salt $\text{Qn}(\text{TCNQ})_2$ [22]. This shows the significant impact of ppm impurities in organic semiconductors. Ryoji Mitsuhashi et al. doped potassium in picene single crystals and reported superconductivity at 2K [23] which shows the possibility of fine tuning of the physical properties of the molecular single crystals by controlled doping of impurities into the crystals.

M. Kotani et al had did some work on highly purified perylene single crystals. They had used the delayed fluorescence (DF) method to monitor the purity of their crystals. They crystallized the perylene until there was no difference in TOF waveform and DF lifetime measurement with further purification. They also used the “time-of-flight” method to measure the mobility of the crystals but the measuring temperature did not go to lower than 150K. However, the electron mobility attained at around $2 \text{ cm}^2/\text{Vs}$ at a temperature of 150K seems comparable with the mobility-temperature graph shown in N. Kart’s work as mentioned above [24].

2.5. Field Effect Transistors (FETs) using Molecular Single Crystals

Field Effect Transistors (FETs) are built using the semiconducting molecular single crystals in an attempt to measure the intrinsic physical properties, particularly the charge carrier mobility, of the molecular single crystals. The surface quality, in terms of roughness and purity, of these molecular single crystals is crucial to obtain high carrier mobility devices [25]. Hence, it is important to maintain the good surface quality of the single crystal during the fabrication of the FETs [26]. As the molecular single crystals are very fragile, building FETs on these single crystals is very challenging. Traditional thin-film processes such as photolithography and sputtering introduce a large density of defects at the single crystal surface by disrupting molecular order. These could cause charge injection barrier at the electrode-crystal interface and interfacial trapping states at the dielectric-crystal interface, which in turn deteriorate the FETs performance [26 - 27].

Fig. 4: Different molecular single crystal FET structures showing (a) Bottom-contact, bottom-gate, (b) Top-contact- bottom-gate and (c) Top-contact, top-gate [9]

There are three types of FET structures using molecular single crystals. They are the bottom-contact, bottom gate, the top-contact, bottom gate and the top contact, top gate as shown in Fig. 4 above. One of the techniques to fabricate top-contact, top gate FET structure involved the direct deposition of the contacts and gate dielectric onto the crystal surface. There are different methods of depositing the source and drain contacts onto the crystal surface, for example thermal or e-beam evaporation of metal patterned onto the crystal surface using a mask [28]. These methods have the advantages of controlled dimension mask patterning and a variety of metal choices for better tuning the metal work function to the HOMO and LUMO of the organic molecules which could result in better charge carrier injection [29]. However, due to highly energetic metal atoms, these methods could

also incur serious damage at the metal-crystal interface resulting in large charge carrier injection barrier [30]. The simplest and least damage method is the direct manual application of a conducting paste on to the crystals. There are fewer choices for the conducting pastes and they are usually a water-based solution of colloidal graphite or solvent-free silver epoxy. [31, 32] The next step in this technique is to deposit the dielectric layer. Conformal coatings of parylene films can be deposited easily onto the single crystal with pre-fabricated source and drain contacts. The final step then involves painting the gate contact over the dielectric layer. [33, 34, 35] This technique is frequently used to fabricate FETs with a top-contact structure. This top-contact structure has the advantage of a smaller contact resistance between the electrodes and the organic semiconductor and this becomes increasingly important as the channel length of the FET decreases. [36, 37]

Another technique to fabricate a top-contact FET structure is the ‘air’ gap transistor. The source, drain and gate structure is pre-fabricated on a substrate using conventional microfabrication methods, and the single crystal is then laminated to such a “stamp”. For this purpose, both hard inorganic silicon and flexible elastomeric polydimethylsiloxane (PDMS) stamps have been used, as shown in Fig. 5. [38 - 40] Molecular single crystal FETs that use air or vacuum gap as the gate dielectric have been made, and it helps in reducing the density of defects created on the crystal surface. [41]

The top contact, bottom gate FET structure could be fabricated by direct growth of molecular single crystals onto an OTS monolayer treated Si/SiO₂ wafer followed by shadow mask patterning source/drain metal electrodes onto the single crystals using thermal or e-beam evaporation methods [42]. The metal electrodes could be

also laminated onto the molecular single crystals by electrostatic forces using the “gold layer glued” or the “multitime gold-wire mask moving” technique [43, 44].

Fig. 5: Schematic for the fabrication and structure of the PDMS "air-gap" transistor [38]

The bottom contact, bottom gate FET structure could be also fabricated by direct growth of molecular single crystals onto a metal electrodes patterned Si/SiO₂ wafer [45]. Direct lamination of the ultra thin flexible tetracene single crystal onto the O₂ plasma treated Si/SiO₂ wafer had also been done [46].

2.6. Molecular Single-Crystals Surfaces and Interfaces

The performance of molecular single crystal FETs can be affected by many factors such as carrier trapping, charge doping, molecular reorientation, and dipole formation, as well as a range of possible chemical interactions that may occur at the crystal-dielectric interface [47]. In the operation of molecular single crystal FETs, very narrow conducting channel, consisting of only few molecular layers extended in the transverse direction, is created at the dielectric-crystal interface. Due to the small polarons within the molecular crystal, the movement of polarons in the conducting channel is extremely sensitive to the semiconducting crystal surface morphology and electronic defects present at the dielectric-crystal interface [27]. Presently, the mobility measured for molecular single crystal FETs is 40 cm²/Vs obtained using rubrene single crystals and pentacene single crystals using 6,13-pentacenequinone (oxide of pentacene) as its dielectric layer [48, 49]. J. Takeya et al. used a F-SAM modified SiO₂ dielectric attempting to relate transistor mobility to dielectric surface hydrophobicity [48]. Oana D. Jurchescu et al. fabricated pentacene single crystal transistors using pentacenequinone as the dielectric, highlighting the importance of dielectric-crystal interface state [49]. Helena Alves et al. created a highly conducting crystal interface simply by stacking the TCNQ and TTF single crystals onto each other [50]. This further highlighted the extreme sensitivity of the molecular single crystals interface to the interacting surrounding ambient.

High contact resistance inevitably will influence the measurement of the molecular single crystal FETs.

Fig. 6: (a) Back-gate device using rubrene single crystal showing rubrene endoperoxide forming at the crystal surface due to photo-oxidation. (b) Chemical equation showing the reaction of oxygen with rubrene molecule [55]

The contact resistance limits the amount charge carriers of injected into the conducting channel and decreases the voltage drop across the conducting channel [51]. It is believed that contact resistance decreases with increasing gate voltage, which causes the mobility extracted from the linear regime to usually be significantly smaller than that from the saturation regime [16]. Additionally, contact resistance becomes progressively more important as the size of the

molecular single crystal FETs decreases. The molecular single crystal FETs performance generally becomes better with decreasing channel length. This is due to an increase in the lateral electric field across the conducting channel which eases the charge carrier injection barrier, hence reducing the threshold voltage. However, there is still limitation on the extent the channel length can be reduced because the high contact resistance, comparing to the negligible resistance of the very short conducting channel, could cause the source-drain current to be extremely small, perhaps out of the equipment measurement range. [16, 52]

Impurities, defined as the minority molecule or atom in the system, can also significantly change the physical properties of the molecular single crystal. This will in turn affect the performance, such as the mobility and on/off ratio, of the molecular single crystal FETs. Impurities might distribute differently in the single crystals. They could either distribute homogeneously in the crystal or form naturally on the crystal surface due to instability of the molecule as shown in Fig. 6 [53 - 55]. Since the conducting channel is at the first few monolayers of the dielectric-crystal interface, the presence of impurities results in the formation of traps at the interface and within the semiconductor material which will alter the relative energy levels and inhibit charge carrier flow [56]. Impurities doped in the crystal could increase its conductivity which leads to poor on/off ratio [56].

The type of crystal packing may affect the performance of molecular single crystal FETs [56]. Xialiou Chi et al. tried to attribute the high mobility ($1.7 \text{ cm}^2/\text{Vs}$) of the tetrachlorotetracene single crystal to the herringbone crystal structure which high mobility single crystals such as rubrene and tetracene also possess [57].

However, Elisey Yagodkin et al. could not get the high mobility for the tetrachlorotetracene single crystal using a vacuum gap transistor and using the 4-point contact measurement [58]. This might be due to the gauge effect in which

V. Podzorov et al. claimed that free radicals produced in the process of hydrocarbon cracking on hot filaments attacked the conducting channel of the vacuum gap transistor, causing a lower mobility [59].

Growth Method	Material	Majority Carrier Type	Charge Carrier Mobility (cm ² /Vs)	Structure	Dielectric	Metal Electrodes
Gas	Rubrene	p	18 ⁴⁸	BC,BG	SiO ₂ F-SAM	Cr, Au
			40 (4-point) ⁴⁸			
	TCT	p	1.7 ⁵⁷	TC,TG	Parylene N	Graphite
			0.02 ⁵⁸	BC,BG	Vacuum Gap	Au
			0.2 (4-point) ⁵⁸	BC,BG	Vacuum Gap	Au
	Perylene	p	2x10 ⁻³ (sat) ²⁴	BC,BG	SiO ₂	Cr, Au
	Anthracene	p	0.02 ⁷¹	BC,BG	SiO ₂	Au
	Tetracene	p	1.6 ³⁹	BC,BG	Air Gap	Ti, Au
	Pentacene	p	40 ⁴⁹	TC,TG	PQ	Ag
	CuPc	p	1 ³⁴	TC,TG	Parylene N	Graphite
			0.6 (4-point) ⁷²			Ag
	Picene	p	1 ⁶¹	TC,BG	Parylene N	Ag
	F ₁₆ CuPc	n	0.6 ⁷³	TC,BG	SiO ₂	Au
	TCNQ	n	0.3 ⁷⁴	BC,BG	SiO ₂ F-SAM	Au
			1.6 (4-point) ⁴⁷		Vacuum Gap	Ti, Au
Solution	Rubrene	p	0.75 ²⁵	TC,TG	Parylene N	Graphite
	DPA	p	0.16 ⁷⁵	TC,BG	SiO ₂	Ti, Au
	TCNQ	n	0.03 ⁷⁶	TC,BG	CL-PVP	Au
Melt	Perylene	p	0.12 (sat) ²⁴	TC,TG	Parylene N	CuI
<p>Abbreviations: BC – bottom contact; TC – top contact; TG – top gate; BG – bottom gate, PDMS – poly(dimethylsiloxane); PQ –pentacenequinone; Au – Gold; Ag – silver; Cr – chromium; Ti – titanium; CuI – cuprous iodide; SiO₂ – silicon dioxide; CL-PVP – poly(4-vinyl phenol); TCT – 5,6,11,12-Tetrachlorotetracene; DPA – 9,10 - diphenylanthracene; CuPc – copper phthalocyanine; F₁₆CuPc – perfluorinated copper phthalocyanine; TCNQ – tetracyanoquinodomethane; sat – mobility extracted from saturated regime</p>						

Table 2: List of mobilities for different molecular single crystal FETs at various conditions

Both Keke K. Zhang et al. and Naoko Kawasaki et al. discovered a mobility dependence on interaction with the environment, such as vacuum, hydrogen, oxygen, in the molecular single crystal “air-gap” transistors made from on rubrene and picene single crystals respectively [60, 61]. Hence the performance of the FETs highly depends on the interactions of the conducting channel in the FETs with its surrounding environment.

A list of highest achievable mobility molecular single crystals from around the world is shown in Table 2. It should be borne in mind that the research groups in different part of world might get different results due to the device sensitivity on climate and fabrication process of the FETs.

2.7. Applications of Molecular Single Crystals

Solution-processable organic electronics [62 - 64] has pushed interest in researching on solution-growth molecular single crystals. The properties of molecular single crystals, particularly their electronic properties, have been studied intensively during the past few years. Could the mobility of organic semiconductors reach a value comparable to that of the inorganic semiconductors? What are the major factors limiting the mobility of organic semiconductors? Are factors like grain boundaries in the organic polycrystal, or overlap of π - π electron orbits due to the structural arrangement of the crystals the only factors limiting the electronic mobility of the organic semiconductor? Researchers and scientists from all around the world are seeking the answers to these questions.

Superconductivity effect was also discovered in molecular crystals made from charge transfer complexes [65] and superconductivity was also observed in alkaline metal strong doped C₆₀ single-crystals at higher temperature [66]. Light-emitting transistors of molecular single crystals were realized [32, 67].

Furthermore, organic light-emitting diode (OLED) have been successfully used for displays [68]. Inverter circuitry has been fabricated on silicon wafer using TCNQ crystals and pentacene thin film as the n-type and p-type materials respectively [69]. Selective patterning of crystals to form arrays of FETs was demonstrated, which seems promising for future applications [70].

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Chapter 3 – Instrument Design, Materials & Characterizations

3.1. Design of Instruments for Crystal Growth

It is essential to have appropriate equipments for research. Good equipment and a proper experimental set-up to conduct clean and simple experiments is necessary for sound conclusions. Building and setting up experimental equipment allows one to better understand the operational principles of instruments and thus design unique experiments that are difficult to set up using typical commercial equipment. Furnaces are essential in crystal growth experiments, which as they often involve heating and slow cooling of the growth system close to the equilibrium state. The ability to control the constant temperature and temperature profile is extremely important in crystal growth experiments. It is often a challenge to modify and regulate large commercial furnaces as the individual components are fixed to the respective furnaces. Therefore, control of the temperature profile in commercial furnaces is difficult. Fig. 7 shows temperature profile measurements of a 3-zone furnace from Lenton.

Fig. 7: Temperature profiles of a 3-zone furnace from Lenton for (a) temperature setting at 0 °C 200 °C 0 °C, (b) temperature setting at -50 °C 200 °C -50 °C and (c) temperature setting at 50 °C 200 °C 50 °C. The measured temperature differs a lot from the temperature setting. The measured temperature profiles at the respective temperature settings were unexpected and unreasonable.

In Fig. 7, the measured temperature profiles differed a lot from the expected temperature at the respective temperature settings in the Lenton furnace. The temperature gradient changes at the zone interfaces were gradual and do not match the preferred step-wise temperature profile ideal for single crystal growth in the Physical Vapor Transport (PVT) process. Hence, for this study custom made furnaces for the single crystal growth process were designed and constructed.

3.1.1. Design and Construction of Apparatus for the Gas Phase Crystal Growth Methods

Fig. 8: Design of furnace table where two-zone gold coated furnaces are hung and work space is created.

The project was started with the construction of the furnace table and instrument holders. The PVT apparatus consisted of two gold plated two-zone tube furnaces hung on the furnace table as shown in Fig. 8.

Fig. 9: Furnaces were control by a temperature feedback system which consist of a power controller (Eurotherm TE10A) and a temperature controller (Eurotherm 3216), for precise temperature control

The furnace temperature was controlled by a temperature controller (Eurotherm 3216) connected to a thyristor which acted as a power controller (Eurotherm TE10A) forming a temperature feedback system as shown in Fig. 9. The two-zone furnace would realize a step temperature profile across the zones which are crucial to PVT crystal growth.

Fig. 10: Photo of the hand-made small transparent furnace which is very useful to purify and crystallize small amounts of powder.

Small, transparent hand-made furnace were also built in the laboratory as shown in Fig. 10. These furnaces come in handy when chemists synthesize only a small amount of new molecules and less than ca. 10 mg of powder is available for purification and crystallization.

3.1.2. Design and Construction of Apparatus for the Solution Phase Crystal Growth Methods

A heater block furnace was constructed for crystal growth using solution methods. An aluminum block with cavity spaces for brown bottles (to prevent any side reactions due to light) was used as the heating medium. A heater mat controlled by the temperature feedback system described above, was stuck beneath the aluminum block. The whole system was thermally insulated with glass wool. Fig. 11 shows the schematic of the heater block furnace.

Fig. 11: Schematic diagram of lab-made aluminum block furnace which can go up to a maximum temperature of 170 °C. It can be used to grow molecular single crystals, such as tetracene, pentacene and C_{60} , in molten naphthalene.

Precise temperature profile control is achieved with this furnace. In the calibration experiment, the furnace was commanded to first ramp to 100 °C at a rate of 50 °C/hour, dwell at 100 °C for 2 hours and then cool to 25 °C at a slow rate of 2 °C/hour. Fig. 12 shows the actual temperature plotted against time. It followed precisely, with minimal temperature fluctuations, the settings in the temperature controller. With this precision and control, the chances of growing high quality single crystals are greatly increased.

Fig. 12: Precise controlled temperature profile from the lab-made heater block furnace for crystal growth using solution growth. The temperature was controlled as follows 1) ramp from room temperature to 100°C at a rate of 50°C/hour, 2) dwell at 100°C for 2 hour and 3) cool slowly to room temperature at a rate of 2°C/hour.

A silicone oil bath with similar temperature profile precision control was also built as shown in Fig. 13. A Commercial rope heater was coiled around the quartz tube

and the feedback thermocouple was placed at the bottom of the round-end quartz tube. The bath is mainly used for crystal growth in molten naphthalene in closed ampoule. Molecular single crystals such as tetracene, pentacene and C_{60} have successfully been grown.

Fig. 13: Schematic diagram of lab-made silicone oil bath which can go up to a maximum temperature of 250 °C. It was used to grow molecular single crystals, such as tetracene, pentacene and C_{60} , in molten naphthalene.

3.2. Structure and Quality Characterization of Molecular Single Crystals

After the molecular single crystals are grown, there is a need to know their crystal structure and quality. Knowing the crystal structure would allow easier interpretation of measurement data. Knowing that the crystals are of high quality would make the assumption of minimal influence of other defects and impurities more realistic. This is important as the measured physical properties would be closer to the materials' intrinsic properties.

There are various ways to characterize molecular single crystals. In this report, various methods are used to characterize the structural and quality of the molecular

single crystals. The characterization methods used were listed and described below.

3.2.1. Structural Characterization Methods

- **Powder X-Ray Diffraction (PXRD)**

Powder X-Ray Diffraction (PXRD) was used to confirm the phases of the single crystals using a Bruker AXS D8 Advance apparatus. The single crystals were crushed into powders and scanned with a Si low background sample holder, especially for low amount of sample, at holder rotation speed of 15rpm, 2θ range of $5^\circ - 60^\circ$, resolution of $0.01^\circ/\text{step}$ and $0.1\text{s}/\text{step}$ in a Bruker AXS D8 Advance Powder X-Ray Diffraction System. The Si low background sample holder aids the sensitive of the measurement as it only require low amount of powdered sample. Crystal phases of most of the molecular single crystals were confirmed using this technique. Software such as Match, EVA, Topaz, and similar has been routinely used for data analysis.

- **Single Crystal X-Ray Diffraction (SCXRD)**

Single Crystal X-Ray Diffraction (SCXRD) was used to confirm the crystal structure of the molecular single crystals using a Bruker SMART APEXII apparatus. Due to the low X-ray diffraction of the organic compounds, the dimensions of the crystals should be in the micrometer range. The crystal structure parameters were calculated from the diffraction pattern spots using software called JANA2006 and cif files were generated containing the crystallographic information of the single crystals. The crystal structures were drawn from the cif files using software called Diamond. Table 3 shows a list of crystal structures of the grown molecular single crystals determined using the PXRD and SCXRD.

Some of the crystal structures are still unknown as the crystals were too small for full crystal structure determination.

Growth Methods	Materials	Morphology	Crystal Structure	Space Group	Characterizations
Gas	Anthracene	Platelet	Monoclinic	P21/a (14)	PXRD
	Tetracene	Platelet	Triclinic	P-1 (2)	PXRD
	Pentacene	Platelet	Triclinic	P-1 (2)	PXRD
	DPA	Needle	Monoclinic	C2/c (15)	PXRD
		Platelet	Unknown	Unknown	PXRD
	Rubrene	Platelet	Orthorhombic	Cmca (64)	PXRD
	Perylene	Platelet	Monoclinic	P21/a (14)	PXRD
	CuPc	Needle	Monoclinic	P21/a (14)	PXRD
	F16CuPc	Ribbon	Unknown	Unknown	Nil
	TCNQ	Platelet	Monoclinic	C2/c (15)	PXRD
	C ₆₀	Block/ Platelet	Cubic	F	PXRD/ SCXRD
	C ₇₀	Block	Unknown	Unknown	PXRD
	TTT	Needle/ Ribbon	Monoclinic	P1211	PXRD/ SCRD
			Orthorhombic	P212121	
	P1T1	Needle	Monoclinic	P121/c1	SCRD
	P2T1	Platelet	Triclinic	P-1	SCRD
Solution	Anthracene	Platelet	Monoclinic	P21/a (14)	PXRD
	Tetracene	Platelet	Triclinic	P-1 (2)	PXRD
	Pentacene	Platelet	Triclinic	P-1 (2)	PXRD
	DPA	Block	Unknown	Unknown	PXRD
	C ₆₀	Block	Cubic	F	PXRD/ SCRD
	P1T1	Needle	Monoclinic	P121/c1	SCRD
	P3T1	Block	Triclinic	P-1	SCRD

Table 3: List of crystal structure of different molecular single crystals obtained from PXRD and SCXRD measurements.

3.2.2. Purity and Quality Characterization Techniques

- **High Performance Liquid Chromatography (HPLC)**

Molecular single crystals were dissolved in chloroform or acetonitrile (ACN) and undergo liquid chromatography in an Agilent 1100 Series HPLC system. A JH08S04-2546 WT 250 x 4.6 mm I.D. S-4 μ m, 8 nm column at room temperature was used. In the column was porous silica beads modified with hydrophobic C₁₈ chains. Due to different affinity of each molecule in the mobile phase, i.e, acetonitrile and water, to the C₁₈ chains, different molecules was separated in the column using the developed HPLC method. The HPLC method mainly consists of the flow rate of the mobile phase, the ratio of the mobile phase, and the UV detection wavelength. The HPLC method is developed for each studied material. Most of the impurities were separated from the host molecules and detected by an UV detector.

- **Liquid Chromatography Mass Spectroscopy (LCMS)**

To perform a quantitative analyze of the host material and separated impurities, a HPLC connected with a mass spectrometer, the Shimadzu LCMS-IT-TOF (Liquid Chromatography Mass Spectroscopy - Ion Trap - Time of Flight) was used. The column, same as the one used for HPLC experiments, was used but the temperature was elevated to 40 °C which resulted in shorter retention time. Ideally, the HPLC technique separates the different molecules and each HPLC peaks should have only one detected mass value. However, different mass values were detected in each HPLC peak. This may be due to side chemical reactions during the separation or detection process. Only the mass values are detected in this technique and the molecular structure was not determined by this technique. Therefore, the molecular structures were assumed intuitively from the mass values.

- **Photoluminescence (PL)**

Photoluminescence (PL) measurements were done using a Witec alpha 300 system. Peaks related to the oxides of rubrene were detected on the oxidized rubrene crystals using PL techniques. The intensities of the peaks associated with the oxides of rubrene increase with increasing heating time at 100 °C in air.

- **Matrix-Assisted Laser Desorption Ionization Time of Flight Mass Spectroscopy (MALDI-ToF-MS)**

Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-ToF-MS) was used to check the purity of some of the crystals. Anthracene, tetracene, pentacene, rubrene and perylene-TCNQ single crystals were placed on carbon tape on a MALDI plate and loaded in Shimadzu Biotech AXIMA TOF² system. A 337nm nitrogen laser was used to ablate the crystal surfaces. Small trace of carbazole were detected in anthracene single crystals revealing the high sensitivity of the mass spectroscopy techniques. Impurities, suspected to be oxides of rubrene and pentacene, were detected on rubrene and pentacene single crystals. However, quantification of each impurity could be done only for selected impurities as different molecules react to ‘fly’ differently under the ablation of the laser. Chemical reactions could occur during laser ablation.

- **Cross-Polarized Light Technique (PLT)**

The cross-polarized light technique (CPLT) was done using a Leica M205 C Stereomicroscope. The crystal were placed in-between two linear polarizing filters. This was used to differentiate the phases in many crystals, in particular for the perylene - TCNQ single crystals. The difference in colour along the same axis reveals the different phases in the crystals. The quality of the crystals was

evaluated using this technique. Rubrene, anthracene, tetracene, perylene, CuPC, F₁₆CuPc, TCNQ and tetrathiotetracene (TTT) single crystals were shown to be of good quality.

- **Scanning Electron Microscopy (SEM)**

The SEM technique was applied to evaluate the surface quality of the crystals using a JEOL JSM-6360A Analytical Scanning Electron Microscope. Straight growth steps and sharp crystal edges could be observed from the scanning electron images (SEI) of the molecular single crystals. Smooth crystal surface could be observed from the SEI, revealing good crystal surface quality.

- **Fourier Transform Infrared Spectroscopy (FTIR)**

Molecular single crystals and precursors were mixed with KBr, pressed into 10 mm diameter, 1mm thick pellets and used for room temperature data collection using a PerkinElmer FTIR Spectrum GX system. Single crystals were also stuck on to a sample holder and an infrared beam was transmit led through the crystals directly. This is to obtain bond vibration information from the bulk crystals. Attenuated total reflection (ATR) FTIR was used to obtain bond vibrations information at the crystal surfaces or interfaces. However, detection of minute impurities in the crystals was unsuccessful using this technique.

- **Atomic Force Microscopy (AFM)**

AFM has been used to measure the surface roughness of the single crystals using Digital Instruments 3100 AFM system. Molecular steps on the molecular single crystals were observed using this technique. Flat and molecularly smooth crystal

surfaces are desirable for fabrication of FETs. Thickness can also be measured for thin crystals using this technique.

- **Differential Scanning Calorimetry (DSC)**

DSC has been used to investigate the reactions of sulphur and tetracene using the TA QSeries DSC Q10 system. Crystals or powders were sealed in a standard pan and the heat flow was measured with changing temperature. Exothermic peaks were detected for the reactions between tetracene and sulphur.

- **Thermogravimetric Analysis (TGA)**

TGA has been used to study the polymerization and decomposition of the parylene N film using TA QSeries TGA Q500 system. Mass loss of the sample was measured with increasing temperature. The degree of mass loss of the sample could give information such as the decomposition or sublimation temperature of the source precursors used for crystal growth.

3.3. Growth of Mono-Component Molecular Single Crystals

Mono-component single crystals, such as anthracene, tetracene, pentacene, and rubrene, were grown from commercially available powders. They are mainly from commercial companies such as Sigma-Aldrich, Fluka, Alfa Aesar and American Dye Source. These commercial powders come in bottles of unknown organic impurity content. Hence, in order to study the intrinsic physical properties of these materials, careful purification, i.e removal of impurities, and single crystal growth of the materials would be essential. Two methods have been employed to achieve this goal. They were the gas phase and the solution phase methods.

3.3.1. From Gas Phase – Physical Vapor Transport (PVT)

The PVT method was used to grow various single crystals. The single crystals grown for this study include anthracene, tetracene, pentacene, perylene, diphenylanthracene, copper phthalocyanine (CuPc), fluorinated copper phthalocyanine (F₁₆CuPc) and Tetracyanoquinodimethane (TCNQ). Binary charge transfer complexes such as perylene – TCNQ single crystals were also grown. The growth of rubrene single crystal and binary transfer complex perylene – TCNQ single crystals is described in detail in this report.

Fig. 14: (a) Schematic Diagram of the Two-zone furnace (b) Temperature-Furnace Length for profile growing rubrene single crystals. The rubrene single crystals are grown near between the two zones.

The growth of rubrene single crystals from rubrene powder (Aldrich) will be reported here as an example. The purity of the commercial material was not specified by the vendor but was analyzed in this study and the material was purified during the crystal-growth process. The horizontal PVT setup shown in the schematic Fig. 14(a) was employed. A two-zone transparent furnace allows the observation of nucleation and growth during the crystal growth process. The temperatures in the middle of the hot, evaporation zone and the cooler, deposition zone were 300°C and 250°C respectively. This is shown in the temperature profile in Fig. 14(b). There is a sharp drop in temperature over a short distance at the interface between the zones. This is close to the step-wise temperature profile desired in the PVT process. Crystals, in the form of needles and platelets, spontaneously nucleated on the wall of a quartz tube. Larger and well-formed crystals were found closer to the evaporation zone at temperatures higher than 250°C and small (below 1 mm) crystals were formed at temperatures below 250°C. Crystals could be grown to size comparable to a ten cent coin shown in Fig. 15. Outside the furnace, along the gas flow direction, at room temperature light orange or even white transparent crystals were always found near the end, inside the quartz tube.

Fig. 15: Rubrene single crystal grown to size comparable to a ten cent coin.

Fig. 16 shows a high quality millimeter-sized rubrene single crystal. The rubrene single crystals were characterized by cross-polarized light microscopy (CPLM), scanning electron microscopy (SEM) and atomic force microscopy (AFM). The uniformity in colour of the CPLM image revealed the high crystallinity and high quality of the single crystal. The secondary electron image (SEI) from the SEM shows extremely straight line and sharp edges which are qualities of a single crystal. The AFM image shows molecular steps on the highly smooth crystal surface.

Fig. 16: (a) Optical image of a rubrene single crystal in the transmission mode. The straight and sharp edges imply good quality of the single crystal. (b) Cross-polarized optical image of a rubrene single crystal. The uniformity in colour of the rubrene crystal indicates that the crystal is of high quality. (c) Secondary electron image of rubrene single crystal using Scanning Electron Microscopy (SEM). The sharp edges and flat surface of the crystal indicate that crystal is of high quality. (d) AFM image of the rubrene single crystal revealing the high surface quality of its surface. It has molecular steps of 0.1 nm.

Fig. 17: Powder XRD data of Rubrene Single Crystals matching the Rubrene PXRD on (a) linear and (b) logarithmic scale [78].

Powder X-ray diffraction (PXRD) techniques were used to confirm the phase of the rubrene single crystals grown. The PXRD data for the rubrene single crystals

grown with the PVT method matches one of the entries in the PDF4 organic database shown in Fig. 17. From the entries, the cif file could be found in the published literature [78]. The rubrene single crystals grown with the PVT method are orthorhombic with space group $Cmca$ (64). The crystal structure of rubrene single crystals is presented in Fig. 18.

Rubrene Crystal Structure (PXRD Matching PDF4 Database)

Fig. 18: Crystal structure of rubrene single crystal. Powder XRD was used to match the crystal structure of rubrene. Crystallography software called Diamond was used to generate the structure from the cif file from the literature [78]. The rubrene single crystal is orthorhombic and its space group is $Cmca$ (64).

3.3.2. From Solution Phase

Anthracene, tetracene, pentacene, diphenylanthracene (DPA) and C_{60} were grown by the solution growth method shown in Table 4. These crystals were grown using the heater block furnace or the silicone oil bath shown in Fig. 11 and Fig. 13. The quality of the crystals grown from solution seems not comparable with that of crystals grown with the PVT method in the experiments.

Conventional solvents, such as toluene and chlorobenzene, boil easily at low temperature. There is interest in growing single crystals at higher temperature. Hence, growing single crystals using a solid state solvent with high boiling point could be interesting.

Naphthalene was chosen as a solvent to grow molecular single crystals. Naphthalene is cheap and has been used as moth balls used to protect clothes in a wardrobe. Single crystals, such as tetracene, pentacene and C_{60} , were successfully grown in molten naphthalene. The crystals grown from molten naphthalene seem to be of good quality as shown in Table 4. However, it was found that there were twinning defects in the C_{60} single crystal grown from molten naphthalene. Growth of C_{60} single crystals from molten naphthalene will be reported in detail as an example below.

Materials	Morphology	Optical Images	solvents
Anthracene	Platelets		toluene
Tetracene	Platelets		naphthalene
Pentacene	Platelets		naphthalene
Diphenylanthracene (DPA)	Blocks		toluene
C ₆₀	Blocks with twinning		naphthalene

Table 4: Mono-component molecular single crystals grown from solution phase. Large platelet anthracene crystals and large block diphenylanthracene crystals were grown from toluene. Platelet tetracene and pentacene and C₆₀ crystals were grown from molten naphthalene.

Fig. 19: (a) Powder X-ray Diffraction (PXRD) of C_{60} single crystals grown by PVT (b) PXRD of C_{60} single crystals grown from naphthalene (c) PXRD of standard silicon powder. Both C_{60} single crystals have the same phase in PXRD analysis. The C_{60} PXRD samples were spiked with some silicon powder to confirm the peak positions.

The Raman and FTIR spectra showed no difference in the structure of the C_{60} crystals grown by the two different methods (not presented in this report). Single crystal X-ray diffraction (SCXRD) and powder x-ray diffraction (PXRD) were done on C_{60} crystals grown from the gas phase and molten naphthalene to determine the crystal structure. The PXRD data show that C_{60} single crystals grown from gas phase (PVT) and solution phase have the same phase as shown in Fig. 19.

Fig. 20: SCXRD diffraction pattern obtained for both PVT and solution grown C_{60} crystals. The PVT crystals exhibited a cubic structure while the phenomenon of twinning can be seen in solution grown crystals, from the doublet diffraction spots in 0kl and h0l planes.

However in Fig. 20, the diffraction pattern, from the single crystal x-ray diffraction (SCXRD), of the C_{60} single crystal grown from molten naphthalene does not match the diffraction pattern of the C_{60} single crystal grown from the gas phase which contradicts the PXRD results. The diffraction pattern of the C_{60} crystals grown from gas phase revealed a cubic crystal structure. The diffraction pattern of the C_{60} crystals grown from molten naphthalene has double spot in the $0kl$ and $h0l$ planes. Hence, it is concluded that twinning occurred within the C_{60} crystals grown from molten naphthalene in a controlled direction.

3.4. Growth of Binary- Component Molecular Single Crystals

3.4.1. From Gas Phase – Physical Vapor Transport (PVT)

In order to better investigate the impurities or foreign molecules affecting the physical properties in the molecular single crystals, a small amount of selected foreign molecules are purposely introduced into the crystal system. If a large amount of foreign molecules is added to the host molecules, new compounds may be formed due to interaction between molecules. Hence, a method of incorporation of foreign molecules with known periodic position in the crystal system was used. That is the growth of binary-component molecular single crystals. The phases of the crystals grown were identified using single crystal XRD, and excellent crystal quality was observed. Anthracene-TCNQ, Tetracene-TCNQ and Perylene-TCNQ charge-transfer compounds have been grown into single crystals. Growth of perylene-TCNQ charge-transfer compounds will be reported here as an example.

Improvements were made to the PVT process to grow binary component molecular single crystals. Growth of perylene-TCNQ charge-transfer compounds with controlled phase and morphology was realized by altering the vaporization rate of the precursors. TCNQ powder and perylene powder were placed in Zone 1 and 2

respectively shown in Fig. 21(a). Employing the temperature profile shown in Fig. 21(b), needle-like black (Perylene)₁-TCNQ (P1T1) single crystals could be obtained. Interestingly, by setting the temperature profile as shown in Fig. 21(c), platelet-like green (Perylene)₂-TCNQ (P2T1) single crystals could be obtained. P2T1 is a newly discovered phase and the crystal structures of the above mentioned perylene-TCNQ charge-transfer compounds are solved using single crystal XRD. The crystal structures of Perylene, TCNQ, P1T1, P2T1 and (Perylene)₃-TCNQ (P3T1) are shown in Fig. 22, Fig. 23, Fig. 24, Fig. 25 and Fig. 26 respectively. It is obvious that the crystal structure of the charge-transfer compound is totally different from its single-component, perylene and TCNQ single crystals. P3T1 single crystals were obtained via solution growth methods and are usually block-like. The platelet-like morphology of P2T1 is desirable in single crystal transistor fabrications.

Fig. 21: (a) Schematic Diagram of the Two-zone furnace (b) Furnace Temperature Profile for growing Dark Needle-like (Perylene)₁-TCNQ (1:1) single crystals (c) Furnace Temperature Profile for growing Green Platelet-like (Perylene)₂-TCNQ (2:1) single crystals. By controlling the sublimation rate of individual molecules, different phases of the crystals could be grown.

Structure and quality determination of the perylene-TCNQ compounds

Perylene Crystal Structure (PXRD Matching)

Fig. 22: Crystal structure of perylene. Powder XRD was used to match the crystal structure of perylene. Crystallography software called Diamond was used to generate the structure from the cif file created from the database. Perylene is monoclinic and its space group is $P2_1/a$ (14).

TCNQ Crystal Structure (PXRD Matching)

Fig. 23: Crystal structure of TCNQ. Powder XRD was used to match the crystal structure of TCNQ with the database. Crystallography software called Diamond was used to generate the structure from the cif file created from database. TCNQ is monoclinic and its space group is C2/c (15).

P1T1 Crystal Structure (SCXRD Matching)

Fig. 24: Crystal structure of (Perylene)₁TCNQ (P1T1). Single crystal XRD was used to solve the crystal structure of P1T1. Crystallography software called Diamond was used to generate the structure from the cif file created from the single crystal XRD experiments. P1T1 is monoclinic and its space group is $P121/c1$. Perylene and TCNQ molecules are stacked alternately in the a -direction.

P2T1 Crystal Structure (SCXRD)

Fig. 25: Crystal structure of $(\text{Perylene})_2\text{TCNQ}$ (P2T1). P2T1 is a new phase which has never been reported. P2T1 was grown from gas phase and could not be obtained from solution phase in the experiments. Single crystal XRD was used to solve the crystal structure of P2T1. Crystallography software called *Diamond* was used to generate the structure from the cif file created from the single crystal XRD experiments. P2T1 is triclinic and its space group is $P-1$.

P3T1 Crystal Structure (SCXRD)

Fig. 26: Crystal structure of (Perylene)₃TCNQ (P3T1). Single crystal XRD was used to solve the crystal structure of P3T1. P3T1 was grown from solution phase and could not be obtained from gas phase in the experiments. Crystallography software called Diamond was used to generate the structure from the cif file created from the single crystal XRD experiments. P3T1 is triclinic and its space group is *P*-1.

The high crystal quality of P2T1 can be shown using cross-polarized light microscopy technique using Leica Optical Microscope shown in Fig. 27. Single colour in the transmission polarized light image revealed high crystalline quality.

Fig. 27: (a) Optical image of P2T1 Single Crystal (b) Cross-polarization image of P2T1 Single Crystal (a) Secondary electron image of P2T1 single crystal (b) AFM image of P2T1 single crystal showing molecular steps revealing the high surface quality of the crystals.

The secondary electron image (SEI) of the P2T1 single crystal from the SEM shows straight lines and sharp edges which also indicate the high crystallinity of the crystal. The AFM image of the P2T1 shows molecular steps at the crystal surface indicating good surface quality.

Fourier-Transform Infrared Spectroscopy (FT-IR) was done for characterization of the crystal phase using a PerkinElmer FTIR spectrum GX system. It was realized that the FTIR spectrum for P2T1 is similar to the FTIR spectrum of P3T1 in

literature [79]. Individual FTIR spectra of the Perylene and TCNQ single crystals grown by PVT were also obtained as shown in Fig. 28.

Fig. 28: FTIR spectra of pure perylene and TCNQ single crystals in the range of (a) $900\text{ cm}^{-1} - 700\text{ cm}^{-1}$ and (c) $1600\text{ cm}^{-1} - 1500\text{ cm}^{-1}$. FTIR spectra of (Perylene)₁-TCNQ (P1T1), (Perylene)₂-TCNQ (P2T1) and (Perylene)₃-TCNQ (P3T1) single crystals in the range of (b) $900\text{ cm}^{-1} - 700\text{ cm}^{-1}$ and (d) $1600\text{ cm}^{-1} - 1500\text{ cm}^{-1}$.

The 811 cm^{-1} and 765 cm^{-1} peaks are believed to be the C-H bending modes of neutral perylene from the FTIR spectrum of pure perylene single crystal as shown in Fig. 28(a). The C-H bending modes of perylene in the (Perylene)₁-TCNQ (P1T1) single crystal are the 815 cm^{-1} and 768 cm^{-1} peaks. The 833 cm^{-1} peak in P1T1 is attributed to TCNQ and is shifted from 862 cm^{-1} in the TCNQ single crystal

compared in Fig. 28(a) and Fig. 28(b). The splitting of the C-H bending modes of perylene in (Perylene)₂-TCNQ (P2T1) and (Perylene)₃-TCNQ (P3T1) single crystals was caused by the two different types of perylene arrangements. For P2T1, it split into 821 cm⁻¹ and 812 cm⁻¹ peaks and also into 775 cm⁻¹ and 765 cm⁻¹ peaks compared to 815 cm⁻¹ and 768 cm⁻¹ peaks respectively in P1T1. For P3T1, it split into 821 cm⁻¹ and 812 cm⁻¹ peaks and also into 776 cm⁻¹ and 766 cm⁻¹ peaks compared to 815 cm⁻¹ and 768 cm⁻¹ peaks respectively in P1T1. The C=C vibration of neutral TCNQ is 1542 cm⁻¹ from the FTIR spectrum of pure TCNQ single crystal as shown in Fig. 28(c). From Fig. 28(d), P1T1 has two TCNQ C=C vibrations at 1541 cm⁻¹ and 1584 cm⁻¹, from the alternating stacking of perylene and TCNQ molecules. However P2T1 has TCNQ C=C vibrations at 1535 cm⁻¹, 1538 cm⁻¹, 1567 cm⁻¹ and 1588 cm⁻¹. And P3T1 has TCNQ C=C vibrations at 1535 cm⁻¹, 1538 cm⁻¹, 1568 cm⁻¹ and 1588 cm⁻¹. These frequencies indicate two different packings of TCNQ and perylene molecules in P2T1 and P3T1 single crystals, which is seen in from the single crystal XRD data. For P2T1, one arrangement was a perylene molecule sandwiched between two TCNQ while the other arrangement was a perylene molecule almost perpendicular to the sandwich stacking as revealed in Fig. 25. For P3T1, one arrangement was two perylene molecules sandwiched between two TCNQ molecules while the other arrangement was the perylene molecule perpendicular to the sandwich stacking shown in Fig. 26.

3.4.2. From Solution Phase

Binary charge transfer compound perylene-TCNQ single crystals were also grown by the solution growth method. Millimeter-sized P1T1 and P3T1 single crystals are shown in Fig. 29. The quality of the charge transfer complex single crystals seems comparable to the single crystals grown from PVT methods. Table 5 shows the single crystal growth parameters of perylene-TCNQ compounds for both gas phase and solution phase. Note that P2T1 can be grown only by gas phase methods while P3T1 can be grown only by solution phase methods in our experiments.

Fig. 29: (a) and (b) Needle-like Perylene-TCNQ single crystals (1:1) were grown by the solution method. (c) and (d) Block-like Perylene-TCNQ single crystals (3:1) were grown by the solution method.

Compounds	Morphology	Crystal Colour	Solvent	PVT Temperature	
				TCNQ	Perylene
P1T1	Needles	Dark green	Toluene	220	220
P2T1	Platelets	Green/ Dark Green	-	180	220
P3T1	Blocks	Dark Green	Benzene	-	-

Table 5: Single crystal growth parameters of perylene-TCNQ compounds

Fig. 30: HPLC data of (a) perylene, (b) TCNQ, (c) perylene-TCNQ (PIT1), (d) (perylene)₂-TCNQ (P2T1) and (e) (perylene)₃-TCNQ (P3T1).

HPLC was done on perylene, TCNQ, P1T1, P2T1 and P3T1 single crystals. The HPLC method was developed for perylene, TCNQ, P1T1, P2T1 and P3T1. The method parameters are list in Table 6.

Mobile Phase	ACN:Water (100)
Flow Rate	1ml/min
Injection Volume	10ul
Solution Concentration	~0.5mg/ml
UV Detection	254nm
Column used	JH08S04-2546WT 250x4.6 mmI.D. S-4um, 8nm No.0425010418(W)
Column Pressure	68 bar
Column Temperature	25 °C

Table 6: A table listing the parameters for the HPLC method developed for analysis of perylene, TCNQ, P1T1, P2T1 and P3T1.

The HPLC data of the perylene-TCNQ salts (P1T1, P2T1 and P3T1) shown in Fig. 30(c), Fig. 30(d) and Fig. 30(e), indicated that the salts do not exist in solution. Two major peaks are detected which correspond to individual perylene and TCNQ in the HPLC data as shown in Fig. 30(a) and Fig. 30(b).

UV-vis absorption measurements were also done on perylene, TCNQ, P1T1, P2T1 and P3T1 in acetonitrile(ACN) as shown in Fig. 31. The UV-vis absorption data also show that the perylene-TCNQ CT compounds in solution exist as individual

perylene and TCNQ, i.e. CT salts of perylene-TCNQ do not exist. This discovery might be significant for the mechanism of crystal growth for charge-transfer compounds using solution methods.

Fig. 31: UV spectroscopy of perylene, TCNQ, (perylene)₁-TCNQ (P1T1), (perylene)₂-TCNQ (P2T1) and (perylene)₃-TCNQ (P3T1) in acetonitrile.

3.5. Molecular Structure Tailoring

Tailoring of molecular structure could have been used widely by the chemists to fine tune the physical properties of materials. However, conventional synthesis methods in organic chemistry often require a lot of process steps and involve the use of solvents. Disposal of used organic solvents has long known to cause environmental hazards. Therefore, a direct, clean and “green” synthesis method was adapted.

Inorganic materials have the advantages of higher stability and better performance while organic materials are cost effective and are easier to fabricate. Hence, there are strong motivations to develop inorganic-organic hybrid material to merge or fuse the advantages of both together into one material.

Polycenes carrying peri-dichalcogenide are known to be superior electron donors [82]. The strong chalcogen-chalcogen and carbon-chalcogen intermolecular interactions are found to be the main mechanisms to lower the first ionization potential of the acenes which will result higher conductivity and better electron donors properties. Direct reaction to produce tetrathiotetracene (TTT) single crystals will be reported here.

Fig. 32: Tetracene and sulphur powder were ground, mixed and loaded in a glass capillary (commercial named as a glass dropper). The glass dropper with the powder mixture was placed in Zone 1 of a two-zone furnace. The temperature at Zone 1 was set to various temperatures, 200 °C, 249 °C, 320 °C and 500 °C. Reactions of tetracene and sulphur will occur to form sulphur-based compounds.

Commercial tetracene and sulphur powder were mixed and ground together in the ratio 5 mol of tetracene to 1 mol of atomic sulphur. As H_2S gas was produced from the reaction between tetracene and sulphur, for safety reasons, an open system was

used for the reaction. A glass dropper loaded with the mixed powder was placed in Zone 1 of a two zone furnace as shown in Fig. 32. The temperature at Zone 1 was raised to 200 °C, 249 °C, 320 °C and 500 °C with constant inert argon gas flow in the furnace. Thereafter, PXRD was done on the leftover source at different temperature shown in Fig. 33. PXRD shows that the powder becomes amorphous above 320 °C which might indicate decomposition or polymerization.

Fig. 33: (a) Powder X-Ray Diffraction (PXRD) of tetrathiotetracene (TTT) leftover source after heated at 200 °C. The first peak at around 7° matches the first peak of tetracene PXRD. Hence, the reaction is not completed. (b) PXRD of TTT leftover source after heated at 249 °C. The tetracene PXRD peak disappeared showing that the reaction had completed. (c) and (d) the TTT leftover source had become amorphous after heated at a temperature more than 320 °C.

Fig. 34: (a) Differential Scanning Calorimetry (DSC) data of sulphur (S) and tetracene ($C_{18}H_{12}$) mixture in the molar ratio of 5:1. The broad peak in the temperature region of 225-250 °C indicates that the reaction is complex. (b) DSC data of sulphur showing dissociation and melting peaks in the temperature region of 100-125 °C. (c) DSC data of tetracene showing no significant heat flow in the temperature range of 25-250 °C.

Differential Scanning Calorimetry (DSC) was performed on a tetracene-sulphur commercial powder mixture, sulphur commercial powder and tetracene commercial powder as shown in Fig. 34. The samples were heated from 25 °C to 250 °C and cooled back to 25 °C at a rate of 3 °C/ min. This is considered a cycle. Two cycles were run consecutively for each sample.

There are two sharp peaks and one broad peak at 114.4 °C, 119.8 °C and 240 °C respectively in the first cycle of the DSC for the tetracene-sulphur commercial powder mixture. There are no peaks in the second cycle. The two sharp peaks at 114.4 °C and 119.8 °C were also observed in the DSC for the sulphur commercial powder which is believed to be associated with the dissociation and melting of sulphur. The broad peak at 240 °C in the first cycle of the DSC for the tetracene-sulphur commercial powder mixture shows that the reaction between tetracene and sulphur is complex.

The overall balanced chemical equation for the reaction between tetracene and sulphur is shown in Fig. 35. However, it is believed that this reaction involves multiple steps implied from the broad peak in the DSC, and the reactions might not be completed.

Fig. 35: Direct synthesis of tetrathiotetracene (TTT) by reacting tetracene with sulphur. This synthesis does not involve any use of solvent. Hence, the reaction is clean and environmental friendly.

The leftover source from the reaction at 249 °C was loaded in Zone 1 of the two zone furnace to grow monoclinic TTT single crystals. The temperature was set at 250 °C at Zone 1, and Zone 2 was at 150 °C. The source was sublimed and carried over by the inert argon gas to Zone 2 where monoclinic TTT single crystals were formed as shown in Fig. 36.

Fig. 36: Tetracene and sulphur powder were ground mixed and placed in zone 1 as source. The temperature was set at 250 °C at Zone 1, and Zone 2 was at 150 °C. The source was sublimed and carried over by the inert argon gas to Zone 2 where monoclinic tetrathiotetracene (TTT) single crystals were formed.

Good refinement of the monoclinic TTT single crystal structure was not obtained from the SCXRD. This might be due to small dimensions or high defect densities of these crystals. However, PXRD data of the monoclinic TTT single crystals seems to match with the calculated SCXRD powder diffraction pattern of the monoclinic TTT single crystals with some of the peaks missing as shown in Fig. 37. This indicates the presence of monoclinic TTT single crystals.

Some crystals were also formed at the end of the furnace. These crystals were confirmed by PXRD and SCXRD to be monoclinic dithiotetracene (DTT) single crystals. Fig. 38 shows the refined crystal structure of the monoclinic DTT single

crystal having space group of P1211. PXRD data of the monoclinic DTT single crystals matches the calculated SCXRD powder diffraction pattern of the monoclinic DTT single crystals shown in Fig. 39. This further confirms the presence of monoclinic DTT single crystals.

Fig. 37: (a) Powder x-ray diffraction (PXRD) pattern of the TTT single crystals which were grown from low temperature (LT) at 250 °C. The PXRD pattern matches quite well with the (b) PXRD pattern calculated from the single crystal x-ray diffraction (SCXRD) data of the TTT single crystals grown at 250 °C.

The PVT method was modified to synthesize and grow new orthorhombic tetrathiotetracene (TTT) single crystals. Tetracene and sulphur powder were ground and mixed together and placed in a two zone furnace as shown in Fig. 40.

Zone 1 was set to 250 °C and zone 2 was set to 500 °C. The mixed powder was sublimed and carried to the end of the furnace where the new orthorhombic tetrathiotetracene single crystals were formed.

DTT Crystal Structure (SCXRD)

Fig. 38: Crystal structure of dithiotetracene (DTT) single crystals. Single crystal XRD was used to solve the crystal structure of DTT. DTT single crystals were grown from the gas phase as describe above. Crystallography software called Diamond was used to generate the structure from the cif file created from the single crystal XRD experiments. DTT is monoclinic and its space group is $P1211$

Fig. 39: (a) Powder x-ray diffraction (PXRD) pattern of the DTT single crystals that were grown from low temperature at 250 °C at the end of the furnace. The PXRD pattern matches quite well with the (b) PXRD pattern calculated from the single crystal x-ray diffraction (SCXRD) data of the DTT single crystals grown at 250 °C.

Fig. 40: Tetracene and sulphur powder were ground, mixed and placed in zone 1 as source. Zone 1 was set at 250 °C and Zone 2 was set at 500 °C. The source was sublimed and carried over by the inert argon gas to the end of the furnace where newly discovered orthorhombic tetrathiotetracene (TTT) single crystals were formed.

The optical images and cross polarization images of the tetracene and orthorhombic TTT single crystals were shown in Fig. 41. The optical images and cross polarization shows that both the tetracene and orthorhombic TTT single crystals are of high quality. The colour changes from orange for tetracene single crystals to green for orthorhombic TTT single crystals which indicate the energy bandgap is reduced.

Fig. 41: (a) Optical image of tetracene single crystal (b) Cross-polarization image of tetracene single crystal (c) Optical image of orthorhombic tetrathiotetracene (TTT) single crystal (d) Cross-polarization image of TTT single crystal

Fig. 42 shows the secondary electron images (SEI) of commercial sulphur powder, commercial tetracene powder, tetracene single crystal and TTT single crystal. The SEI show the morphology of the commercial powders. The sulphur commercial powder has particles in cone-flower shape and the tetracene commercial powder has particles in platelet shape. The SEI of the crystals show the obvious transformation from the respective commercial powder and the high quality smooth crystal surfaces. The smooth crystal surfaces are important criteria for making good FETs.

Fig. 42: (a) Secondary Electron Image (SEI) of sulphur commercial powder. The sulphur commercial powder has particles of cone-flower shape. (b) SEI of tetracene commercial powder (c) SEI of triclinic tetracene single crystal having high quality smooth crystal surface desired for FETs. (d) SEI of orthorhombic TTT single crystal. The morphology is ribbon-like and the crystal surface is smooth.

The crystal structures of the tetracene and tetrathiotetracene (TTT) single crystals were shown in Fig. 43 and Fig. 44. Both of the crystals have crystal structures that are completely different, with just substitution of four hydrogen atoms with four sulphur atoms. The tetracene single crystal is triclinic and has a space group of P-1 (2). The TTT single crystal is orthorhombic. It has a space group of P212121. Different crystal structures with different molecular interactions make drastic changes on the physical properties.

Tetracene Crystal Structure (SCXRD)

Fig. 43: Crystal structure of tetracene single crystals. Powder XRD was used to match the crystal structure of tetracene. Tetracene single crystals were grown from the gas phase in the experiments. Crystallography software called Diamond was used to generate the structure from the cif file created from the database. Tetracene is triclinic and its space group is $P-1$ (2).

TTT Crystal Structure (SCXRD)

Fig. 44: Crystal structure of tetrathiotetracene (TTT) single crystals. Single crystal XRD was used to solve the crystal structure of TTT. TTT single crystals were grown from the gas phase as described above. Crystallography software called Diamond was used to generate the structure from the cif file created from the single crystal XRD experiments. TTT is orthorhombic and its space group is $P2_12_12_1$.

3.6. Parylene Dielectric Coating System

Fig. 45: A lab-made reactor for vapour deposition of conformal parylene film. A lab-made small furnace was used for sublimation of the solid dimer paracyclophane (di-para-xylylene) at 120 °C. A commercial high temperature furnace from Thermo was used for creating the prolysis zone at 700 °C. A tight sealed vacuum chamber was used as the polymerization zone.

A parylene dielectric coating system was developed for transistor fabrication as shown in Fig. 45. Carbon or silver paste was painted on the crystal surfaces as source and drain electrodes, forming the channel in between. Next, conformal parylene N polymer film was deposited on the crystals as the dielectric. Then, a gate was painted on the film between the channels. This forms the top contact, top gate field-effect transistor.

Fig. 46: Process flow of the parylene coating system. The parylene dimer source powder was first vaporized in the vaporization zone and diffused to the pyrolysis zone. In the pyrolysis zone, the parylene dimer molecules undergo pyrolysis at 700 °C, forming the monomer free radicals. The free radicals diffused and polymerized into polymer film at the polymerization zone at room temperature. The whole system was at a pressure of $\sim 10^{-3}$ Torr.

The basic process flow of the parylene coating system is shown in Fig. 46. The parylene system was pumped down to $\sim 10^{-3}$ Torr. The parylene dimer source (solid dimer paracyclophane (di-para-xylylene)) was vaporized and diffused to a 700 °C high temperature furnace labeled as the pyrolysis zone. The high temperature at the pyrolysis zone caused the dimer molecules to pyrolyze into highly reactive free radicals. The pyrolysis reaction is shown in Fig. 47. These free radicals then diffused to the deposition chamber and polymerized into a conformal polymer film at room temperature.

Fig. 47: Pyrolysis of solid dimer paracyclophane (di-para-xylylene) into monomer para-xylylene free radicals. The monomers will then undergo free radical polymerization, forming a conformal parylene film.

Fig. 48: Relationship between the parylene N precursor mass used and the thickness of the parylene N film formed using the parylene coating system.

Fig. 48 shows the relationship between the mass of the parylene N precursor used and the thickness of the transparent parylene N film formed. The relationship is

almost linear. Table 7 gives a list of the capacitance per unit area of the film calculated for the respective film thickness with the formula shown below.

$$C_i = \frac{\kappa \cdot \epsilon_0 \cdot 10^{-4}}{\text{film thickness}}$$

where

C_i is the capacitance per unit area

κ is the relative dielectric constant of the transparent parylene N film

ϵ_0 is the permittivity of free space, 8.854×10^{-12} F/m

d is the thickness of the transparent parylene N film

The capacitance was calculated using a dielectric constant (ϵ) of 2.67 from the literature [77]. The thicker the film the lower will be its capacitance. The calculated capacitance is in F/cm².

Parylene N precursor mass used (g)	Thickness of parylene dielectric layer formed (nm)	Standard deviation (nm)	Capacitance (10 ⁻⁹ F/cm ²)
0.20	635.44	7.35	3.72
0.25	795.33	10.18	2.97
0.30	886.18	7.75	2.67
0.35	1132.88	22.17	2.09
0.40	1325.10	28.45	1.78

Table 7: Mass of parylene dimer used as starting material resulting in different thickness of the parylene N polymer film. The respective capacitances of the film of different thickness were calculated using a dielectric constant of 2.67 from the literature [77].

Atomic force microscopy (AFM) was done on the 1.1 μm thick parylene N film, as the surface roughness is crucial to the fabrication of FETs. There are a lot of dust particles on the film detected by the AFM technique shown in Fig. 49(a). Very rough dielectric surfaces could lead to gate leakage current through the thinnest part of the dielectric. The average roughness of the parylene N film was found to be 7.269nm from the dust-free region as shown in Fig. 49(b). The parylene N film is considered smooth.

Fig. 49: Atomic Force Microscopy (AFM) image of the 1.1 μm thick Parylene N film (a) showing a lot of dust particles found on the film and (b) showing an average roughness of 7.269 nm on the highlighted area.

Chapter 4 - Purity Assessment

4.1. Impurity Distribution in Single Crystals

Impurity distribution in molecular single crystals could be imagined to be of two types. Impurities could be formed at the surface of the crystal as shown in Fig. 50(a), for example, a layer of oxide at the crystal surface. Impurities or defects could also be randomly or evenly distributed throughout the crystal shown in Fig. 50(b). The impurity distributions within the crystal could affect its physical property differently.

Fig. 50: Models of the distribution of the impurities or defects within a crystal. The black dots represent impurities or defects. (a) A layer of impurities formed at the crystal surface, such as oxide of the host molecule. (b) Impurities distributed randomly or evenly throughout the crystal.

4.2. Bulk Purity Investigation

Researchers are familiar with commercial inorganic semiconducting materials having metal basis purity of 99.999% (5N) or 99.9999% (6N). The physical properties of the inorganic single crystals could be adversely affected by minute impurities, at ppm or even ppb amount. It is therefore interesting to investigate the relation between high charge carrier mobility of molecular single crystals and their purity. Rubrene was selected for this study as it possess the highest mobility (around 40 cm²/Vs for a 4-point contact single crystal air-gap transistor) in the field of semiconducting molecular single crystals. The well-known material is one of the most studied. Physicists, chemists and material scientists from around the world had showed great interest on this material.

4.2.1. Work of Liquid Chromatography and Mass Spectroscopy

High Performance Liquid Chromatography (HPLC) was performed on commercial rubrene powder and rubrene single crystals. Bright red rubrene solutions of fixed concentration were prepared by dissolving commercial rubrene powder or rubrene single crystals in chloroform. The HPLC method for rubrene was developed and is listed in the Table 8 below.

Mobile Phase	ACN:Water (98:2)
Flow Rate	1ml/min
Injection Volume	10ul
Solution Concentration	~0.5mg/ml
UV Detection	254nm
Column used	JH08S04-2546WT 250x4.6 mmI.D. S-4um, 8nm No.0425010418(W)
Column Pressure	60 bar
Column Temperature	Room temperature

Table 8: A table listing the parameters for the HPLC method developed for analysis of rubrene

As shown in Fig. 51, two major peaks were observed in the rubrene HPLC chromatogram at around 15 min and 36 min. The peak at around 15 min was named Peak 1 and the peak at around 36 min was named Peak 2. Peak 1 and Peak 2 were believed to belong to the oxidized form of rubrene and rubrene respectively. The degradation of rubrene to the oxidized form of rubrene in solution as the days passed was analyzed. Bleaching of the bright red colour solution to colourless solution overtime was observed. Peak 1 increased while Peak 2 decreased as the days passed. This indicated that the solution was changing and Peak 1 was peak indicated an oxidized form of rubrene.

Fig. 51: HPLC chromatogram of rubrene solution in chloroform kept for 0 to 6 days on the laboratory bench. The oxidation of rubrene is presented here as a bleaching of the red solution. The peak at around 36min is associated with rubrene while the peak at around 15 min is associated with the oxidized form of rubrene.

In order to identify the major peaks (Peak 1 and Peak 2), photoluminescence measurements were done on samples which were collected manually from the HPLC. From Fig. 52, photoluminescence was observed from Peak 2 but not from Peak 1. The position of the photoluminescence peak of Peak 2 was blue shifted from the photoluminescence peak of commercial rubrene dissolved in toluene. This could be due to the different solvents in the samples of Peak 2 and commercial rubrene.

Fig. 52: Photoluminescence measurements of the major peaks collected manually from the rubrene HPLC measurement. The black curve (Peak 1) is associated with the peak around 15min in the HPLC measurement. The red curve (Peak 2) is associated with the peak around 36min in the HPLC measurement. The green curve is the luminescence peak resulted from the commercial rubrene dissolved in toluene in the photoluminescence measurement. The luminescence peak from the Peak 2 of HPLC in the photoluminescence measurement gives evidence of the presence of rubrene molecules. The peak shift of the red curve (Peak 2) to the green curve (Commercial Rubrene) might be due to the different solvents used in the measurement.

Photoluminescence (PL) measurements were also done on the (110) surface of solid state rubrene single crystals shown in Fig. 53. The pristine rubrene single crystals were grown in forming gas and the oxidized rubrene single crystals were

grown in air. A 488nm laser beam was incident on the crystal surfaces and photoluminescence was backscattered from the crystal surface. The red curve shows the oxidized rubrene and the black curve shows the pristine rubrene in Fig. 53. Part of the spectra of the oxidized rubrene was similar to the pristine rubrene. The peaks at 650nm and 720nm were believed to be related to the oxidized form of rubrene on the crystal surface.

Fig. 53: Photoluminescence (PL) data of the (110) surface of solid state rubrene single crystals. The black line represents PL detected from the pristine rubrene and the red line represents PL detected from the oxidized rubrene

LCMS was done on rubrene single crystals and commercial powder. The rubrene samples were prepared in the same way as in the HPLC experiments. The quantitative amount of endoperoxide on the surface of crystals was not investigated because the LCMS measurements the crystals need to be dissolved in a solvent (chloroform) and oxidation of rubrene in solution needs to be avoided, which was impractical in the experiments. Still, efforts were made to minimize light exposure of the rubrene solution samples during preparations by using brown vials and wrapping the vials in aluminum foil. The HPLC method used in the LCMS experiments was similar to the other HPLC experiments except that the column temperature used was controlled at 40°C. This results in shorter total retention time in the initial HPLC process of the LCMS experiments. The two major peaks (Peak 1 and Peak 2) were still observed. It was found that higher column temperature could improve peak resolution and reduce total retention time. However, it is important to note that higher temperature might accelerate the chemical reaction or even activate new reactions.

Fig. 54: Chromatogram of commercial rubrene powder. Curve (a) represents the peaks as measured by the UV detector of the LCMS system. The curves (b)-(g) show the appearance of molecular masses of (b) 533 m/z, (c) 547 m/z, (d) 565 m/z, (e) 531 m/z, (f) 535 m/z and (g) 549 m/z.

Fig. 54(a) shows the Total Ion Chromatogram (TIC) of commercial rubrene powder dissolved in chloroform solution, and Fig. 55(a) shows the TIC of rubrene single crystal dissolved in chloroform solution. Molecular masses of 533 m/z, 547 m/z, 565 m/z, 531 m/z, 535 m/z and 549 m/z were detected in commercial rubrene. Molecular masses of 533 m/z, 547 m/z and 565 m/z were detected from rubrene single crystals. It is clearly seen that most impurities have been successfully removed in rubrene single crystals during the crystal growth process using physical vapor transport (PVT). A list of masses and their assumed associated chemical formulae detected in commercial rubrene powder and rubrene single crystals is shown in Table 9. Only rubrene and its oxidized form were detected in rubrene single crystals. It is also interesting to note that 533 m/z which is associated to the

rubrene molecule was also detected in Peak 1. This indicates that the oxidation reaction of rubrene is complex and unstable during flowing in the LCMS system. Table 10 listed the detected masses with the associated assumed molecule structures present in commercial rubrene and rubrene single crystal. Table 10 and Fig. 56 show the assumed molecules detected and the proposed possible chemical reactions.

Fig. 55: Chromatogram of rubrene single crystal. Curve (a) represents the peaks as measured by the UV detector of the LCMS system. The curves (b)-(d) show the appearance of molecular masses of (b) 533 m/z , (c) 547 m/z and (d) 565 m/z .

Peak #	Retention Time	Base Peaks m/z	Possible Formula	Commercial Powder	Single Crystal
1	~5.8 min	549	C ₄₂ H ₂₈ O	Yes	No
		531	C ₄₂ H ₂₆		
2	~6.5 min	549	C ₄₂ H ₂₈ O	Yes	No
		531	C ₄₂ H ₂₆		
3	~7.9 min	549	C ₄₂ H ₂₈ O	Yes	No
		531	C ₄₂ H ₂₆		
4	~8.8 min	531	C ₄₂ H ₂₆	Yes	No
5	~9.8 min	531	C ₄₂ H ₂₆	Yes	No
6	~10.2 min	565	C ₄₂ H ₂₈ O ₂	Yes	Yes
		547	C ₄₂ H ₂₆ O		
		533	C ₄₂ H ₂₈		
7	~10.7 min	549	C ₄₂ H ₂₈ O	Yes	No
		533	C ₄₂ H ₂₈		
8	~14.7 min	431	-	Yes	No
9	~15.9 min	338	-	Yes	No
10	~18.1 min	535	C ₄₂ H ₃₀	Yes	No
11	~20.9 min	533	C ₄₂ H ₂₈	Yes	Yes

Table 9: Molecular masses detected by the LCMS (liquid chromatography with mass spectroscopy) system in particular HPLC peaks.

Molecular Mass of the Protonated Molecules m/z [g/mol]	Assumed Molecular Structures
533
531
535
549
565

Table 10: Assumed molecular structures of some molecules associated with LCMS peaks

Fig. 56: Proposed reactions during the LCMS detection process

4.3. Surface Purity Investigation

4.3.1. Sensitivity of MALDI-ToF-MS

MALDI-ToF-MS was done on molecular single crystals to investigate the purity at the crystal surface. Carbon tapes were struck onto the cleaned MALDI plate and the single crystals were placed on the carbon tapes for measurements. A 337nm nitrogen laser was used to ablate the crystal surface. The result is shown in Fig. 57 below. Considering the ppm sensitivity of the MALDI-ToF-MS technique, signal peaks can be associated to the molecules of interest if there is a sudden increase in peak area compared with the peaks surrounding it. In addition, the peak resulting from the molecule is usually surrounded by peaks from its isotopes which will aid in identifying very small peak signals.

Fig. 57: Mass spectrum of anthracene single crystal from MALDI-ToF-MS experiment. A major peak at mass of 178 m/z was detected, which matches the molecular mass of anthracene. A minute amount of 167 m/z , which matches the molecular mass of carbazole, was also detected in the single crystals

The sensitivity of the MALDI-ToF-MS technique could be seen in the experiments on anthracene single crystals. Minute amounts of carbazole could be detected in anthracene single crystals grown from commercial powder, gas phase and solution phase as shown in Fig. 57. 178 m/z represents the mass value of anthracene while 167 m/z represents the mass value of carbazole after ionization. Carbazole content was also detected in the literature [20]. Hence, it is possible to evaluate the purity of the single crystals using the MALDI-ToF-MS technique.

4.3.2. Work of MALDI-ToF-MS and FTIR Measurements

Fig. 58: Mass spectrum of rubrene single crystal from MALDI-ToF-MS experiment. Major peak at mass of 533 m/z was detected which matches the molecular mass of rubrene with a positive proton added during ionization in the mass spectrometer.

The mass spectrum of a rubrene single crystal was shown in Fig. 58 above. A major peak at 533.01 m/z was detected in the mass spectrum and was the molecular mass of rubrene molecule. Impurity peaks such as 334.88 m/z and 481.43 m/z were also observed in the mass spectrum. Fig. 59 shows a zoomed in view of the impurity peak at 565.33 m/z, which was believed to be associated with the rubrene endoperoxide molecules. 565.33 m/z was the molecular mass of rubrene endoperoxide.

Fig. 59: Zoomed in mass spectrum of rubrene single crystal from MALDI-ToF-MS experiment. A very small peak at 565.33 m/z was detected, which may be associated with rubrene endoperoxide.

Similar procedures, as with the rubrene MALDI-ToF-MS experiments, were repeated in the experiments of MALDI-ToF-MS on pentacene single crystals and commercial powder. The mass spectrum of a pentacene single crystal was shown in Fig. 60 below. A major peak at 277.86 m/z was detected in the mass spectrum and was similar to the molecular mass of the pentacene molecule. Impurity peaks such as 294.95 m/z and 309.04 m/z were also observed in the mass spectrum.

Fig. 60: Mass spectrum of pentacene single crystal from MALDI-ToF-MS experiment. Major peak at mass of 277.86 m/z was detected which matches the molecular mass of pentacene. Smaller peaks of 294.95 m/z and 309 m/z were detected and were believed to be associated with oxidized form of pentacene.

Fig. 61 shows a zoomed in view of the impurity peaks of 294.95 m/z, 309.04 m/z and 324.14 m/z which were believed to be associated with the different forms of pentacenequinone, containing single oxygen, double oxygen and triple oxygen respectively.

Fig. 61: Zoomed in mass spectrum of pentacene single crystal from MALDI-ToF-MS experiment. Smaller peaks of 294.95 m/z, 309.04 m/z and 324.14 m/z were detected which may be associated to different forms of pentacenequinone, with single oxygen, double oxygen and triple oxygen respectively.

Table 11 shows the impurities that were detected in the rubrene and pentacene single crystal surface and the commercial powder. In the table is listed the impurity: host molecule intensity ratio. Note that the impurity: host molecule intensity ratio did not take the isotopes of other molecules into consideration. The molecules listed in the table are the assumed molecular structures and more characterization work should be done in the future for confirmation. The results found for pentacene were similar to those in the literature [80].

Materials	Forms	Impurity Mass (m/z)	Assumed Molecular Structure	Impurity/Host Mass Ratio
Rubrene	Commercial Powder	548.99		0.005
	Single Crystals	549.13		0.004
	Commercial Powder	565.57		0.001
	Single Crystals	565.33		9.42e-4
Pentacene	Commercial Powder	293.95		0.114
	Single Crystals	294.95		0.030
	Commercial Powder	307.95		0.130
	Single Crystals	309.04		0.011
	Commercial Powder	324		0.019
	Single Crystals	324.14		0.005
	Commercial Powder	340		0.007
	Single Crystals	-		-

Table 11: List of impurity masses detected using MALDI-ToF-MS. The molecules drawn in the list are the assumed molecular structures.

In order to investigate on the purity of the single crystal at the surface and in the bulk, the FTIR technique was used. A black board with a small hole was used as the sample holder in these experiments. The rubrene single crystal was pasted on to the sample holder (covering the hole), and infrared beam will pass through the crystals measuring the absorption after the crystals. Thus, chemical information of the bulk could be obtained.

The ATR-FTIR technique was then used to obtain the chemical information from the crystal surface. The rubrene single crystal was pressed onto an optically transparent window with high refractive index. Due to the occurrence of total internal reflection, the infrared beam will just probe the surface of the crystal as it passes through the high refractive index optically transparent window. In this way, chemical information from the crystal surface could be obtained.

Fig. 62 shows the results comparing the FTIR from the bulk of the rubrene single crystal and the surface of the rubrene single crystal.

Peaks at 876 and 1190 cm^{-1} were detected and assigned to $-\text{O}-\text{O}-$ and $-\text{C}-\text{O}-$ stretching mode in FTIR for rubrene endoperoxide. However, the purity and form of the rubrene endoperoxide which might affect the FTIR vibration spectrum was not reported in the paper [81]. In the FTIR of $^{18}\text{O}_2$ enriched ascaridole, a peak at 730 cm^{-1} was detected and assigned to the $-\text{O}-\text{O}-$ stretching mode [83]. Therefore, the 730 cm^{-1} peak detected in Fig. 62(a) might be related to the $-\text{O}-\text{O}-$ stretching mode of the oxides of rubrene on the rubrene surface. Extra peaks are detected in the FTIR from the surface of the rubrene single crystal compared to the FTIR from the bulk of the rubrene single crystal.

The purity of semiconducting single crystals is well-known to adversely influence the material physical properties in inorganic semiconductor. The semiconductor industry is familiar with 99.999% (5N) and 99.9999% (6N) metal basis pure

silicon single crystals. Learning from the inorganic semiconductor field, the purity of the molecular single crystals has been investigated. Attempts to detect organic impurities in molecular single crystals with HPLC, LCMS, MALDI-ToF-MS and FTIR techniques were made.

Fig. 62: FTIR spectra comparing the chemical bonding in rubrene bulk and rubrene surface in the respective spectra ranges (a) $900 - 600\text{ cm}^{-1}$ (b) $1100 - 900\text{ cm}^{-1}$ (c) $1600 - 1300\text{ cm}^{-1}$ (d) $3200 - 2950\text{ cm}^{-1}$. Extra peaks were detected in different parts of the FTIR spectrum on the rubrene surface, indicating some chemical changes could happen at the surface. Note that the 730 cm^{-1} peak detected in (b) might be related to the -O-O- stretching mode.

Chapter 5 - Physical Properties Measurements

5.1. Introduction

Fundamental studies of carrier transport properties in organic semiconductors should lead to low cost applications in flexible organic electronics such as foldable displays, organic solar cells and printed microelectronic circuits. In particular, the increase in electron and hole mobilities from the range of 10^{-5} to above $10\text{ cm}^2/\text{Vs}$ was achieved. The exploration of new and higher-quality crystalline materials promises numerous new applications, especially in high-frequency electronics.

However, the intrinsic transport mechanism is still debatable and the limit of charge carrier mobility, a parameter critical for device applications, is not yet known due to the presence of impurities and other defects at far higher levels than in typical inorganic semiconductors. This chapter explores the possibility of controlling the transport properties by material selection, molecule engineering and surface doping of molecular semiconductors.

5.2. Single Crystal Field-Effect Transistors (FETs) Fabrication Processes

Different types of field-effect transistors (FETs) have been fabricated. They are the silicon dioxide FETs, air-gap FETs and parylene N FETs. For rubrene, tetracene, pentacene and TCNQ which have very flat surfaces, PDMS stamps with prefabricated source, drain and gate are used. FETs with silicon dioxide as dielectric were also prepared on F₁₆CuPc, perylene, TCNQ, P1T1 and P2T1 single crystals. For most studied materials also FETs with parylene as a dielectric have been prepared. The transport properties have been measured in air and in situ during the flow of oxygen or hydrogen [60].

Fig. 63 shows the structure of a silicon dioxide single crystal field-effect transistor (FET). It is a bottom gate, top contact configuration. The single crystals were grown onto a silicon wafer with 600nm silicon dioxide which is used as a dielectric layer for the FET. Another method was to cleave the crystals with magic tape from 3M and fresh cleaved surfaces was laminated on the silicon wafer. Gold pads were patterned onto the single crystals using thermal evaporation through a transmission electron microscopy (TEM) grid as the mask. This FET structure is a bottom gate, top contact configuration.

Fig. 63: Silicon dioxide Field-effect Transistor (FET) structure. It is a bottom gate, top contact configuration. The thickness of the silicon dioxide dielectric is around 600 nm and the thicknesses of the source/ drain gold pads are around 100nm.

To make the air-gap FET, PDMS stamps were made with patterns of different channel dimensions on them. Then, 20 nm gold films were deposited on the forming the source, drain and gate of the FET. An as-grown molecular single crystal having flat and smooth surface was laminated onto the source and drain. The FET structure is a bottom gate, bottom contact configuration as shown in Fig. 64.

Fig. 64: Air-gap Field-effect Transistor (FET) structure. It is a bottom gate, bottom contact configuration. The thickness of the air/ vacuum dielectric is around 4 μm and the thicknesses of the gate/ source/ drain gold pads are around 20nm.

To make the parylene N FET, a single crystal was struck on a glass slide with a tape. Source and drain contacts were then painted on the crystal with silver or carbon pastes. Parylene N dielectric was then deposited on the crystal surface with the source and drain contacts on it. Gold wires were used to lead the source and drain contacts away from the crystal to an open space on the glass slide. This is to protect the crystal from any physical damage due to connections. Lastly, the gate electrode was painted on the channel formed between the source and drain contacts, with a gold wire leading away from the crystal again. Copper wires, for rough connections to the Keithley 2636A, were then connected to the gold wires with the carbon paste. The FET structure is a top gate, top contact configuration as shown in Fig. 65. Fig. 66 shows the lab-made working parylene N transistor for a rubrene single crystal.

Fig. 65: Parylene N Field-effect Transistor (FET) structure. It is a top gate, top contact configuration. The contacts used can be carbon paste or silver paste.

Fig. 66: Pictures of a rubrene single crystal parylene N transistor made on glass slide.

5.3. Single Crystal Field-Effect Transistors (FETs) Measurements and Setups

Fig. 67: Circuitry of a transistor when connected to Keithley 2636A during measurement. SMU stands for Source Measurement Unit in the Keithley 2636A. Each SMU consists of one voltage source, one ammeter and one voltmeter.

A Keithley 2636A was controlled by Matlab software for FET measurements. Fig. 67 shows the circuit connections for the FET measurements. The Keithley 2636A has two source measurement units (SMU). Each SMU consists of one voltage source, one ammeter and one voltmeter. The voltage source could provide DC voltage from $\pm 1 \mu\text{V}$ to $\pm 202 \text{ V}$. The voltmeter could measure DC voltage from $\pm 1 \mu\text{V}$ to $\pm 204 \text{ V}$. The ammeter could measure DC current from $\pm 1 \text{ fA}$ to $\pm 1.53 \text{ A}$.

With such precision capabilities, the instrument is sufficient to measure our working devices.

The charge carrier mobility was calculated from the linear region of the output characteristic curves of the FETs. The equation used for this calculation is shown below.

$$\mu = \frac{L}{C_i W V_{SD}} \frac{dI_{SD}}{dV_G}$$

where

μ is the charge carrier mobility

L is the channel length

W is the channel width

C_i is the capacitance per unit area

V_G is the applied gate voltage

V_{SD} is the applied source-drain voltage

I_{SD} is the measured source-drain current.

Table 12 shows the list of materials tested with silicon dioxide FETs, air-gap FETs and parylene N FETs, with the measured experimental charge carrier mobility compared with the ones in the literature. Note that all the measured mobility values, including the ones in the literature, are from two-point contact FETs.

Charge carrier transport in an FET, takes place at the semiconductor-dielectric interface region; thus any modification of the physical or chemical properties of this region affects the charge carrier transport of the device. Air gap transistors have been made on rubrene, tetracene, pentacene and TCNQ surfaces. However on copper phthalocyanine, that surface possess numerous growth steps, and FETs

made with the PDMS stamps have not exhibited field effect behavior. Therefore, the parylene dielectric has been used specially for needle-like crystals. It was observed that the mobility for all crystals, in particular for rubrene, depends strongly on the state of the surface.

Crystals	Dielectric	Electrodes	Carrier Type	Mobility (cm ² /V.s)	Mobility (cm ² /V.s) (Literature)
Rubrene	Air-Gap	Au	p	19	18 ⁴⁸
	Parylene N	C	p	5.3	
Pentacene	Air-Gap	Au	p	0.055	40 ⁴⁹
	Parylene N	C	p	0.02	
Tetracene	Air-Gap	Au	p	2	1.6 ³⁹
	Parylene N	C	p	0.1	
Perylene	SiO ₂	Au	p	0.04	0.12(sat) ²⁴
	Parylene N	C	p	~10 ⁻⁶	
TCNQ	Air-Gap	Au	n	0.1	0.3 ⁷⁴
	SiO ₂	Au	n	0.26	
	Parylene N	C	n	~10 ⁻⁵	
DPA	Parylene N	C	p	~10 ⁻⁴	0.16 ⁷⁵
TTT	Parylene N	C	p	0.01	-
CuPc	Parylene N	C	p	0.75	1 ³⁴
F ₁₆ CuPc	SiO ₂	Au	n	0.6 ⁷³	-
P1T1	SiO ₂	Au	n	0.05	-
	Parylene N	C	n	1.5 x 10 ⁻³	
P2T1	SiO ₂	Au	p	0.01	-
		Ag	n	3 x 10 ⁻³	
	Parylene N	C	p	~10 ⁻⁴	
Abbreviations: C – Carbon; Au – Gold; Ag – silver; SiO ₂ – silicon dioxide; TTT –Tetrathiotetracene; DPA – 9,10 - diphenylanthracene; CuPc – copper phthalocyanine; F ₁₆ CuPc – perfluorinated copper phthalocyanine; TCNQ – tetracyanoquinodomethane; P1T1 - (Perylene) ₁ -TCNQ; P2T1 - (Perylene) ₂ -TCNQ					

Table 12: List of mobilities of different molecular single crystals achieved compared to the literature. Note that the mobilities were calculated from 2-point contact FETs.

5.4. Investigation of Single Crystal – Parylene N Dielectric Interface

The charge carrier mobility of the materials measured with parylene N as a dielectric is usually at least an order of magnitude lower than the ones measured with silicon dioxide FETs or air-gap FETs. For instance, the highest mobility of the tetracene air-gap FET was $2 \text{ cm}^2/\text{Vs}$ while the highest mobility of the tetracene parylene N FET was only $0.1 \text{ cm}^2/\text{Vs}$, and the highest mobility of the rubrene air-gap FET was $19 \text{ cm}^2/\text{Vs}$ while the highest mobility of the rubrene parylene N FET was only $5.3 \text{ cm}^2/\text{Vs}$.

Parylene during deposition and polymerization on the crystal surfaces forms interfacial traps that could greatly hinder the charge transport. Hence, defect and impurity control in the conducting channel of the transistors is crucial in tailoring the material mobility. This is interesting because the single crystal FETs were fabricated with the intent to measure the intrinsic mobility of the materials. However, apparently it was heavily dependent on the type of dielectric used or the processes used to deposit the dielectric. Therefore, from the material science point of view, it is important to understand the fabrication process used to make the silicon dioxide FETs, air-gap FETs and parylene N FETs.

From the operations of the FETs, it is known that the conducting channel is formed at the semiconductor – dielectric interface. Therefore, there is a strong urge to probe on to this interface to further understand the FET measurements.

The investigation starts with the parylene N dielectric. The three main steps, initialization, propagation and termination, of the parylene N polymerization process are shown in Fig. 68. It was suspected that the free radical polymerization products might have some proportion of small oligomer molecules. These small oligomer molecules could be doped at the crystal surface. Hence,

thermogravimetric analysis (TGA) was used to detect the presence of the small oligomer molecules.

Fig. 68: Polymerization process of parylene N showing the three main steps of the free radical polymerization, initialization, propagation and termination. The process occurred at pressure of around 10^{-2} Torr. The polymer formed might consist of a huge range of n and m values which include small oligomer molecules. Note that when $n = 1$ and $m = 0$ or vice versa, the polymer becomes the dimer precursor molecule.

The TGA of the parylene N film is presented below in Fig. 69. The black line shows the weight percentage change with increasing temperature while the red line shows the derivative of the black line. The peak at $440\text{ }^{\circ}\text{C}$ shows the temperature having the highest mass loss, which should be the decomposition temperature of

the parylene N film. At around 100 °C, the mass of the parylene film started to decrease. This indicates the presence of small oligomer molecules in the parylene film. These small oligomer molecules might dope the crystal surface and will decrease the performance of the FETs.

Fig. 69: Thermogravimetric analysis (TGA) of parylene N polymer film. The black line shows the change in weight percentage with increasing temperature and the red line shows the derivative of the black line. The peak indicates that the highest mass loss occurred at around 440 °C, which is believed to be the decomposition temperature of the polymer film. The slight initial decrease in mass indicates that there might be residual monomers or molecules in the polymer film. These residual molecules might result in unintentional doping of the semiconducting molecular single crystals during the deposition of the dielectric.

First Peel

Fig. 70: Magic tape peeling on parylene N coated crystal to separate the parylene N film and the crystal. It is interesting that there is a thin layer of parylene N polymer film on the crystal surfaces after the first peel. On the second peel, parylene N film could be observed on the magic tape. Note that the parylene N polymer film alone could not be cleaved with magic tape peeling.

At the initialization step of the polymerization, a large number of free radical molecules are created. These free radical molecules would attack the crystal surface by forming new chemical bonds at the surface. This may be the reason for the poorer performance of the parylene N FET. Hence, a technique using magic tape peeling to separate the parylene N film and the crystal was used. Subsequently, ATR-FTIR and MALDI-ToF-MS were adopted to probe the interface for new chemicals. The magic tape peeling technique is described in Fig. 70.

Fig. 71: Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) data of Parylene N – Rubrene interface in wavenumber range of (a) $1500\text{--}1300\text{ cm}^{-1}$ and (b) $3200\text{--}2800\text{ cm}^{-1}$. ATR-FTIR data of Parylene N – Tetracene interface in the wavenumber range (c) $1500\text{--}1300\text{ cm}^{-1}$ and (d) $3200\text{--}2800\text{ cm}^{-1}$. The parylene coated single crystals were peeled once with magic tape to remove the first layer of parylene film.

There is always a thin layer of parylene N film left on the crystal surface after the first peel. This is interesting because the parylene N film itself could not be cleave with the magic tape peeling technique. Therefore, it is natural to suspect that there might be new chemical bonds formed between the parylene N and the crystal surface. It was expected that new aliphatic alkane bonds would be formed when the free radicals attack the polyaromatic hydrocarbon (PAH).

The molecular single crystals used in the ATR-FTIR experiments are rubrene and tetracene, shown after the first peel in Fig. 71. The ATR-FTIR data present the region where aliphatic bond vibration is expected. However, no new vibrational peaks were detected at the measured surfaces. The ATR-FTIR of the parylene N – crystal interface seems to be a superposition of the ATR-FTIR spectrum of the parylene N surface and the respective crystal surfaces.

MALDI-ToF-MS was also used to detect any new chemicals formed at the Parylene N – crystal interface. Conducting double-sided carbon tape was struck onto the MALDI plate. The single crystals were placed on the carbon tape. A 337 nm laser was then used to ablate the crystal surface, vaporizing the material at the surface. Fig. 72 below shows the mass spectra of the pristine rubrene single crystal, the parylene-coated rubrene after first peel and parylene-coated rubrene after second peel.

All the mass spectra in Fig. 72 looked similar. There are no obvious new mass peaks detected at the parylene N – crystal interface.

Both ATR-FTIR and MALDI-ToF-MS could not detect any chemical changes at the parylene N – crystal interface compared to the pristine crystal surface. However, these results could not imply that there are absolutely no chemical changes at the interface. This is because there are a few other possible reasons for not being able to detect the chemical changes at the interfaces using the above characterization techniques.

- 1) The quantity needed to be detected might be out of the detection limit of the characterization machines.
- 2) The new chemical bond vibrations might be very similar to the bond vibrations of rubrene and parylene N polymer and thus difficult for ATR-FTIR technique to detect.

- 3) As the MALDI-ToF-MS was calibrated to detect a mass range of 50-700 m/z accurately, the entity of interest might be out of the mass range as it might be a high mass molecule.

Fig. 72: MALDI-ToF-MS data of the pristine rubrene single crystal, parylene-coated rubrene after the first peel and the second peel. There were no obvious differences between the pristine rubrene surface and the parylene N – crystal interface. However, this does not mean that there are no new chemical bonds formed at the interface. This is because the quantity needed to detect might be out of the detection limit of the MALDI machine.

The high value of the charge mobility, in the range of tens of cm^2/Vs , reported for rubrene [48] is not an intrinsic property of the bulk organic crystal but is determined by the surface states. The charge carrier mobilities are reported in Table 12. The highest mobility has been measured in rubrene using an air gap

transistor. It is concluded that the interaction of dielectric with single crystals surface is responsible for charge trap formation on the surface which lowers the charge carrier mobility. Therefore, the current efforts to tailor the molecular structure of organic semiconductors to achieve high-mobility charge-carrier transport should be complemented by efforts to control the state of the surface of the organic semiconductors by defect and impurity control.

5.5. Mobility and Bandgap Measurements of Perylene-TCNQ Charge-transfer (CT) Compounds

Fig. 73: (a) Output and (b) transfer curve of PIT1 single crystal FETs using 1.1 μm thickness perylene N film as the dielectric. The channel length and width of PIT1 and were 1.06 mm and 0.0862 mm respectively. The electron mobility was calculated to be $1.5 \times 10^{-3} \text{ cm}^2/\text{V.s}$.

Growth of binary charge transfer compounds may be used as a method to tailor the band gap and charge carrier mobility of semiconducting materials that might be useful for solar cell applications. An increase in the mobility of single crystals of charge-transfer (CT) perylene-TCNQ compound mobility was observed for perylene N FETs but not for silicon dioxide FETs. The performance of the (perylene)₁-TCNQ single crystal FETs is shown in Fig. 73 below.

The band gap of the charge transfer compounds is reduced from that of the present crystals as shown in Fig. 74. UV-vis absorption measurements were also done with solid-state single crystals. UV-vis absorption measurements on solid-state perylene, TCNQ and P2T1 single crystals were presented in Fig. 74. The perylene single crystal was found to have a bandgap of 2.67 eV as shown in Fig. 74(a). The TCNQ single crystal was found to have a bandgap of 2.55 eV as shown in Fig. 74(b). And the P2T1 single crystal was found to have a bandgap of 2.23 eV as shown in Fig. 74(c).

Single crystal FETs were also made on silicon wafers with a 600nm silicon dioxide layer as the dielectric. The best FETs performances of perylene, TCNQ, P1T1 and P2T1 were shown in Fig. 75. The mobility was calculated from the linear region of the curves. The perylene single crystal FETs has a mobility value of $0.04 \text{ cm}^2/\text{V.s}$, on/off ratio of 10^4 and threshold voltage of -50V. The TCNQ single crystal FETs has a mobility value of $0.10 \text{ cm}^2/\text{V.s}$, on/off ratio of 10^3 and threshold voltage of -33V. The P1T1 single crystal FETs has a mobility value of $0.05 \text{ cm}^2/\text{V.s}$, on/off ratio of 10^3 and threshold voltage of -36V. The P2T1 single crystal FETs has a mobility value of $0.01 \text{ cm}^2/\text{V.s}$, on/off ratio of 10^3 and threshold voltage of -29V. There was no FETs performance for P3T1 single crystals.

Fig. 74: (a) Absorption spectrum of perylene single crystal showing bandgap at around 2.67 eV. (b) Absorption spectrum of TCNQ single crystal showing bandgap at around 2.55 eV. (c) Absorption spectrum of P2T1 single crystal showing bandgap at around 2.23 eV.

Fig. 75: Output and transfer curves of (a, b) perylene, (c, d) TCNQ, (e, f) PIT1 and (g, h) P2T1 measured from the FETs on a silicon wafer with a 600nm silicon dioxide layer. The channel length and width of perylene, TCNQ, PIT1 and P2T1 were separately 12.52 μm and 93.07 μm , 14.72 μm and 37.80 μm , 9.86 μm and 22.22 μm , 6.40 μm and 24.17 μm .

5.6. Conductivity and Field-Effect Transistors (FETs) Measurements of Tetrathiotetracene (TTT)

Fig. 76: Output and transfer curves of (a,b) tetracene and (c,d) Tetrathiotetracene single crystal FETs. The dielectric was 1.1 μ m thick parylene N film. The channel length and width of the tetracene FET were 0.311 mm and 0.515 mm respectively. The channel length and width of the TTT FET were 0.562 mm and 0.0368 mm respectively.

Parylene N field-effect transistors (FETs) were made from tetracene single crystals and tetrathiotetracene (TTT) single crystals. The best FETs performance of tetracene single crystals and TTT single crystals were shown in Fig. 76. The mobility was calculated from the linear region of the curves. The mobility of the tetracene FETs is calculated to be 0.1 cm²/V.s and the mobility of the TTT FETs is calculated to be 0.01 cm²/V.s.

There was also minimal field-effect in TTT FETs compared to tetracene FETs as shown in Fig. 76(a) and Fig. 76(c). The off current of the tetracene FETs were around 10^{-11} A while the off currents of the TTT FETs were around 10^{-8} A. The off current of the TTT FETs were 3 orders of magnitude higher than the off current of the tetracene FETs. The conductivity of TTT single crystals was much higher than that of the tetracene single crystals. The conductivity of TTT single crystals was calculated using the equation as shown below.

$$\sigma = \frac{I_{SD}}{V_{SD}} \frac{L}{W \cdot t}$$

where

σ is the conductivity

I_{SD} is the source-drain current

V_{SD} is the source-drain voltage

L is the channel length

W is the channel width

t is the crystal thickness.

The TTT crystals were grown onto a silicon wafer. Gold was thermally evaporated using a transmission electron microscopy (TEM) copper grid as a pattern mask onto the crystal. A two-terminal TTT single crystal device was shown in Fig. 77. Next, an I-V measurement was done. Atomic force microscopy (AFM) was used to measure the crystal thickness for the conductivity calculation.

Fig. 77: Two-terminal TTT single crystal device. The yellow squares are the patterned gold pads and the ribbon is the TTT single crystal. The thickness of this crystal was measured to be around 120 nm. Its conductivity was calculated to be $2.63 \times 10^{-3} \text{ Scm}^{-1}$, which is quite conducting for organic crystals.

The thickness of the TTT single crystal in the two-terminal TTT single crystal device as shown above in Fig. 77 was measured to be around 120nm. The conductivity for was calculated to be $2.63 \times 10^{-3} \text{ Scm}^{-1}$, which is quite conducting for organic crystals.

Chapter 6 – Conclusions

In order to grow high quality single crystals, furnaces with high precision control of temperature were made. The furnaces were controlled by a PID temperature controller (Eurotherm 3216) and a power controller (Eurotherm TE10A) for precise temperature control.

Numerous high quality mono-component and charge-transfer (CT) binary-component molecular single crystals have been grown using solution phase and gas phase methods. High boiling point solvents such as naphthalene were used successfully to grow difficult crystal such as pentacene, which is very insoluble in most solvent. However, consistent twinning defects were observed in C₆₀ single crystal grown from naphthalene. High performance liquid chromatography (HPLC), liquid chromatography mass spectrometry (LCMS), Matrix-assisted laser absorption/desorption mass spectrometry (MALDI), photoluminescence (PL), cross-polarized light microscopy (CPLM), attenuated total reflection fourier transform infrared spectroscopy (ATR-FTIR), atomic force microscopy (AFM), powder X-ray diffraction (PXRD) and single crystal X-ray diffraction (SCXRD) measurements were done to characterize the quality and purity of the single crystals.

Most of the single crystal structures have been determined with PXRD and SCXRD. New crystal structures for tetrathiotetracene (TTT) and (perylene)₂-TCNQ (P2T1) were discovered and solved using SCXRD.

Oxides on rubrene single crystal surfaces were detected using HPLC, LCMS, MALDI, ATR-FTIR and PL. The oxides of rubrene were believed to be responsible for its high charge carrier mobility.

Many single crystal field-effect transistors (FETs) of different structures were made. The three main FETs structures were:

- the bottom gate, top contact FETs with silicon dioxide as the dielectric (silicon dioxide FETs),
- the bottom gate, bottom contact FETs with air gap as the dielectric (air-gap FETs), and
- the top gate, top contact FETs with parylene N polymer film as the dielectric (parylene N FETs).

Physical properties such as mobility and bandgap were changed through molecular engineering and through growth of binary-component molecular single crystals. Solvent-less synthesis method for high conducting tetrathiotetracene (TTT) were developed from modified physical vapor transport (PVT). The method is clean and green and is a direct reaction between tetracene and sulphur.

CT binary-component molecular single crystals, such as (perylene)₁-TCNQ (P1T1) and P2T1, with controlled phases and morphologies were grown with modified PVT method. The bandgap of the single crystals of the CT compound were reduced compared with those of their individual component molecules. Moreover, the mobilities of the CT compounds, comparing with their individual counterparts perylene and TCNQ in this case, were observed to increase in parylene N FETs but not in silicon dioxide FETs.

It was observed that the mobilities of the parylene N FETs were always at least an order of magnitude lower than the silicon dioxide FETs or the air-gap FETs. Therefore, chemistry at the molecular crystal – parylene N dielectric is of particular interest. TGA was done on the parylene N polymer film and small oligomer molecules were detected. ATR-FTIR and MALDI were done to detect new molecules or new chemical bonds at the interface but no obvious differences

were found. Chemical reactions at the interface during deposition of parylene N polymer from free radical polymerization are possible. However, the amount that was needed to detect might be out of the detection limit or range of the characterization instruments.

Mobilities comparable to the highest reported in the literature were achieved for rubrene ($19 \text{ cm}^2/\text{V.s}$), tetracene ($2 \text{ cm}^2/\text{V.s}$) and F16CuPc ($0.6 \text{ cm}^2/\text{V.s}$) FETs in this project. For all the single crystal FETs that were measured, the mobility range was still in the range of $\sim 10^{-6}$ - $\sim 19 \text{ cm}^2/\text{V.s}$. Mobility in the range of tens is still higher than the mobility of amorphous silicon. Hence, this magnitude of mobility will open up possibilities for applications where amorphous silicon was used.

It is concluded that the measured mobilities from the single crystal FETs do not represent the intrinsic mobility of the materials. The measured mobility highly depends on the surface states of the single crystals which are largely affected by the fabrication process of the single crystal FETs. The physical properties of these molecular single crystals are high sensitive to impurities and defects in the single crystal whose impurities level is still far higher than its inorganic counterpart. Therefore it is expected to be possible to achieve even better performance of organic devices if the technological process were to be improved. It is recommended that more research work should be done on interfaces or surfaces of molecular single crystals, relating the impurities or defects on the crystal surface to its surface states and to its physical properties.

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