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MOLECULAR ENGINEERING OF PERYLENE DERIVATIVES FOR OPTO-ELECTRONIC APPLICATIONS

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Doctor of Philosophy Thesis.

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2010



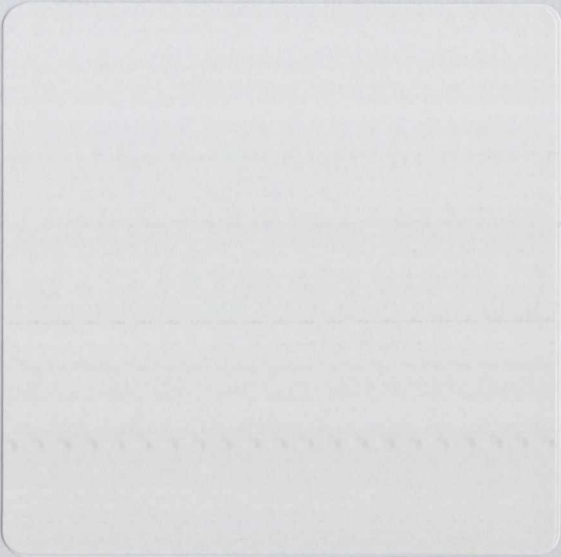
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DECLARATION

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This thesis is dedicated to my Creator, my family and my supervisor.

Abstract

The overall objective of this material science study is to investigate the physical, chemical and optical properties of perylene derivatives with a view to understanding how these properties affect their applications in optoelectronic devices. Practical questions are prompted by the need to develop, characterise and improve organic molecular materials for applications in opto-electronic devices to meet growing demands.

This thesis presents a materials science study of perylene derivatives, a novel class of π -conjugated small organic molecules with a wide variety of promising optoelectronic applications owing to their outstanding properties. A molecular modelling with Hyperchem predicted the absorption spectra, electronic spectra, geometry optimised structures and properties of some commercial and new perylene derivatives namely 1,6,7,12-tetraphenoxy-N'N'Bis-(2,6-diisopropylphenyl)-perylene-3,4,9,10 bis(dicarboximide) or perylene red, N'N'Bis(2,6-xylyl)perylene-3,4,9,10-bis(dicarboximide) or perylene orange indenoperylene dicarboximide or perylene violet, dibenzocoronene tetracarboxdiimide or perylene yellow, 3,4,9,10-tetra-(12-alkoxycarbonyl)-perylene or perylene blue, 3,4,9,10-tetra-(alkoxy-t-butyl)-perylene (TBPB) and 3,4,9,10-tetra-(alkoxy 3,5 dibutyl phenoxy)-perylene (BPPB). The quantitative structure-activity relationship properties of mass, volume, partition coefficient, hydration energy, polarisability and molar refractivity were also modelled. The refractive index was determined to be 1.1 and thus in opto-electronic applications, perylene derivatives would undergo minimal refractive losses.

Perylene blue was successfully synthesised and characterised alongside the commercial products of perylene red, perylene violet, perylene yellow and perylene orange. Predicted properties from modelling were confirmed empirically. Perylene blue showed improved solubility due to addition of alkyl side groups and also displayed aggregation control due to the bulky side groups. The results showed that bulky functional groups reduce aggregation in small molecules. The solubilisation exhibited by the molecule makes it desirable for polymer blending or film casting thus reducing the cost of device fabrication. The perylene derivatives have an average exciton binding energy of 1.04 eV thus suggesting mainly Frenkel type excitons. This makes the derivatives attractive candidates for optoelectronic applications in which transfer of energy can take place without transfer of charge.

All the perylene derivatives studied have quantum efficiencies close to unity, absorb and fluoresce in the visible range, are photochemically stable and are thermally stable up to 300 °C making those attractive candidates for ordinary day optoelectronic applications. Structural studies confirmed different nano aggregates in nanopillar forms of perylene red, nanospike forms of perylene orange, nanocrystals and nanobelts structures of perylene violet, nanocones forms of perylene yellow and some nanostructures of perylene blue. The nanostructures are a result of the effect of the different side chains around the perylene core. These nanostructures are used to explain the properties of the materials in relation to their possible applications in diverse optoelectronic applications.

In the selected optical limiting application, the perylene derivatives showed high absorption and/or scattering cross section and optical limiting abilities with non-linear scattering from perylene blue, perylene orange and perylene violet whilst emission was evident from perylene orange and reverse saturable absorption from perylene red all at 1g/l concentration in chloroform solution. Their different behaviour for the same application is explained in terms of the structures of the materials. This makes the molecules promising candidates in two photon absorption applications.

Acknowledgements

I wish to express my deep gratitude to my supervisor Professor Werner Blau for according me the opportunity to study for a PhD and for all moral, financial, motivational and fatherly support he has given me overall.

I am also greatly indebted to members of the Groups BU and CoCo for the assistance they rendered during the course of the study. Particular mention goes to Professor Jonathan Coleman who set me off with solubility theory, Dr. Manuel Reuther who tried to turn me into a synthetic chemist, Dr. Jun Wang for assistance with optical limiting and proof reading of this thesis, Dr. Umar Khan for all his assistance professionally, as a friend and also as a perfect sounding board with very wise stories, Dr. Hellen Carthcart for assistance with dichroism, Niall McEvoy who tirelessly and patiently introduced me to the AFM at the expense of his own time and Trevor Woods of Materials Ireland for help with MI equipment.

The School of Physics staff has been very helpful right across the board. The mention of names here will produce another thesis. And if any one of the Physics staff does not think they assisted me with the thesis, just ask me and thank you for just being staff members of the School of Physics.

I wish to extend a million "thank you" statements to Professor Hugh "Huge" Byrne of Dublin Institute of Technology's FOCAS department for allowing me to work with his colleagues and their equipment. I wish to mention here Dr. Isabela Nayednova for the AFM and Dr. Luke Oneill for initial lessons with Hyperchem.

I wish to express gratitude to Manuela Lunz, Alexandra Racovich and Paraic Keane for assisting me with lifetime measurements.

I thank my children who readily gave me very good breaks from "research stuff" and always wondered why adults had to go to school. I am exceptionally grateful to my beloved wife for having to put up with a studying husband, her support as usual is invaluable. I extend my thanks to family and friends who have also been very supportive in their own ways.

Last but definitely not least, I thank the Father for strengthening me throughout, the Spirit for retentive memory and the Son through whom excellence is revealed.

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Chapter 1

Background and Motivation

1.1 Materials science and nanotechnology

In order to develop new products and technologies that make our lives safer, more convenient, more enjoyable and more sustainable, we need an understanding of how to make the best use of the materials we already have, and how to develop new materials that will enable us to cope with future demands and challenges. Materials Science and Engineering Technologies involves the study of the structure, properties and behaviour of all materials, the development of processes to manufacture useful products from them, and research into recycling and environmentally friendly disposal. The fundamental questions that material scientists ask themselves are: why does each material exhibit its behaviour and how can the properties of the material be exploited to make something better or cheaper?

Everything we use is made from materials derived from the earth. Early earthly materials include metals and ceramics(1). These were later joined by polymers, semiconductors and composites. All these materials have revolutionised our lives and advanced materials continue to do so by offering advanced performance and new possibilities of design and application. Among the latest advanced materials list are high strength and highly conducting (both thermally and electrically) carbon nanotubes(2, 3) and their composites useful in cars, aircraft, sports equipment(4) and intergrated circuits(5, 6). The author has been involved in a parallel project on the reinforcement of ceramic materials with carbon nanotubes for intergrated circuits and this work is summarised in the appendix.

Most recently (2004)(7, 8), graphene has also joined ranks with advanced materials and is attracting a lot of research(9-13). Another notable recent addition to advanced materials are new electronic materials for digital communication used mostly in mobile phones and optical networks. Active functional materials, commonly known as SMART materials(14, 15) having one or more properties that can be significantly changed in a controlled fashion by external stimuli, are also among recent advanced materials and have applications in skis and snowboards that absorb vibrations, miniature loudspeakers, buildings that respond to weather conditions and noise reduction systems in cars and planes(16-18). All these technological advancements have been made possible by materials science defined as the study of structures, microstructures, properties, processing and applications

of materials. Material science is the backbone of the latest and fastest growing scientific field of "nanotechnology", the study of control of matter at an atomic and molecular scale covering all aspects of science and technology expected to make most products lighter, stronger, cleaner, less expensive in addition to improved accuracy and precision where measurements are involved.

1.2 Organic opto-electronics

Organic materials are chemical compounds based on carbon (C) and hydrogen (H) atoms and sometimes also bonded with few other chemical species. The term "organic semiconductors" is used to describe organic materials with the ability of conducting electrons. The electrical conductivity of such materials lie between those of metals and insulators spanning a very broad range of $10^{-9} - 10^{-3} \Omega^{-1}\text{cm}^{-1}$. The discovery of the photoconduction of anthracene (19, 20) in 1906 is a historical benchmark for the study of organic compounds. Apparently classic and technological inorganic semiconductors like germanium and silicon were also discovered during the same early 19th century (21-23). It is not surprising that research in organic semiconductors lapsed for four decades at the expense of the inorganic semiconductors. The potential of organic semiconductors was only realised in the late 1980s(24) when the use of organic semiconductors in electronic devices such as organic light emitting diodes (OLEDs), field effect transistors (FETs) and as photoconductors in xerographic applications was envisioned(25-27). The semiconductors applied in xerography are responsible for the photogeneration of charge carriers as well as charge transport. Since then, research in organic semiconductors has exploded and is growing rapidly. The discovery of fullerenes(28-30) also initiated a wave of research that includes carbon nanotubes(2, 31-33) whilst the observation of electrically stimulated fluorescence(34, 35) has opened a way for molecular electronics and opto-electronics; the study of electronic devices that source, detect and control light.

Over the last two decades, there has been an explosion of information pertaining to organic opto-electronics(27, 36-44). Hence organic based devices are currently experiencing an accelerated development as dictated by the optical storage, display and photovoltaics. The fabrication of organic semiconducting materials opto-electronic devices, the existence of a huge information age market, driven by rapid developments in both manufacturing process technology encompassing novel nano designs and new materials has caused organic opto-electronics to reach a self sustaining momentum which fuels further growth as the

next generation in most key technologies. The most important peculiar advantages of organic semiconductors over inorganic ones are as follows:

- Organic materials are usually used as thin films and so can be processed over large areas;
- Relatively small amounts of organic materials (less than 100nm film thickness) are needed making large scale production easier;
- Organic materials can be chemically tuned to change properties like charge transport, aggregation, solubility, band gap and even structural properties to mention a few;
- Organic materials offer a plethora of chemical structures and functionalities so promoting active material science research for alternative competitive materials with desired properties like tuning the energy levels;
- The production and processing of opto-electronics devices based on organic materials is possible at low process temperatures and is cheaper than those based on their inorganic counterparts;
- Organic materials in OLEDs are brighter than a conventional television screen, with brilliant colours, large viewing angle, switching times fast enough for real time image displays and lifetimes over 10000 hours;
- Low dielectric constants are characteristics of organic materials which makes reflection losses at interfaces much lower than the inorganic semiconductors;
- The internal fluorescence efficiency for most organic semiconductor dyes is close to unity with emission peaks red shifted to the absorption edge so avoiding re-absorption losses in the devices;
- Most organic semiconductor dyes have high absorption coefficients in the visible range of the electromagnetic spectrum and hence can be very attractive for photovoltaics.

These advantages have expanded the field of organic opto-electronics to include this non-exhaustive list of devices; photodiodes, photovoltaics, phototransistors, photomultipliers, integrated optical circuits, photoresistors, photoconductive camera tubes, charge coupled imaging devices, injection laser diodes, quantum cascade lasers, optocouplers, displays, optical sensors, optical limiters and optical switches.

1.3 Types of organic semiconductors

Inorganic semiconductors consist of covalent or ionic bonds whilst organic semiconductors are based on independent molecules characterised by weak Van

der Waals interactions. This makes design of organic materials readily possible at molecular level and of particular mention are organic conjugated pi-electron systems which have received attention as very promising opto-electronic active materials(45-50). The development of such materials by material scientists involves the correct choice of structural units with charge transport or optical properties in addition to the mechanical, thermal and electrochemical properties. The most important requirement for all these organic semiconducting materials is their ability to form stable smooth films by thermal evaporation or solution processing methods.

Depending on their molecular weight, these conjugated organic materials can be divided into two classes; oligomers and polymers. Both share many common opto-electronic properties but differ mainly in the film formation techniques. Oligomers, also known as small molecules, are low molecular weight materials and are most commonly deposited by the thermal vacuum technique or more recently by vapour phase deposition. Polymers have high molecular weights and are large molecules composed of repeating structural units typically connected by covalent chemical bonds. To produce a thin film, polymers are usually dissolved in a suitable solvent to obtain a viscous solution which is then deposited onto an appropriate substrate by spinning, dipping, stamping, doctor blading, ink-jet printing or casting. Both oligomers and polymers be used either separately or in hybrid and mixed form(51).

Oligomers have a thermal decomposition temperature much higher than their sublimation temperature, typically between 200°C and 400°C. Thus repeated sublimation can be used to purify oligomers. Polymers cannot be deposited or purified by thermal evaporation because their decomposition temperature is generally lower than their sublimation temperature hence polymeric device preparation is solution based. A big advantage of polymers is hence their adaptability to low cost large scale device production(52, 53). Recently(54-56), oligomers that can be solution processed have been developed and one such case is reported in Chapter 4 of this thesis.

Another difference between oligomers and polymers is in their pi-electron overlap. Organic semiconducting materials have a pi-electron sytem delocalised over the whole molecule and characterised by frontier orbitals called the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (HOMO). The HOMO and LUMO determine the opto-electronic properties of both polymers and oligomers. This pi-electron system is saturated as the LUMO is a fully occupied bonding pi-orbital whilst the LUMO is an unoccupied antibonding pi-orbital, thus intermolecular covalent bonds cannot be formed, rather these molecules are bonded by weak Van der Waals forces (57). For oligomers, the narrow bands due to

each of the molecular pi-orbitals have a small intermolecular overlap. Polymers have broad quasi-continuous energy bands of the pi-electron states along their chains. Charge is therefore not localised resulting in a small interchain overlap so limiting mobilities to the most costly hopping steps. Thus highest mobilities are achieved in oligomers (57).

The operating voltages for polymers are lower than for oligomers, but controlled doping has enabled small molecules to compete here with polymers(57). Continued material science study of polymers and oligomers has made research very competitive between the two. One of the key factors for focusing on oligomeric materials is the existence of a small number of known conducting polymers(58) and the difficulty involved in producing the same.

The possibility of a wide variety of chemical structures and functionalities amongst organic semiconductors has resulted in more types of the same. In addition to polymers and oligomers, other classes and/or sub-classes include dendrimers(59, 60), organo-minerals(61), dyes(62), pigments(63), liquid crystals(64, 65) to mention a few. Academic research, industrial research and even academic-industrial collaborations of the above-mentioned materials is currently aggressively pursued worldwide.

1.4 Justification and motivation

In order to make most products lighter, stronger, cleaner, less expensive and more precise, there is a need for materials science study as outlined in section 1.1. Materials science study of organic semiconductors based optoelectronic devices has recently gained great attention due to their superior advantages over their inorganic counterparts as outlined in sections 1.2 and 1.3 above. These advantages can be summarised as the low cost in device production, simple packaging, compatibility with flexible substrates and the immense variety of molecular semiconductors. The promise of being able to optimise, by a synthetic method, molecular materials for desired properties is a driving force behind this work. Gaining more knowledge on the structure and properties of currently existing materials and relating the same to current and possible applications also motivates this work.

Whilst polymers can be used for device fabrication at a lower cost than oligomeric materials, this study focuses on oligomeric materials at the expense of the existence of a small number of known conducting polymers and the challenge of producing conducting polymers. The pressure for technological applications has focused researchers' interest on specific systems that are promising but at the

same time causing considerable challenges. Amongst such promising semiconducting oligomeric materials, pentacenes(66-69), phthalocyanines(70-72), oligothiophenes(73-76) and perylene derivatives(77) have enjoyed the most attention over the last two decades. P-n junctions are a very important integral part of organic semiconducting opto-electronic devices and n-type semiconductors are a key component to the same. Of the oligomeric materials mentioned enjoying the most attention recently, pentacenes, oligothiophenes and phthalocyanines are p-type and have become well known, yet n-type oligomeric organic semiconducting materials are not fully developed and not extensively studied. The work in this thesis is based on the material science study of five different families of perylene derivatives. The materials science study involves an extensive characterisation of four of the family of perylene derivatives and a synthesis and characterisation of one element of the fifth family. Projected device fabrications based on the characterisation are then recommended.

When originally discovered, perylene derivatives were used as vat dyes and pigments mainly due to their colour which appeals to human beings. Perylene derivatives rose on the scene as interesting organic semiconductors in the mid-1980s, with the demonstration of a low voltage and efficient thin film light emitting diode by Ching Tang and Steven van Slyke at Kodak (78). Although that particular first demonstration was not of sufficiently high performance to replace existing inorganic technologies, it opened the door to the possibility of using organic thin films as a foundation for a new generation of optoelectronic devices. Since then, perylene derivatives have been transformed from vat dyes and pigments to "functional dyes" as explained in section 2.2.1. The "functional dye" aspect of the perylene derivatives is also explored in this research.

As promising n-type organic semiconducting materials for opto-electronic devices, perylene derivatives boast of such superior characteristics as thermal stability, photostability, electroactivity among others as outlined in section 2.2.2. Recently, two photon absorption (TPA) has been discovered in some perylene derivatives. Optical limiting is the foundational study leading to TPA studies. This work also focuses on the study of the optical limiting properties of more perylene derivatives not studied elsewhere to date.

Most perylene derivatives are generally insoluble making production methods costly via thermal sublimation or vapour pressure deposition. In addition aggregation is a paramount property of most perylene derivatives and quenches the fluorescence quantum yield so affecting the performance of perylene derivative based opto-electronic devices. This work focuses on the modelling and synthesis of soluble perylene derivatives with improved aggregation control to exploit cost

advantage of organic semiconducting opto-electronic device fabrication with solution processing methods.

1.5 Thesis outline

This thesis describes work done on the application of conventional investigation techniques to determine the physical structure, chemical, optical and electronic properties, among other physical phenomena, of both commercially available and new perylene derivatives. This materials science study led to an understanding of the morphology and transport characteristics of these organic molecules as well as pointing out the subsequent nanodevice fabrication for possible opto-electronic applications. Both theoretical and experimental investigations are reported. Theoretical investigations are based on modelling using HyperChem, a molecular modelling package for windows. Experimental investigations are based on the usual conventional techniques which are outlined in Chapter 2.

Chapter 1 explains the need for materials science and the important role it plays in science and nanotechnology. An introduction to organic semiconductor opto-electronics materials is also provided in the same chapter. The justification for and motivation behind this research is also explained. An outline of the thesis is given in the same chapter.

Chapter 2 describes the background and general characteristics of perylene and its derivatives. Common production methods of perylene derivatives and their applications are briefly explained. A brief overview of the experimental techniques and relevant theory employed in this research is also provided and the materials used in this research are given.

Chapter 3 reports on the molecular modelling using Hyperchem. The geometry optimisations, vibronic spectra and electronic spectra of selected perylene derivatives are presented. The dipole moments and polarisabilities of the perylene derivatives are compared. The quantitative structure activity-relationship (QSAR) properties of the perylene derivatives are also presented in this chapter.

Chapter 4 describes the synthesis, characterisation and optical limiting properties of a perylene derivative that has controlled aggregation as well as improved solubility.

In chapter 5, the thermal properties and photophysics of the perylene derivatives are presented. The photophysics includes uv-vis absorption, fluorescence and cyclic dichroism. A study of the life times and quantum yields is

also presented therein. The anisotropy of physical properties is shown to be reflected in the variable angle spectroscopy findings.

Chapter 6 reports on the structural properties of the perylene derivatives. Atomic force microscopy, transmission electron microscopy and scanning electron microscopy are the techniques used for structural studies. The investigation of perylene derivatives as possible two photon absorption materials is reported.

Chapter 7 is a summary of the work done for the PhD and highlights the significant findings. Recommendations for future work are also made in this chapter.

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Chapter 2

Materials and Experimental Techniques

2.1 Introduction

This chapter provides an introductory overview of perylene and its derivatives. The general characteristics, common production methods and applications of perylene derivatives are highlighted in this chapter. Conventional experimental and characterisation techniques used in this research are explained in this chapter. The end of the chapter provides a summary of the specific materials used and studied in this work.

2.2 Perylene derivatives

2.2.1 From vat dyes to high performance pigments and functional dyes

Perylene is a polycyclic aromatic hydrocarbon (PAH) which occurs as a brown solid and has the chemical formula $C_{20}H_{12}$. Perylene occurs pervasively in both marine and freshwater sediments as a major component of other PAHs (1) and is strongly believed to originate principally from anaerobic diagenesis of organic matter, but its precursor material remains enigmatic (2-4). The basic chemical structure of the perylene molecule is shown in Fig. 2.1 and can be considered to be made up of two naphthalene molecules joined by single C - C bonds at positions 1 and 8. The centre ring is therefore not a benzene ring as this would cause sp^3 hybridisation of two of the C atoms resulting in the loss of some of the molecule's aromaticity (5).

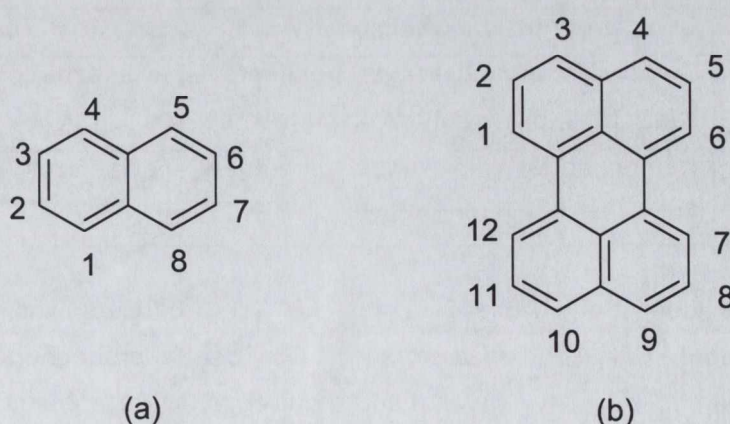


Figure 2.1 Basic chemical structures of naphthalene (a) and perylene (b)

Perylene is highly fluorescent and has current applications as a blue emitting dopant in OLEDs, an organic photoconductor and also as a fluorescent lipid probe. The perylene molecule is both thermally and chemically stable. Due to the thermal and chemical stability as well as the aromaticity, perylene has been made to form the core of many other PAHs. Positions pairs 3,4 and 9,10 are known as peri-positions whereas position pairs 6,7 and 12,1 are called the bay positions. A variety of “functional groups” or chromophores can be added via chemical reactions to the different positions so resulting in an even wider variety of perylene based molecules.

The first perylene derivatives were discovered in 1913 by M. Kardos(6) and were used as vat dyes for textiles. To date some perylene derivatives are still referred to as perylene dyes. The development and commercial use of these perylene based substances as pigments was not realised until the late 1950s and today the perylene pigments have found use in the coloration of automotive paint and in mass coloration of synthetic fibre and engineering resins(7). They have been consequently classified as high performance organic pigments originally defined as fluorescent particulate organic pigments that demonstrate high performance properties in their end use applications(8). There are however still more perylene dyes than perylene pigments. The synthetic manufacturing of dyestuff and pigments has been a major propellant of the 19th century industrial revolution mainly because colour appeals to human beings. Table 2.1 shows the production site for main high performance pigment producers(8).

Table 2.1 Main producers of high performance pigments.

PRODUCER	MAIN PIGMENT CLASS
BASF	Perylenes, isoindolenes/isoindoinones, quinophthalone, phthalocyanine specialties, anthraquinones
BAYER	Quinocridones, dioxazines, perylenes, phthalocyanine specialties
CLARIANT	Quinocridones, dioxazines, perylenes, special azos, hp naphthols
CIBA	Quinocridones, dioxazines, perylenes, special azos, phthalocyanine specialties, other polycyclic pigments
DIC/SUN	Quinocridones, dioxazines, perylenes, special azos, hp naphthols phthalocyanine specialties

It is evident from Table 2.1 that the few producers who dominate this market all produce perylene based pigments. Confidential production know-how has been accompanied by heavy investment requirements. As a result, recent times have seen the use of organic dyes and pigments for colouring textiles and other

consumer goods expanding to the field where they are now known as part of "functional dyes". Tang and van Slyke's 1985(9) copper phthalocyanine and perylene derivative photovoltaic cell is a well known "turning point" of perylene derivatives from dyes and pigments to functional dyes. In the functional dye context, the aesthetic appearance is no longer the most important role but rather both the chemical and physical properties like light emission, absorption, photoelectric, photochemical activity and light induced polarisation (10). It is not amazing that both production methods and fields of application for perylene derivatives have expanded widely as summarised in section 2.2.3.

2.2.2 General characteristics of perylene derivatives

Perylene derivatives have attracted much attention amongst small molecule organic semiconductors for a wide range of very promising optoelectronic applications; from solar cells(11), through field effect transistors(12), optical switches, chemical sensors, liquid crystal displays(13) to organic light emitting diodes(OLEDs) (14). The wide variety of applications is only possible due to the unique characteristics of perylene derivatives. When originally discovered, it was their colour, very appealing to humans, which found them having use as vat dyes and eventually pigments. Their thermal stability and light fastness aided to such applications. As organic pi-conjugated materials with a perylene aromatic core, the perylene derivatives boast of strong absorption and intense fluorescence in the visible range with brilliant colours (15, 16). They have large carrier mobilities(17), are suitable for epitaxial growth(18) and can be chemically tuned allowing for their extensive use as functional dyes(10). This family of materials has outstanding chemical, thermal and photochemical stabilities. Perylene imides, a popular family of perylene derivatives, represent a class of n-type semiconductors with high electron affinity among large-band-gap materials and therefore are potential photoactive and electro-active organic materials(13). Ongoing material science study of perylene derivatives aims at incorporating potential devices into all plastic integrated circuits for low end and low cost optoelectronics(19).

Original perylene derivatives were highly insoluble, which limited their applications. Recently production methods have focused on producing soluble perylene derivatives without compromising other properties and so expanding their range of applications. Another common property of perylene derivatives is aggregation due to them being pi-systems. In solid state based devices, this has a tendency to quench the fluorescence. Other synthetic routes in which bulky groups are added to the perylene core have resulted in the reduction of aggregation.

Very recently, the two photon absorption properties of perylene derivatives have come to light. TPA based applications are very numerous as explained in Chapter 4's section 4.1.

2.2.3. Production methods and applications of perylene derivatives

As described in section 2.2.1, a wide range of functional groups or chromophores can be attached to any of the perylene positions shown in Fig. 2.1. These chromophores then control the physical and chemical properties of the resulting perylene derivatives which in turn determine their possible applications. Thus the full potential for perylene derivatives in such functional applications is still emerging and is obviously beyond the scope of our imagination and this thesis. The fact that there are different possible chromophores determines the production method and one can imagine as wide a range of production methods as there are types of chromophores. Some selected production methods and applications are summarised in this section.

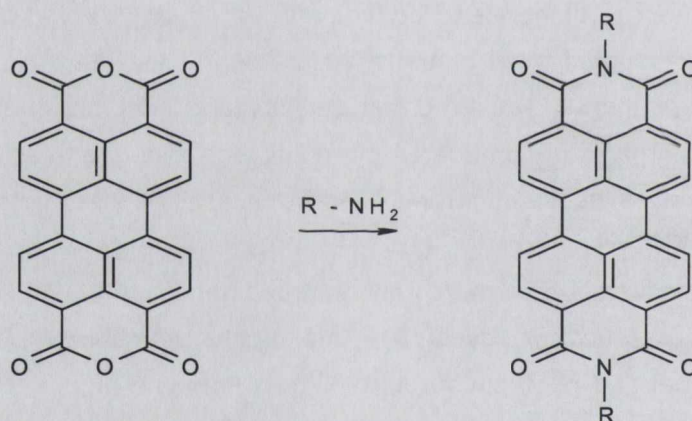


Figure 2.2. Synthesis of bis-imides perylene derivatives from PTCDA

The most common and well studied perylene derivative is the 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA), an archetypal molecule whose basic properties have been studied for over ten years(20-28). PTCDA is commonly used as the parent molecule in most syntheses of perylene derivatives. Figure 2.2 shows the scheme for the production of imide based perylene derivatives which are also the most common type. R can be a hydrogen (H) atom or any alkyl group (aromatic, aliphatic or combined). One can now imagine how many different types of perylene derivatives can result from just this type of synthesis.

This synthesis involves the condensation reaction of PTCDA with a primary amine(29, 30). The choice of the solvent for this reaction depends on the reactivity of the amine. For reactive amines, *e.g.* alkyl amines, water or DMF can be used at

100 – 160°C (31). For less reactive amines such as aromatic amines with reaction temperatures of 160 – 180°C, solvents such as quinoline or molten imidazole are necessary and zinc acetate can be used to catalyse the reaction; it has been suggested that the aforementioned solvents have an ability to solubilise the anhydride. One of the reasons why perylene derivatives are used for pigment application is their low solubility which also was a handicap for the development of their chemistry. Even though their strong fluorescence was discovered in the 1940s, practical applications were limited due to low solubility. The introduction of alkyl groups at the N atoms as shown in Figure 2.2 improves solubility. Whilst the scheme in Fig. 2.2 is used to produce symmetrical imides, it can be developed to produce mono-imides as well as non-symmetrical imides (31-33). In addition to the diimide product in Fig.2.2 being useful for the synthesis of multi-chromophores (34), it is also a very useful intermediate from which different functional perylene dyes are derived (10) leading to whole big classes of perylene based near infra-red dyes(35), thermotropic dyes(36), star polymers(10) and dendritic dyes(37). Current investigations on applications of perylene based imides include optical switching(38), photoreceptors, chemical sensors, electroluminescent devices(39, 40) and colourful liquid crystal displays. Imides derivatives of perylene have also attracted a lot of attention due to potential applications in solar cells(41).

Whilst the condensation of PTCDA with an amine is the most popular and almost the starting point of subsequent perylene derivatives, other methods exist and depend on the desired end product and its function. One of the common limitations of perylene derivatives is the formation of aggregates. Whilst this may be a limitation in some cases, it may be desirable in other applications. Where it is not desired, aggregation may be reduced by addition of appropriate bulky groups at the correct positions. By introducing four arylalkoxy substituents at the bay areas, Wurthner was able to synthesise perylene derivatives with twisted fluorophores for supramolecular chemistry(42) towards the derivation of self-assembled nanoelectronic and nanophotonic devices(43). Wurthner et. al also synthesised one dimensional luminescent nano-aggregates of perylene bisimide by attaching very bulky groups at the N nodes of the bisimide(44). The resulting aggregates compared well with the archetypal PTCDA and are very promising as semiconducting wires and in (nanoscopic) LEDs. Nolde et. al also synthesised core-extended perylene diimides with branched alkyl chains so increasing the solubility and lowering the isotropization temperature of the liquid crystalline phase for better processing as well as achieving a more effective π - π interaction leading to highly ordered supramolecular architectures with high charge carrier mobilities(45). The core extension was done along both the long and short aromatic axes. Muller and

Mullen also achieved extension of the core and shifted absorption both side of the red to yellow and violet (46), the resultant products of which are characterised in depth in this study.

Aggregation can quench the fluorescence of perylene dyes(47, 48). Langals et.al was able to control self-organisation of perylene dye molecules by introducing bulky peripheral groups producing monoimides and non-symmetrical diimides without affecting the fluorescence quantum yield. A variety of synthesis methods is described in his paper (49).

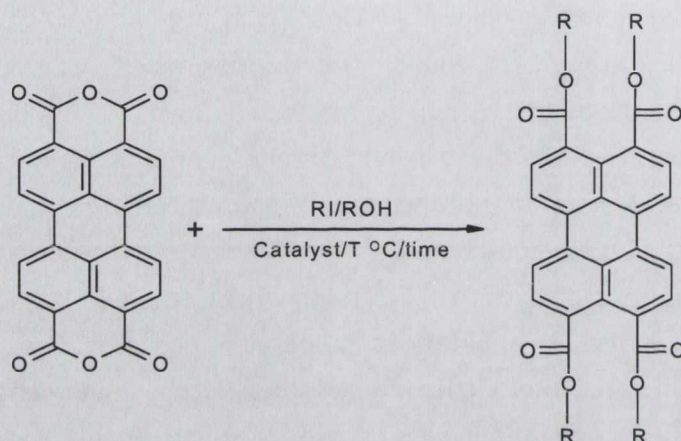


Figure 2.3 General chemical reaction for the production of 3,4,9,10-tetra-(*n*-alkoxycarbonyl-perylenes)

Figure 2.3. shows the structure of another interesting family of perylene derivatives is the alkoxy carbonyls namely 3,4,9,10-tetra-(*n*-alkoxycarbonyl)-perylenes where *n* is the number of carbon chains in the alkyl group. Besides the usual inherent perylene attributes of fluorescence and stability, this family also shows liquid crystal behaviour with electron transport capability so complementing known columnar hole transporters. The synthesis route involves refluxing PTCDA with a suitable halogenide or tosylate and alcohol, at a temperature $T\text{ }^{\circ}\text{C}$ controlled by their boiling points, over an appropriate catalyst such as potassium carbonate (17) which is a much easier synthesis compared to the original method (50). The reaction time depends on the boiling point of the halogenide or tosylate and can range from 2 days to one week. Benning et al. confirmed the absence of liquid crystallinity for $n=10$. In this thesis, a member of this family with $n=12$ is synthesised and comprehensively characterized as described in chapter 4 and in part confirming Benning's result.

2.3 Characterisation techniques

The experimental techniques employed in this research are conventional techniques and were performed using standard methods and instruments without any modifications. This section outlines experimental techniques applied commonly to the whole research.

2.3.1 Atomic Force Microscopy (AFM)

The atomic force microscope (AFM), also known as the scanning force microscope (SFM) was invented by Binnig, Quate and Berber in 1986(51). The AFM, like all other scanning probes, makes use of a very sharp probe moving over the surface of a sample in a raster scan. There are about two dozen types of scanned proximity probes where a local property like height, optical absorption or magnetism is measured with a probe placed close to the sample. In the case of the AFM, the local property is the height whilst the probe is a tip on the end of a cantilever which bends in response to the attractive or repulsive force between the tip and the sample.

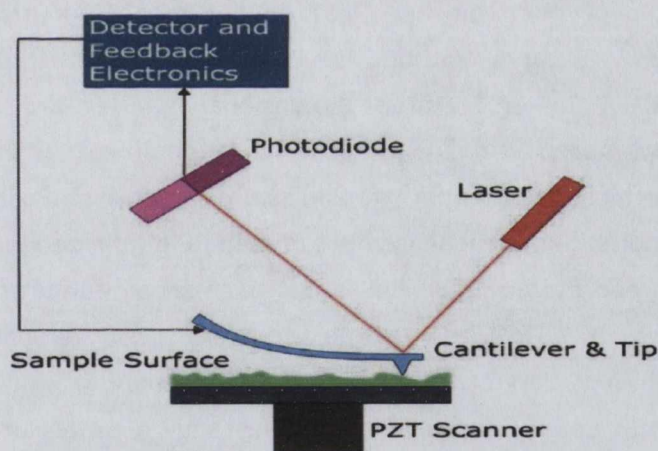


Figure 2.4 Concept of AFM with schematic of tip on a cantilever touching a sample(52)

Figure 2.4 illustrates how the AFM operates. When the cantilever flexes, light from the laser is reflected onto the split photodiode. In principle the AFM resembles a record player as well as the stylus profilometer, but incorporates some of the following refinements that enable it to achieve atomic scale resolution; sensitive detection, flexible cantilever, sharp tips, high resolution tip-sample positioning and force feedback. A difference signal measures the change in the cantilever bending.

In the most common and popular repulsive or "contact" mode, as a raster scanner drags the tip over the sample, some detection measures the vertical deflection of the cantilever indicating the local sample height. Hence in contact mode the AFM measures hard-sphere repulsion forces between the tip and the sample. In the non-contact mode the AFM derives topographic images from measurements of attractive forces and the tip does not touch the sample(53). Tapping mode involves moving the oscillating tip towards the surface until it begins to lightly touch or tap the surface. Tapping mode overcomes problems associated with friction, adhesion electrostatic forces and other difficulties by alternately placing the tip in contact with the surface to provide high resolution and then lifting the tip off the surface to avoid dragging the tip across the surface. Contact mode imaging is heavily influenced by frictional and adhesive forces compared to non-contact and tapping modes. Non-contact mode generally provides low resolution and can be hampered by the contaminant layer which can interfere with oscillation. Other modes also exist but are not commonly used. These include lateral force, magnetic and thermal scanning.

Compared to other imaging techniques, the AFM has several advantages and that has made it grow into a very popular imaging method. The AFM provides extraordinary topographic contrast direct height measurements and unobscured views of surface features without any coating, unlike in scanning electron microscope (SEM). In AFM, three dimensional images are obtained without expensive sample preparation and yield more complete information than two dimensional samples obtained by transmission electron microscopes (TEM). The AFM provides unambiguous measurement of step heights independent of reflectivity differences between materials which optical microscopy cannot do. With scanning tunnelling microscopy (STM), the voltage and tip-to-substrate spacing are integrally linked whereas in AFM they can be controlled independently.

The AFM is applied to solve processing and materials problems in a wide range of technologies affecting electronics, telecommunications, biological, automotive, aerospace and energy industries. Materials under investigation include thin and thick film coatings, ceramics, composites, glasses, synthetic and biological membranes, metals, polymers and semiconductors. Phenomena like abrasion, adhesion, cleaning, corrosion, etching, friction, lubrication, plating and polishing have been studied using the AFM since the AFM not only images the surface in atomic resolution, but can also measure the force at nano-newton scale. It is not surprising that AFM related publications have greatly increased.

2.3.2 Scanning Electron Microscopy

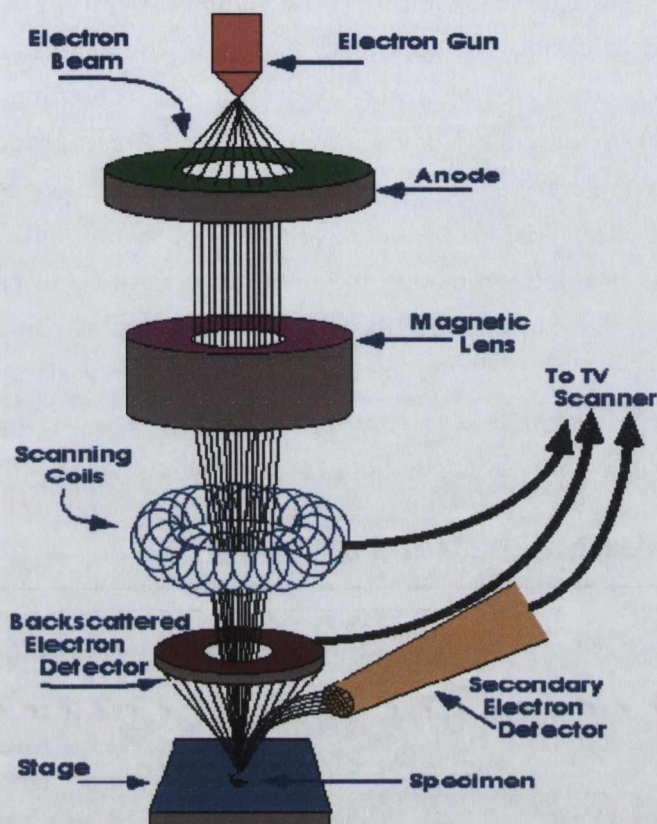


Figure 2.5 Schematic of the SEM(54)

Structures of tiny substances can be visually analysed using optical microscopes. When the wavelength of the radiation used becomes the same order as that of the object under study, diffraction effects then limit the distinctness of the boundaries of the object or the image being processed by the instrument. Corrective techniques exist but the battle is ongoing and uphill. The scanning electron microscope (SEM) circumvents diffraction limits and can be used to analyse particles at subatomic and nano-metre scale. Max Knoll produced the first SEM image in 1935 (55). Two to three years later, Manfred von Ardenne did some practical work but did not produce the SEM instrument (56-58). The first SEM known as the "Stereoscan" was first marketed in 1965 (59).

Figure 2.5 is a schematic of an SEM. The SEM is an instrument which can produce a greatly magnified image using electrons in the place of light. The SEM scans a focused beam of electrons across a sample surface. An electron gun is the source of primary electrons. Electromagnetic fields and lenses are employed to focus the beam of primary electrons towards the sample. On interacting with the

sample the primary beam of electrons causes electrons and X-rays to be ejected from the sample. The ejected electrons are called secondary electrons. Some of the primary electrons are backscattered from the sample. A system of detectors collect the backscattered electrons, the secondary electrons, the X-rays, some light due to cathode-luminescence as well as transmitted electrons converting them to a signal to produce a final image on a monitor screen. The SEM can produce well resolved images revealing 1-5 nm detail on samples. The magnification can be as high as X250000 which is about 250 times that of known light microscopes to date.

Limitations of the SEM include the need for a vacuum to produce electrons, so samples must be stable under high vacuum. The samples can only be solid and sample size is limited by the SEM sampling chamber. Only electrically conductive samples can be viewed or analysed using an SEM so there is need to coat non-conductive samples with a conductive metal before analysis.

2.3.3 Transmission Electron Microscopy

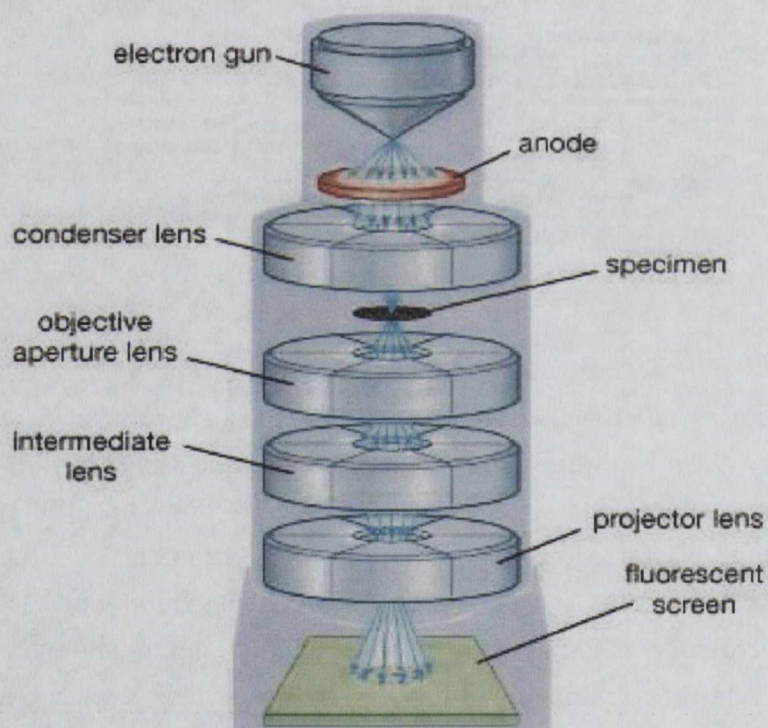


Figure 2.6 Schematic of a TEM(60)

The transmission electron microscope (TEM) was the first electron microscope invented to deal with the diffraction limits or shortcomings of optical microscopes. The first TEM was built in 1931 by Max Knoll and Ernest Ruska. The operational principles are almost the same as those of the SEM described in section

2.3.2 except that the image results only from the transmitted electrons. Figure 2.6 shows a schematic of the TEM. It consists of an electron gun, which produces the electron beam, a condenser system which focuses the beam onto the object or sample and the image-producing system consisting of the objective lens, movable specimen stage, and intermediate and projector lenses, which focus the electrons passing through the specimen to form a real image.

The TEM technique has a few drawbacks. Most materials require extensive sample preparation to produce an electron transparent thin enough sample. This makes TEM analysis a relatively time consuming process with a low throughput of samples. The structure of the sample may also be changed during the preparation process. TEM field of view is relatively small, raising the possibility that the region analyzed may not be characteristic of the whole sample. It is thus necessary to image sample over many positions. The electron beam may damage the sample, particularly in the case of biological materials. Resolution of the HRTEM is limited by spherical and chromatic aberration, but a new generation of aberration correctors has been able to overcome spherical aberration(61).

2.3.4 Thermo gravimetric Analysis

The term "thermal analysis", originally used by Tamman (62, 63), refers to a variety of techniques in which the temperature dependence of a chosen physical property of a sample is continuously measured whilst the sample is subjected to a pre-determined temperature profile. Thermal analysis techniques are used in virtually every area of modern science and technology. The basic information that these techniques provide, such as crystallinity, specific heat and expansion, are relied on heavily for the research and development of new products. Thermal analysis techniques also find increasing use in the area of quality control and assurance, where demanding requirements must be met in an increasingly competitive world. Thermal analysis instruments are used in universities for applications ranging from basic undergraduate studies to the most sophisticated postgraduate research.

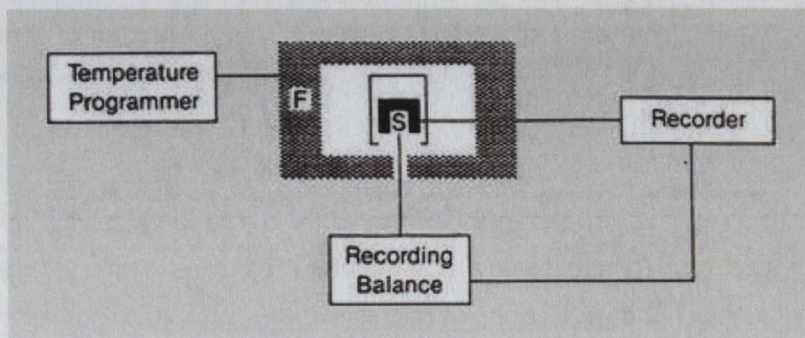


Figure 2.7 Schematic of the thermo gravimetric analyser(64)

Thermo gravimetric analysis (TGA) examines the process of weight changes as a function of time, temperature, and other environment conditions that may be created within the apparatus. Common parts of a TGA instrument include a sensitive thermo-balance attributed to Honda (65, 66), which monitors the weight of the sample, a digital recorder which records the variation in weight during a TGA run, a ceramic material heating furnace, F as shown in Fig.2.7, in which the sample S is placed in a crucible, a temperature programmer and a computer monitor to display the data. The data is usually displayed graphically as a weight loss versus temperature or time, and sometimes as the derivative of the weight loss. TGA can be run under different atmospheres like in air or in an inert environment, as in argon or nitrogen, important where oxidation would be a nuisance in the course of studying the material's temperature dependent properties.

TGA is applicable in the determination of the thermal stabilities of materials under the required atmospheres. When coupled with FTIR, it is possible to tell what materials or groups of elements have been lost at each loss stage in the TGA. This coupling of TGA with FTIR is applied in this thesis. Lifetimes of materials can also be determined from TGA. The oxidation and reduction of the materials can be also be monitored using TGA. Solvent residues can be elucidated from the derivative TGA curve and the presence of volatile components in a sample can be estimated. The presence of trapped solvents and their effect on thermal stability of materials can be studied using TGA. The kinetic features of all types of loss or gain can be analysed for predictive studies or to gain knowledge of the controlling chemistry. Generally thermal events like melting, crystallization and glass transition do not bring a change in mass, but thermal changes accompanying mass change like decomposition, sublimation, reduction, desorption, absorption and vaporisation can be measured by TGA.

2.3.5 Differential scanning calorimetry

Differential scanning calorimetry (DSC) is one of the thermal analysis methods. DSC is a technique in which the difference in energy inputs into a substance and a reference material is measured as a function of temperature whilst both the substance and the reference materials are subjected to a controlled temperature program. In power-compensation DSC the temperatures of the sample and reference are controlled independently using separate, identical furnaces. The temperatures of the sample and reference are made identical by varying the power input to the two furnaces; the energy required to do this is a measure of the enthalpy or heat capacity changes in the sample relative to the reference. In heat-flux DSC, the sample and reference are connected by a low resistance heat-flow

path (a metal disc) as shown in Fig.2.8. The assembly is enclosed in a single furnace. For power-compensation DSC, the heat flow rate is normally plotted on the ordinate with endothermic reaction upwards whilst in heat flux DSC the curve has the endothermic reaction downwards.

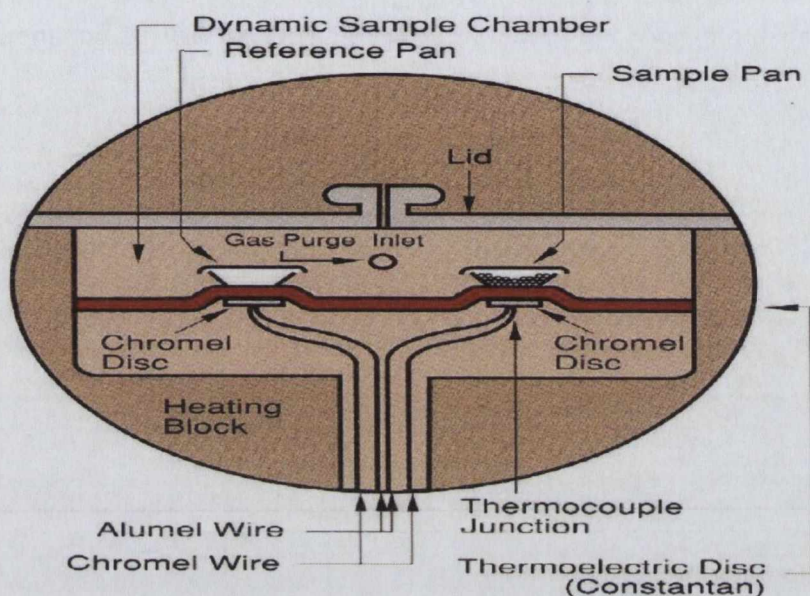


Figure 2.8 Experimental set-up for heat flux DSC(64)

Figure 2.8. shows the general set up for a heat-flux DSC experiment. The main assembly of the DSC cell is enclosed in a cylindrical, silver heating block, which dissipates heat to the specimens via a constantan disc which is attached to the silver block. The disc has two raised platforms on which the sample and reference pans are placed. A chromel disc and connecting wire are attached to the underside of each platform, and the resulting chromel-constantan thermocouples are used to determine the differential temperatures of interest. Alumel wires attached to the chromel discs provide the chromel-alumel junctions for independently measuring the sample and reference temperatures. A separate thermocouple embedded in the silver block serves as a temperature controller for the programmed heating cycle. An inert gas is passed through the cell at a constant flow rate of about 40 ml min^{-1} .

DSC can be used to obtain the glass transition temperature of amorphous and semi-crystalline polymers, melting points of materials, crystallization time and temperature, the percentage of crystallinity, heats of fusion and reactions, specific heat and heat capacity, oxidative stability, rate and degree of curing, reaction kinetics, percentage of purity and thermal stability.

2.3.6 Open aperture Z-scan

The Z-scan technique is the most popularly used method for investigating non-linear optical properties of certain media including non-linear absorption, scattering and refraction(67). The Z-scan method is an easy and relatively simple way for measuring nonlinear absorption coefficients as well as nonlinear refractive indices for a wide variety of optically interesting materials.

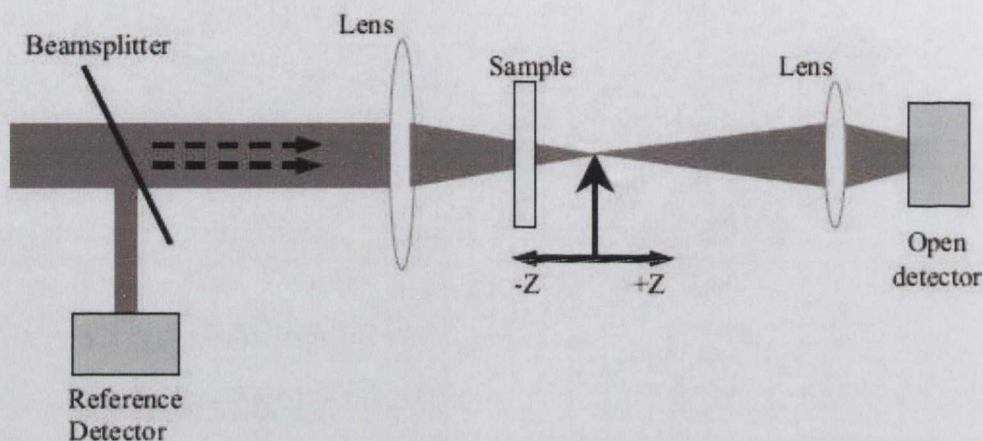


Figure 2.9 Schematic diagram for open-aperture Z-Scan(68)

In open-aperture Z-scan, the sample material is translated along the axis of a focused Gaussian laser beam and changes in the beam's characteristics, such as far field intensity, is measured as the sample changes position (Fig 2.9). The real and imaginary parts of the third order susceptibility can be deduced from the intensity versus Z-scan curve as explained in the theory on open-aperture z-scan relevant to this thesis given and first applied in Chapter 4 (see section 4.2.3) and further applied in Chapter 6.

2.3.7 Photophysical Processes

Photophysical processes result from the photo excitation by electromagnetic radiation and subsequent relaxation of a molecular system from one state to another via either a radiative or non-radiative transitions with no chemical modification of the species. Common radiative photophysical processes involving photons are absorption (A), photoluminescence or fluorescence (F) and phosphorescence (P) whilst common radiationless transitions are vibrational relaxation (VR), intersystem crossing (ISC) and internal conversion (IC). The electronic levels and transitions involved with the photophysical processes in organic materials are usually represented schematically in a Jablonski diagram as shown in Figure.2.10.

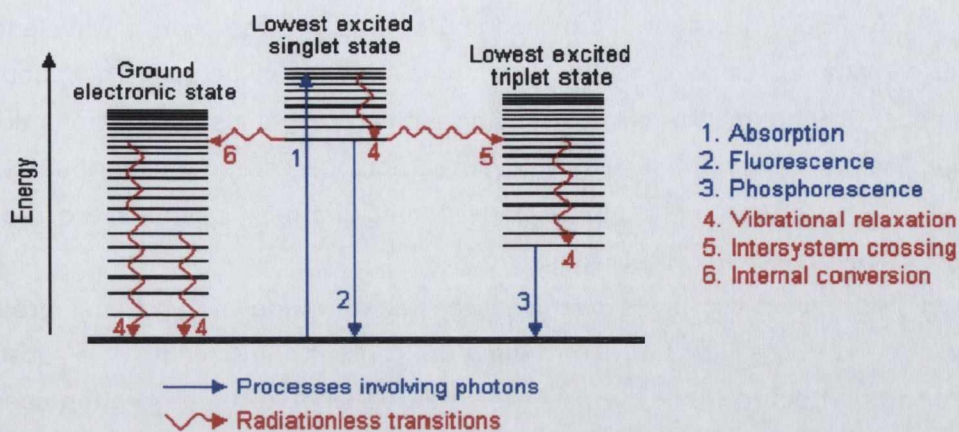


Figure 2.10 Jablonski diagram showing electronic levels and photophysical processes.

Absorption (A)

The colour of objects is determined by the visible light they absorb. Visible or ultraviolet light is absorbed by the valence or outer electrons which are promoted from their ground or normal states to higher energy or excited states. The energies of the orbitals involved in the electronic transitions have fixed values. Due to quantisation of energy, the absorption peaks in the ultraviolet/visible (UV-Vis) spectrum are expected to be sharp but this is rarely observed due to superposition of vibrational and rotational transitions (available to absorbing materials) on the electronic transitions, giving a combination of overlapping lines.

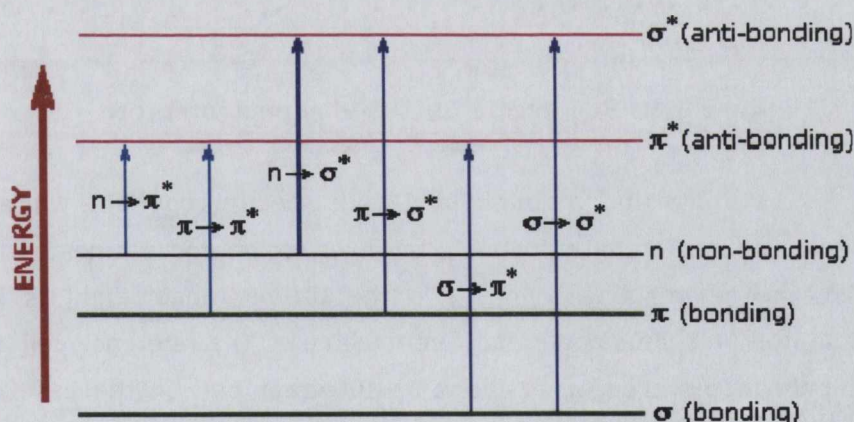


Figure 2.11 Possible electronic transitions of π , σ and n electrons.

Valence electrons exist in three types of electron orbitals namely single (σ bonding orbitals), double or triple (π bonding orbitals) and non-bonding orbitals (lone pair electrons). Sigma (σ) bonding orbitals tend to be lower in energy than π bonding orbitals which in turn are lower than non-bonding orbitals. With the correct frequency of electromagnetic radiation being absorbed, transitions occur from one of the above-mentioned orbitals to any empty orbital usually an anti-bonding orbital

σ^* or π^* (Fig.2.11). Transitions from bonding orbitals are too short a wavelength to measure easily, hence most of the common absorptions involve $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and $\sigma \rightarrow \pi^*$ transitions. The occupation of non-bonding molecular orbitals by electrons does not change the bond order between relevant atoms i.e. does not contribute to the binding energy of the molecule. In anti-bonding orbitals, electrons are repulsive and act to destabilise the whole molecule.

UV-Vis spectroscopy is useful in the identification of functional groups in molecules and in assaying i.e. determining the content and strength of a substance. Most excitation occurs from the ground state only and so the absorption spectrum can give information on the energy distributions for the first and second excited states. Excited state absorption is also possible and is a dominant process responsible for nonlinear optical responses. In this research, all these applications of UV-Vis are employed in characterising the molecules under investigation.

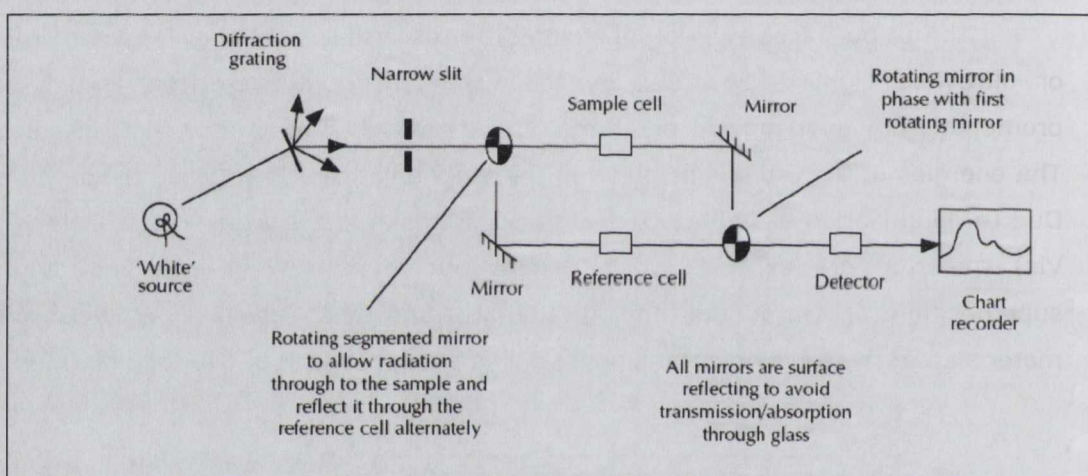


Figure 2.12 Schematic for UV-Vis spectrometer.

Figure 2.12 shows the schematic for UV-Vis spectroscopy. The white source is a hydrogen or deuterium lamp for the ultraviolet region and a tungsten/halogen for the visible range enabling scanning in the UV-vis range. Light is incident simultaneously through the sample and reference cells. The reference cell is either the solvent only in the case of solutions or substrate only in the case of solid samples. The spectrometer compares the light passing through the sample and reference cells. The transmitted radiation is detected and the absorption spectrum is recorded by scanning the wavelength of the light passing through the cells. Single and double beam instruments both exist, the difference being that in single beam instruments, the reference and sample are scanned separately but the spectrum is recorded much faster than in double beam spectrometer. The recorded

spectrum can then be analysed and information is drawn from the analysis. The Beer-Lambert law is the most commonly applied law in the analysis.

Beer's law states that the light absorbed for dilute solutions is directly proportional to the number of absorbing species i.e. to the concentration of the absorbing molecules. Lambert's law states that the fraction of the absorbed radiation is independent of the radiation intensity. The Beer-Lambert law is a combination of these two laws and is given as:

$$A = \log_{10}\left(\frac{I_0}{I}\right) = \epsilon bc \quad (2.1)$$

where A is the absorbance, I_0 is the incident intensity, I is the transmitted intensity, ϵ is the molar absorptivity in $\text{L mol}^{-1} \text{ cm}^{-1}$, b is the path length in cm and c is the concentration of the solution in mol L^{-1} . Equation 2.1 can be applied to calculate ϵ and λ_{max} , the wavelength at which maximum absorption occurs. The two parameters are often enough to identify a substance and when they are known, the concentration of the solution can be calculated.

Flourescence (F)

The emission of light by a substance is referred to as luminescence, this occurs when an electron in an excited state returns to the ground state losing its energy as a photon. Three types of luminescence exist namely fluorescence, phosphorescence and chemiluminescence. Fluorescence, also known as photoluminescence (PL) occurs when a molecule returns to the electronic ground state from an excited singlet state by emission of a photon and can be described by the equation:

$$S_1 = S_0 + h\nu \quad (2.2)$$

where h is Planck's constant, ν is the frequency of the light emitted, S_0 and S_1 are the ground state and excited state energies respectively. Emission takes place from lowest levels of the excited state to the various vibrational levels of the ground state, hence the fluorescence spectrum gives information about the vibrational energy distribution of the ground state. Molecules relax non-radiatively prior to emission, thus the energy of the emitted photons is always lower than that of the excitation energy. The red shift in emission with respect to the absorption is known as the Stokes shift. Emission rates of fluorescence are typically 10^8 s^{-1} so that typical fluorescence lifetimes, τ , are about 10 ns.

Fluorescence is governed by various rules two common ones being Kasha's rule and the mirror image rule. Kasha's rule states that the emission spectra are independent of the excitation wavelength. In the mirror image rule, the emission is the mirror image of the $S_0 - S_1$ transition (not the total absorption spectrum). These rules are further explored and explained in the results associated with the materials studied in this research.

The efficiency of the fluorescence process is given by the fluorescence quantum yields, defined as the ratio of the number of photons emitted to the number of photons absorbed and is given by:

$$Q = \frac{k_r}{k_r + \sum k_{nr}} \quad (2.3)$$

where Q is the fluorescence quantum yield, k_r and k_{nr} are the corresponding radiative and non-radiative rates respectively. Non-radiative decay does not involve the emission of a photon. The maximum value of Q is unity (100%) where every photon absorbed results in a photon emitted, i.e. radiationless decay rate is much smaller than radiative decay rate ($k_{nr} \ll k_r$). Compounds with quantum yields of 0.10 are considered quite fluorescent, thus perylene derivatives with quantum efficacies close to 1 are very fluorescent materials.

The lifetime of an excited state is defined by the average time the molecule spends in the excited state prior to returning to the ground state. Assuming $n(t)$ to be the number of excited molecules at a time t , the decay in $n(t)$ will be given by:

$$\frac{dn(t)}{dt} = -(k_r + k_{nr})n(t) \quad (2.4)$$

which can also be expressed as:

$$n(t) = n_0 \exp(-t/\tau) \quad (2.5)$$

The experimenter actually observes intensity, and since intensity is directly proportional to the number of photons, equation (2.5) can be re-written in terms of intensities in the form:

$$I(t) = I_0 \exp(-t/\tau) \quad (2.6)$$

Thus the lifetime can be calculated from the slope of a plot of $\log I(t)$ versus t . The observed lifetime is the inverse of the total decay rate, $(k_r + k_{nr})^{-1}$. The lifetime of the fluorophore in the absence of the nonradiative process is called the intrinsic lifetime and is given by:

$$\tau_n = \frac{1}{k_r} \quad (2.7)$$

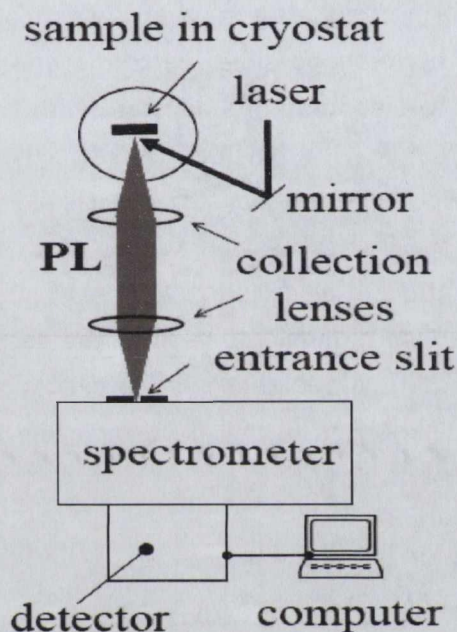


Figure 2.13 Schematic of a fluorescence spectrometer.

Fluorescence instruments generally contain a source of light, a sample holder, a detector and a readout device usually a computer. Fig. 2.13 shows the schematic for the instrumentation. Sometimes a cooling system like cryostat or heating system is included if low or high temperature dependence is required respectively. The light source excites the sample which on returning to the ground state gives up energy by luminescence. This energy is detected by the detector and recorded or displayed on the readout device. In ordinary fluorescence (F) or photoluminescence (PL) spectroscopy, the light source is fixed and the spectrum measured by scanning the spectrometer. In photoluminescence excitation spectroscopy (PLE), the detection is done at the peak emission and the frequency of the light source is varied, effectively measuring absorption. In time-resolved spectroscopy, short pulse light source and very fast detector are used and in this manner lifetimes can be measured.

Fluorescence is useful in band gap determination, impurity level detection, defect detection, quantum yields and studies of recombination mechanism and

material quality. A modification of the usual fluorescence technique can be used to determine lifetimes and relaxation processes.

Internal Conversion (IC) and Vibrational Relaxation (VR)

When a molecule that absorbs UV-Vis radiation does not fluoresce, it can only have lost its energy by some other means referred to as radiationless transfer of energy or non-radiative process. One such process involves the intra-molecular redistribution of energy between possible electronic and vibrational states. The molecule can return to the electronic ground state with the excess energy being converted to vibrational energy so placing the molecule in an extremely high vibrational level of the electronic ground state. Such a process is referred to as Internal Conversion (IC). This excess energy is lost by collision with other molecules so termed Vibrational Relaxation (VR) (See Fig.2.10). IC occurs between excited states with same spin multiplicity as from the second singlet state to the first singlet state. It thus is a radiationless de-excitation and an isoenergetic process. VR involves dissipation of energy from molecule to its surroundings and cannot occur for isolated molecules.

Intersystem Crossing (ISC)

There is another non-radiative process which involves a combination of intra- and inter-molecular energy redistribution. The spin of an excited state can be reversed leaving the molecule in an excited triplet state of a lower energy than the excited singlet state. The process is known as intersystem crossing (ISC) and is also shown in Fig.2.10.

Phosphorescence (P)

A molecule in the excited triplet state may not use ISC to return to the ground state, but could lose energy by emission of a photon. This is termed phosphorescence (see Fig.2.10). A triplet/singlet transition is much less probable than a singlet/singlet transition. The lifetime of an excited state is very large (up to 10 s) in comparison to the average lifetime of excited singlet states. Hence emission from triplet/singlet transitions can continue after the initial irradiation. Phosphorescence competes with other radiationless transfer so it is usually observed only at low temperature or in highly viscous media.

2.3.8 Fourier transformation infra-red spectroscopy

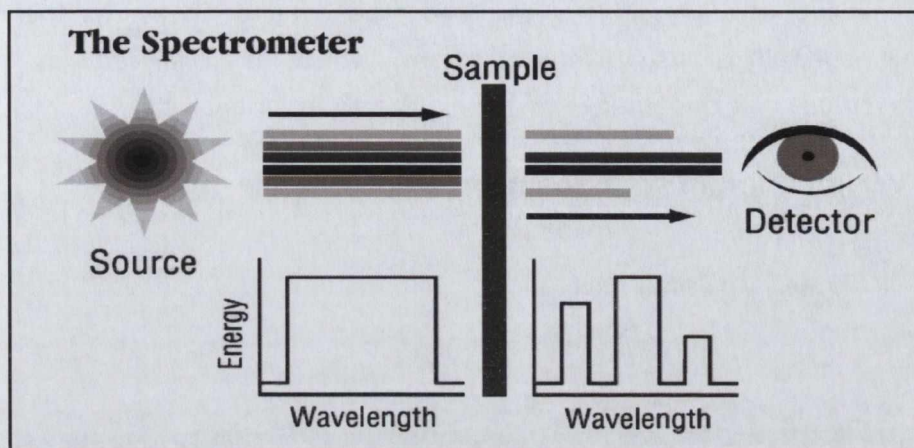


Figure 2.14 Schematic of FTIR(69)

The basic operational principles of Fourier Transform Infra-Red (FTIR) spectroscopy involve passing infra-red radiation through a sample (solid, liquid or gas). As shown in the FTIR schematic in figure 2.14, some of the infra-red radiation is absorbed by the sample and some is transmitted through the sample. The resulting spectrum is representative of the molecular absorption and transmission and so acts as a fingerprint of the sample. Hence FTIR is useful in identifying materials, quality or consistence of materials, amounts of components in a mixture and vibrational characteristics of functional groups.

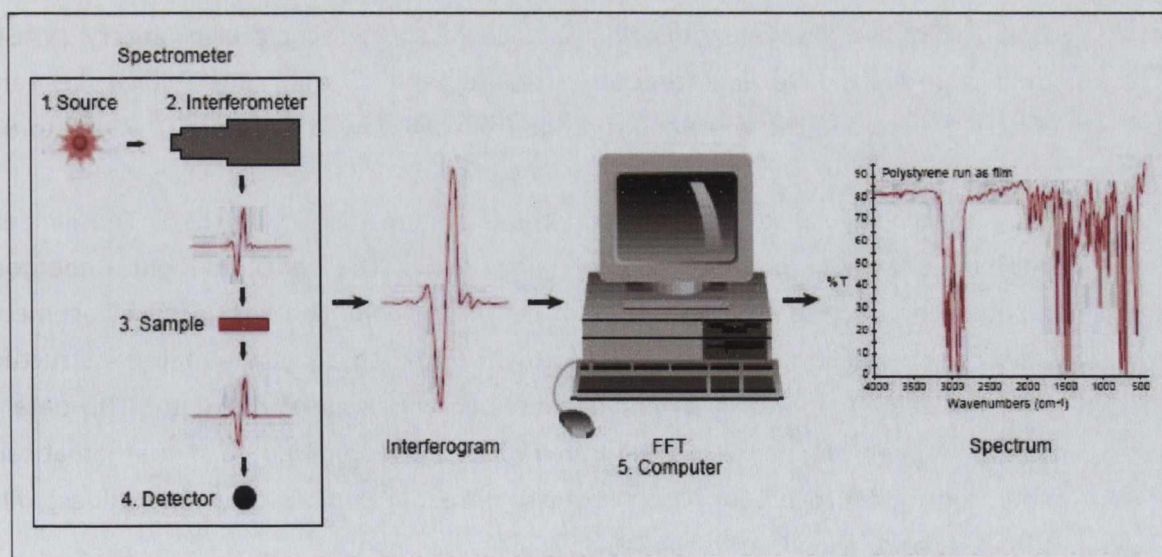


Figure 2.15 The FTIR instrumental process(69)

The instrumental process is represented in Figure 2.15 and is as follows; the source produces the infra-red radiation which enters the interferometer for

"spectral encoding". The resulting inter-ferogram is directed at the sample and is transmitted and reflected by the sample. At this stage specific frequencies uniquely characteristic of the sample are absorbed. The detector measures the final or resulting special digitised inter-ferogram which is analysed by Fourier Transformations in a computer to produce a spectrum for analysis.

2.3.9 Variable angle spectroscopic ellipsometry

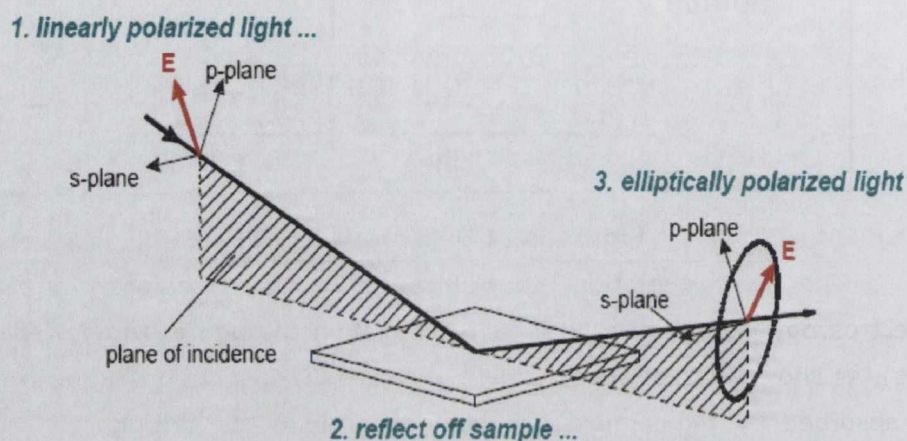


Figure 2.16 Basic configuration of reflection ellipsometry

The development of new lithographic processes, new fundamental science, and new metrology in the semiconductor, optical and data storage industries has necessitated the need to determine optical properties of thin films and bulk materials at short wavelengths. Variable angle spectroscopic ellipsometry (VASE) offers non-destructive and precise measurement of thin film thicknesses and refractive indices in the wavelength range from 140 nm to 1700 nm (0.73 eV to 8.9 eV).

A sample ellipsometry measurement is shown in Figure 2.16. The incident light is linear with both p- and s- components. The reflected light undergoes amplitude and phase changes for both p- and s- polarized light, and ellipsometry measures these changes. To extract useful information about the material structure, it is necessary to perform a model dependent analysis of the data. The data is measured over the entire wavelength range and compared to a mathematically generated model to obtain film thickness, refractive indices (n and k values), film roughness and/or uniformity.

2.3.10 HyperChem

HyperChem is a molecular modelling package created by HyperCube Inc. It has a very wide variety of comprehensive applications. In this research, HyperChem is used to predict the possibility of synthesising new perylene derivatives by considering geometry optimisations. It is also employed to predict vibronic and electronic spectra of both "possible" and already existing perylene derivatives studied herein. Predictions of the HOMO and LUMO of the perylene derivatives are also possible using the same package. The dipole moments and polarisabilities are calculated using HyperChem and compared for the materials studied. HyperChem is also employed here to determine the quantitative structure-activity relationship of the molecules. Theoretical findings based on HyperChem are then compared with the experimental findings from the experimental techniques described in Section 2.3.

2.4 Specific Materials Used

The materials used in this research include a wide range of solvents for a variety of purposes ranging from characterisation of the perylene derivatives, through preparation of cleaning solutions like the popular base piranha, to use in the synthesis of new materials. The two solutes used were mainly employed for synthesis with 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA) as the parent molecule and potassium carbonate (K_2CO_3) as the catalyst. Five perylene derivatives are extensively characterised in this study.

2. 4.1 Solvents and solutes

Apart from the de-ionised water which was produced in-house, all other solvents and solutes were supplied by Sigma-Aldrich (www.sigmaaldrich.com). Most of the solvents were spectro-photometric grade and/or of very high purity. Tables 2.2 summarise the physical properties of the solvents and solutes. In this table, the following abbreviations apply: MW = molecular weight, bp = boiling point, mp = melting point, ρ = density, δ = Hildebrand solubility parameter, P = Polarity index, ϵ_r = dielectric constant, D = dipole moment and η = viscosity. All temperature dependent parameters are quoted as at room temperature.

Table 2.2 Physical properties of solvents and solutes

Material	Formula	MW (g/mol)	bp (°C)	mp (°C)	ρ (g/ml)	P	δ (MPa)^{1/2}
Acetone	C ₃ H ₆ O	58.08	56.0	-94.0	0.79	5.1	19.7
Ammonia	NH ₃	17.03	-	-	0.78	-	-
Chloroform	CHCl ₃	119.38	61.5	-63.0	1.48	4.1	18.7
De-ionised water	H ₂ O (DI)	18.02	100.0	-	1.00	9.0	48.0
Deuterated acetone	C ₃ D ₆ O	64.12	55.5	-93.8	0.87	-	-
Deuterated chloroform	CDCl ₃	120.38	60.9	-64.0	1.50	-	-
Dichloromethane (DCM)	CH ₂ Cl ₂	84.93	39.8	-97.0	1.33	3.1	20.2
Dimethyl- formamide (DMF)	C ₃ H ₇ NO	75.08	153.0	-61.0	0.97	6.4	24.7
Dimethyl-sulfoxide (DMSO)	C ₂ H ₆ SO	78.13	189	17.5	1.10	7.2	26.4
Ethanol	C ₂ H ₆ O	46.07	78.0	-114.0	0.79	5.2	19.4
Hydrochloric acid (32%)	HCl	36.46	>100.0	-	1.20	-	-
Isopropanol	C ₃ H ₈ O	60.10	82.0	-89.5	0.79	3.9	24.5
N-methyl-2- pyrrolidinone (NMP)	C ₅ H ₉ NO	99.13	202.0	-24.0	1.03	-	22.9
Methanol	CH ₄ O	32.04	64.7	-98.0	0.79	5.1	22.3
Potassium carbonate	K ₂ CO ₃	138.21	-	891.0	2.43	-	-
Pyridine	C ₅ H ₅ N	79.10	115.0	-42.0	0.98	5.3	21.7
Tetrahydrofuran (THF)	C ₄ H ₈ O	72.11	66.0	-108.0	0.89	4.0	18.5
Toluene	C ₇ H ₈	92.14	110.0	-93.0	0.87	2.4	18.3
Trichloroethane (TCE)	C ₂ H ₃ Cl ₃	133.40	75.0	-35.0	1.34	-	15.8
1-dodecanol	C ₁₂ H ₂₅ O	186.33	261.0	24.0	0.83	-	-
1-iodo-dodecane	C ₁₂ H ₂₅ I	296.23	159.0	-3.0	1.20	-	-
3,4,9,10-perylene- tetracarboxylic- dianhydride (PTCDA)	C ₂₄ H ₈ O ₆	392.32	-	>300.0		-	-

Table 2.2 Continued

Material	Formula	ϵ_r	D (Debye)	η
Acetone	C_3H_6O	21	2.88	0.32
Ammonia	NH_3	-	-	-
Chloroform	$CHCl_3$	4.8	1.15	0.57
De-ionised water	H_2O (DI)	80.0	1.85	1.00
Deuterated acetone	C_3D_6O	-	-	-
Deuterated chloroform	$CDCl_3$	-	-	-
Dichloromethane (DCM)	CH_2Cl_2	9.1	1.60	0.44
Dimethyl-formamide (DMF)	C_3H_7NO	38.3	3.82	0.92
Dimethyl-sulfoxide (DMSO)	C_2H_6SO	47.2	3.96	2.00
Ethanol	C_2H_6O	24.3	1.69	1.20
Hydrochloric acid (32%)	HCl	4.60	1.03	1.90
Isopropanol	C_3H_8O	18.0	1.68	2.30
N-methyl-2-pyrrolidinone (NMP)	C_5H_9NO	32.2	4.30	1.70
Methanol	CH_4O	33.0	1.70	0.60
Potassium carbonate	K_2CO_3	-	-	-
Pyridine	C_5H_5N	12.0	2.37	0.94
Tetrahydrofuran (THF)	C_4H_8O	7.5	1.63	0.55
Toluene	C_7H_8	2.4	0.31	0.59
Trichloroethane (TCE)	$C_2H_3Cl_3$	7.5	-	0.87
1-dodecanol	$C_{12}H_{25}O$	-	-	-
1-iodo-dodecane	$C_{12}H_{25}I$	-	-	-
3,4,9,10-perylene- tetracarboxylic-dianhydride (PTCDA)	$C_{24}H_8O_6$	-	-	-

2.4.2 Perylene Derivatives

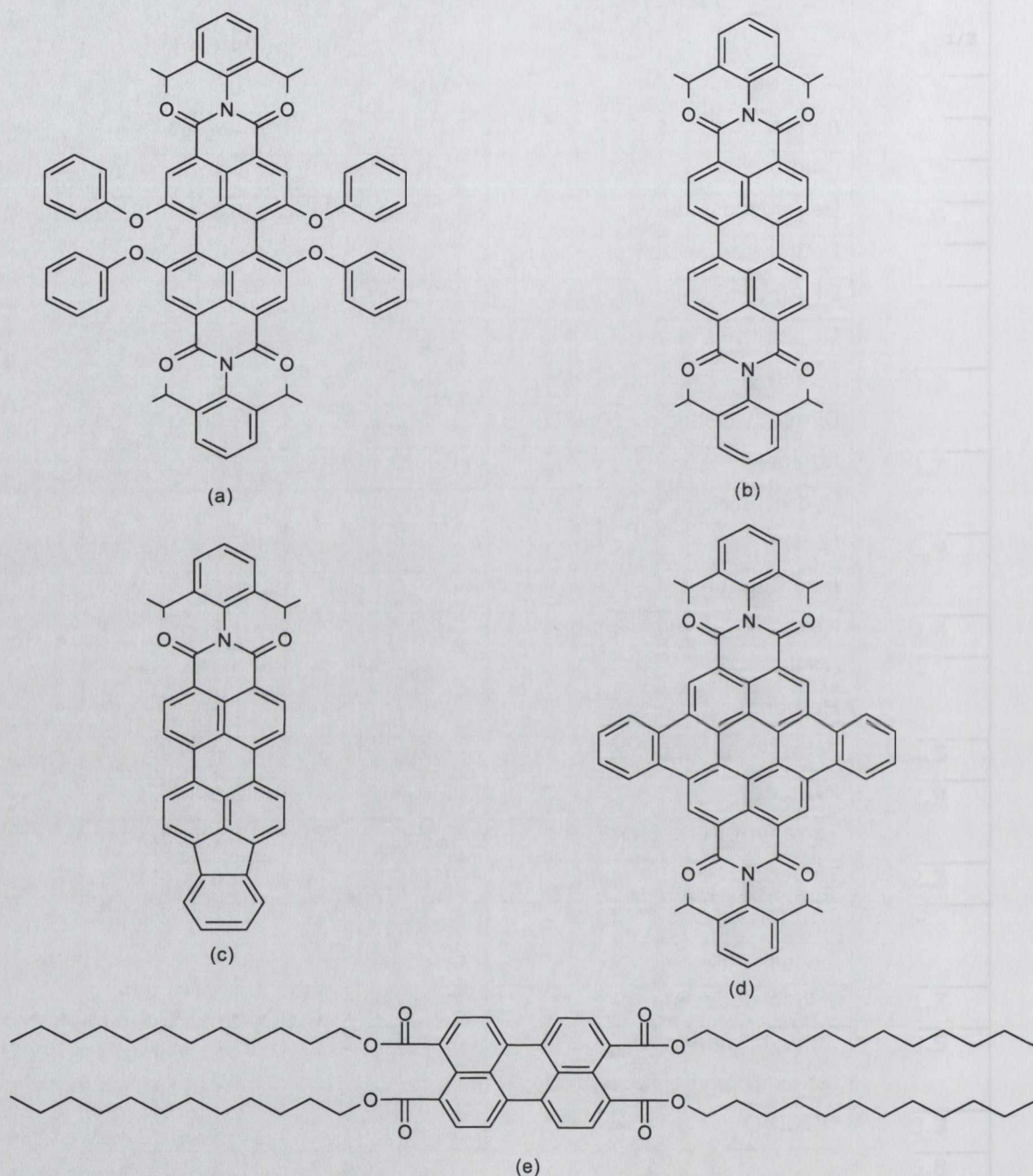


Figure.2.17: Chemical structures of the perylene derivatives studied herein
(a) 1,6,7,12-tetraphenoxy-N'N'Bis-(2,6-diisopropylphenyl)-perylene-3,4,9,10-bis(dicarboximide) or perylene red (PR) (b) N'N'Bis(2,6-dimethylphenyl)perylene-3,4,9,10-bis(dicarboximide) or perylene orange (PO) (c) indenoperylene dicarboxmonoimide or perylene violet (PV) (d) Dibenzocoronene tetracarboxdiimide or perylene yellow (PY) (e) 3,4,9,10-tetra-(12-alkoxycarbonyl)-perylene or perylene blue (PB).

In this research, five very similar compounds are studied. The chemical structures of the five perylene derivatives are given in Figure 2.17. All have a perylene core with seemingly slight modifications of side chains and the positions to which they are attached. These differences are not trivial but give rise to very significant differences in the electronic and physical properties of the materials as explained in the thesis. Materials (a) through to (d) were obtained from BASF Germany whilst material (e) was synthesised in-house.

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Chapter 3

Molecular Modelling of perylene derivatives

3.1 Introduction

Theoretical calculations are an important tool to guide and support current and future materials science laboratory studies. Absorption spectra can be predicted and insight into the nature of absorptions can be gained. Trends that may aid the direction of future research can be extracted. The expected behaviour and characteristics of existing and potential new materials can be predicted. Molecular modelling is a collective term referring to theoretical methods and computational techniques to mimic the behaviour of molecules. It includes techniques for deriving, representing and manipulating the structures and reactions of molecules as well as those properties that are dependent on the three dimensions. In molecular modelling, the lowest level of information is individual atoms or a small group of atoms unlike in quantum chemistry where electrons are considered explicitly. Molecular modelling thus reduces the complexity of the system so allowing many more particles to be considered. Applications of molecular modelling include investigating the structure, dynamics and thermodynamics of molecular systems be they organic, inorganic, biological or polymeric.

There has been an increasing interest in the study of polycyclic aromatic hydrocarbons (PAHs) and their potential and promising applications for the creation of new dyes have yet to be exhausted. PAHs are components of natural pigments with no artificial analogs (1, 2) and the reason for the high concentrations of PAHs, especially perylene, in marine sediments is their ability to recover (3, 4). Successful PAHs applications include the production of quantum electronics materials (5-9). The large size and high symmetry of perylene and most of its derivatives provides an interesting database of PAHs candidates for detailed studies (10). Perylene derivatives are currently gaining increasing interest due to their huge variety of possible future electronic and photonic applications in diodes (11), waveguides (12), quantum well structures (13), energy transfer dye lasers (14-16), solid state lasers (17, 18), optical amplifiers (19), luminescent solar concentrators (20), luminescent converters for blue light emitting diodes (19) and electron transport materials for solar cells (21). It is this wide and varied extend of opto-electronics applications that make perylene derivatives worth the investment and research attention.

In this chapter, the fundamental molecular modelling results using Hyperchem on selected perylene derivatives are presented. The results include geometry optimization, vibronic spectrum, electronic spectrum and quantitative structure-activity relationship (QSAR) among other inferences drawn from the same. These theoretical results are later compared to experimental results herein and also in a later Chapter 5.

3.2 Theory

3.2.1 Geometry Optimisation

Molecular mechanics is concerned with searching the molecular potential energy surfaces of molecules for equilibrium structures sometimes referred to as minima. Geometry optimisation is the term given to the process of finding minima on potential surfaces where the minima represent equilibrium states. At a minimum point, the first derivative of a function f with respect to a variable x is zero and the second derivative is positive. This is also true for all variables if the function depends on more than one variable. Mathematically this is represented in equations (3.1) and (3.2)(22)

$$\frac{\partial f}{\partial x_i} = 0 \quad (3.1)$$

$$\frac{\partial^2 f}{\partial x_i^2} > 0 \quad (3.2)$$

The variables x_i are the Cartesian or the internal coordinates of the atoms in the case of quantum or molecular mechanics. This energy minimisation in molecular modelling must precede any computational analysis in which molecular or quantum mechanics are applied. Since minimisation of a function $-f$ is equivalent to maximisation of the function f , the term optimisation is preferred to either minimisation or maximisation (23). Geometry optimisation in molecular modelling has the following applications; to characterise a potential energy surface, obtain a structure for a single-point quantum mechanical calculation which then provides a large set of structural and electronic properties and to prepare a structure for molecular dynamics. Geometry optimisation can also be used to predict the possibility of producing new molecules. If the structure conforms to steric hindrance, the molecule may be synthesised but if the structure is inconsistent, then steric hindrance is so pronounced that it may not be a feasible synthesis as the energy barrier cannot be overcome. There can be a large number of minima on the energy

surface but there is only one "global energy minimum" which is the minimum with the lowest energy surface(22). Molecules can move from one minimum state to another through transitions.

3.2.2 Vibrational and electronic spectra

Molecular modelling can be used to predict the structure and properties of compounds based on mathematical models. Some of such properties as can be predicted are the electronic and vibronic spectra.

A molecular vibration is excited when the molecule absorbs a quantum of energy, E , corresponding to the vibration's frequency, f , according to the relation in equation (3.3)

$$E = hf \quad (3.3)$$

where h is Planck's constant. During a molecular vibration, the atoms in a molecule are in a state of periodic motion whilst translational and rotational motions for the whole molecule remain constant. The vibrations of a molecule can be very complicated but quantum mechanics dictate that non-linear molecules have $3N-6$ normal modes of vibration whereas linear molecules have $3N-5$ normal modes of vibration. The difference is due to the fact that rotation about the molecular axis of linear molecules cannot be observed. In this research only non-linear molecules are studied. The normal modes of vibration of polyatomic molecules are independent of each other, each involving simultaneous vibrations of different parts of the molecule. This is typically observed in this research with the perylene derivatives. A fundamental vibration is excited when a quantum of energy is absorbed by the molecule in its ground state. When two quanta are absorbed the first overtone is excited, and so on to higher overtones.

The vibrational states of a molecule can be probed in a variety of ways. The most direct way is through infrared spectroscopy, as vibrational transitions typically require an amount of energy that corresponds to the infrared region of the spectrum. Raman spectroscopy, which typically uses visible light, can also be used to measure vibration frequencies directly. Thus in modelling the vibronic spectrum, the calculated frequencies are the same as would be obtained in both infra red spectroscopy and Raman spectroscopy whilst the calculated intensities are only identical to those obtained in infra red spectroscopy. This allows for theoretical and experimental comparison as shown in later in this chapter.

Two major types of vibrations exist which are stretching due to a change in the bond lengths and bending due to a change in bond angles. Bending vibrations include rocking due to a change in an angle between a group of atoms, wagging

due to a change in the angle between the planes of groups of atoms, twisting due to a change in the angle between the planes of two groups of atoms and out-of-plane or scissoring due to atom moving in and out of the plane of the other atoms. In a rocking, wagging or twisting coordinate the angles and bond lengths within the groups involved do not change. Rocking is distinguished from wagging by the fact that the atoms in the group stay in the same plane.

The electronic spectrum of a compound results from emission or absorption of electromagnetic radiation during changes in the configuration of atoms, ions or molecules as opposed to vibrational, rotational, fine structure or hyper-fine spectra. The theory of electronic spectrum has been provided in Chapter 2's section 2.3.7. Electronic spectra can also be predicted by mathematical methods employed in molecular modelling. Experimental spectra can then be compared to the theoretically predicted ones.

The Parameterised Model number 3 (PM3)(22) is a semi-empirical method for the quantum calculation of molecular electronic structure in computational chemistry. It is based on the Neglect of Differential Diatomic Overlap (NDDO) integral approximation. The PM3 employs similar formalism and equations as the Austin Model 1 (AM1) method. The differences are that PM3 uses two Gaussian functions for the core repulsion function, instead of the variable number used by AM1 (which uses between one and four Gaussians per element) and the numerical values of the parameters are different. Another difference lie in the philosophy and methodology used during the parameterization; whereas AM1 takes some of the parameter values from spectroscopical measurements, PM3 treats them as optimizable values.

3.2.3 Quantitative structure-activity relationship (QSAR) properties

The major thrust of materials science is to understand and explain the functions of molecular systems in molecular terms as well as relating the functions to the properties of the molecules. The development of molecular modelling techniques has aided the prospects of understanding the properties, functions and reactivity of systems in terms of molecular structure. Quantitative structure-activity relationships (QSARs) are attempts to correlate structural or property descriptors of compounds/molecules with chemical or biological activity. The properties can be obtained empirically but recently computational methods have been employed. Equation (3.4) is a general form which relates the properties to the activity of a molecule.

$$\text{Activity} = f(p) \quad (3.4)$$

where f is some function and p are structure derived properties of the molecule(22).

Molecular modelling can be used to discover and design new molecules. In most materials science studies, the modelling is done to predict the properties based on a "designed" or expected structure of a molecule. Once the synthesis has been done, the empirical results can be compared with the theoretical predictions. There is a wide range of descriptors of molecular properties, however in this research, the following QSAR were obtained using Hyperchem; mass, volume, surface area, log P , polarisabilities, refractivity and hydration energy.

The mass of the molecule M is calculated by summation of individual atomic masses m_i that make up the molecule as is given by equation (3.5)

$$M = \sum_i m_i \quad (3.5)$$

The atomic volume contributions are calculated by numerical integration grid technique where the volume of an atom whose van der Waals radius R is given in equation (3.6)(23)

$$V = \frac{4}{3}\pi R^3 \quad (3.6)$$

The molecular volume is thus the sum of the individual atomic contributions. The molecular surface areas are similarly calculated considering that the surface area of an atom is the first derivative of its volume.

For an organic solute in equilibrium with water and a polar solvent, there exists a parameter P called the partition coefficient which is approximately constant and is a ratio of the concentration of the solute in the polar solvent to that of the solute in the water defined by equation (3.7)

$$P = \frac{\text{solute in polar solvent}}{\text{solute in water}} \quad (3.7)$$

Originally discovered by Hansch (24) to relate biological activity to a molecule's electronic characteristics and hydrophobicity, log P has now become a popular QSAR for chemical activity especially where atoms are substituted.

The permanent dipole $p_e(\text{permanent})$ is one that a molecule has in free space with no fields present. The molecular dipole moments may be due to non-uniform distributions of positive and negative charges on the various atoms. The direction of the resulting dipole moment is dictated by convention to point from the more electronegative area of a molecule to the region of least electronegativity as displayed in figures 3.2 to 3.8 for the perylene derivatives studied. When a weak electric field E is applied to in a direction parallel to a molecule's electric dipole moment, it causes charge re-distribution and the induced dipole $p_e(\text{induced})$ is given by equation (3.8)

$$p_e(\text{induced}) = p_e(\text{permanent}) + \alpha E \quad (3.8)$$

where α is the dipole polarisability defined as the relative tendency of a charge distribution to be distorted from its normal shape by an external electric field. The charge distribution may be an electron cloud of an atom or molecule say with total charge Q and electron cloud radius a . The external electric field maybe due to a nearby ion or a dipole. If d is the radius of the atom or molecule, α can be defined as in equation (3.9)

$$\alpha = \frac{Qa}{E} = 4\pi\epsilon_0 a^3 \quad (3.9)$$

where ϵ_0 is the permittivity of free space(23).

Molar refractivity MR is one QSAR that can be used to model steric effects. It is defined by equation (3.10) (22)

$$MR = \frac{(n^2-1) MW}{(n^2+1) \rho} \quad (3.10)$$

where n is the refractive index, ρ is the density of the organic material and MW is its molecular weight. The refractive index does not vary much from one organic molecule to another and as molecular weight divided by density is the volume, MR thus is an indication of steric effects.

3.3 Modelling

The molecular modelling was performed on the selected perylene derivatives shown in Fig.2.17. Perylene and it's archetypal derivative, PTCDA, shown in figs.2.1b and 2.2 respectively were used as standards. In addition to these, two more "alkoxy" based perylene derivatives shown in Fig.3.1 were also modelled with a view towards possible synthesis and steric effects, hence the bulky groups substitution.

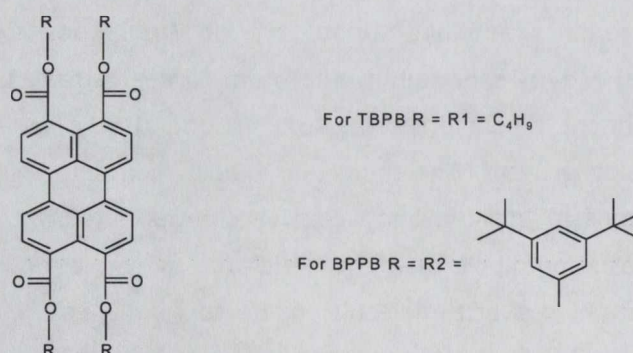


Figure 3.1 Structure of bulky groups substituted "alkoxy" based perylene derivatives 3,4,9,10-tetra-(alkoxy-t-butyl)-perylene (TBPB) and 3,4,9,10-tetra-(alkoxy 3,5 dibutylly phenoxy)-perylene (BPPB).

3.3.1 Geometry optimisation

The molecules were drawn using the Chemistry Sketching package MDL ISIS Draw 2.5 SP4. Hyperchem was employed to open the sketch files of the molecule. The hydrogen atoms were added and model building performed. The MM+ (25) molecular mechanics was set up before computing the geometry optimisation, applying the Polak-Ribiere (26) conjugate gradient with a termination condition of RMS gradient of 0.1 kcal/mol or 1680 points in vacuo. At convergence, the HIN file was saved and properties such as the dipole moment, bond length and angles, HOMO/LUMO, inertial axis, different renderings, isosurfaces and molecular graphs including total charge density could be displayed. Any subsequent modelling was only performed with the geometrically optimised molecular structure. All exported pictorial files were done using metafile for high resolution on paper.

3.3.2 Vibronic and electronic spectra

To obtain the vibrational spectrum, the geometrically optimised structure was opened into the Hyperchem workspace. The ball and stick rendering was selected. The Parameterised Model number 3 (PM3)(22) quantum method was selected for simplicity even though in reality any semi-empirical quantum method would be applicable and produce similar results. The vibrations were computed using the Restricted Hartree-Fock (RHF) (22, 23) spin pairing with an accelerated convergence to an iteration limit of 50 and a convergence limit of 0.01. Once completed, the vibrational spectrum could be displayed and forbidden and allowed vibrations could be observed. Hyperchem displayed the frequency of vibrations, their intensities and an option to view animations was present.

For the electronic spectrum, the single point computation was performed on the geometrically optimised structure with none for configuration interaction to allow observation of the HOMO and LUMO. The Austin Model 1 (AM1) semi-empirical method was then setup with a singly excited configuration interaction selecting six each of occupied and unoccupied orbitals. Another single point computation was performed immediately followed by a computation of the electronic spectrum from which could be extracted forbidden transitions, allowed transitions, intensities and frequencies.

3.3.3 QSAR

The QSAR properties were obtained by computation of QSAR on the geometrically optimised structure. The selected properties were partial charges, approximate surface area, mass, volume, hydration energy, log *P*, refractivity and polarizability. A choice of QSAR properties of surface area and volume was possible

between van der Waals and solvent accessible surface with the solvent probe radius fixed at 1.4 Å.

3.4 Modelling results and discussion

3.4.1 Geometry optimisation

The geometry optimised structures for the perylene derivatives modelled are shown in ball and cylinder as well as sticks rendering in Figs. 3.2 through to 3.8. The figures include inertial axes and dipole moment direction for each derivative. The length of the dipole is not to scale and doesnot indicate the strength of the dipole. Hyperchem allows charge density visualisation on isosurfaces and in the same figures the molecular electrostatic potential are displayed as 3-D mapped isosurface. For the HOMO and LUMO potentials, green represents positive and purple represents negative.

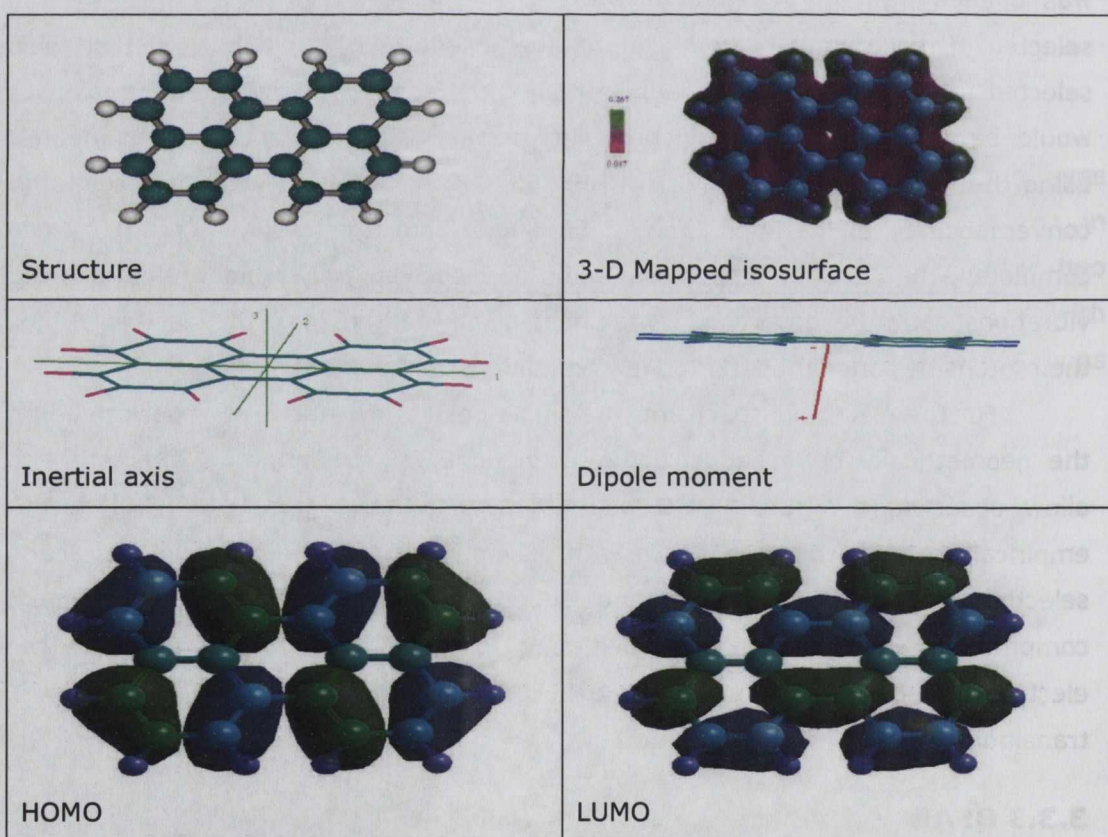


Figure 3.2 Geometry optimised properties for perylene

Perylene forms the core or building block for all derivatives studied herein and its properties are well known as described in section 2.2. In the same section, it has been explained that PTCDA is a well studied archetypal perylene

derivative(27). Alongside each other, the two can be used as standards against new derivatives. In this research, perylene and PTCDA are modelled both as standards as well as confirm the authenticity of the modelling program (Hyperchem) used.

Figure 3.2 shows some of the geometry optimised properties of perylene. Hyperchem gives the molecular point group for perylene as D_{2h} which is consistent with previously obtained data(27). It thus has a centre of inversion and therefore its dipole moment is expected to be zero as found in this research (see Table 3.16.). The electron density is localised on the peripheral atoms as previously found(28). As also shown by the inertial axis, perylene is a planar molecule. The HOMO and LUMO orbitals distribution are very similar with those found elsewhere(29) differing in values. This is explained later in this section concerning all the perylene derivatives studied here.

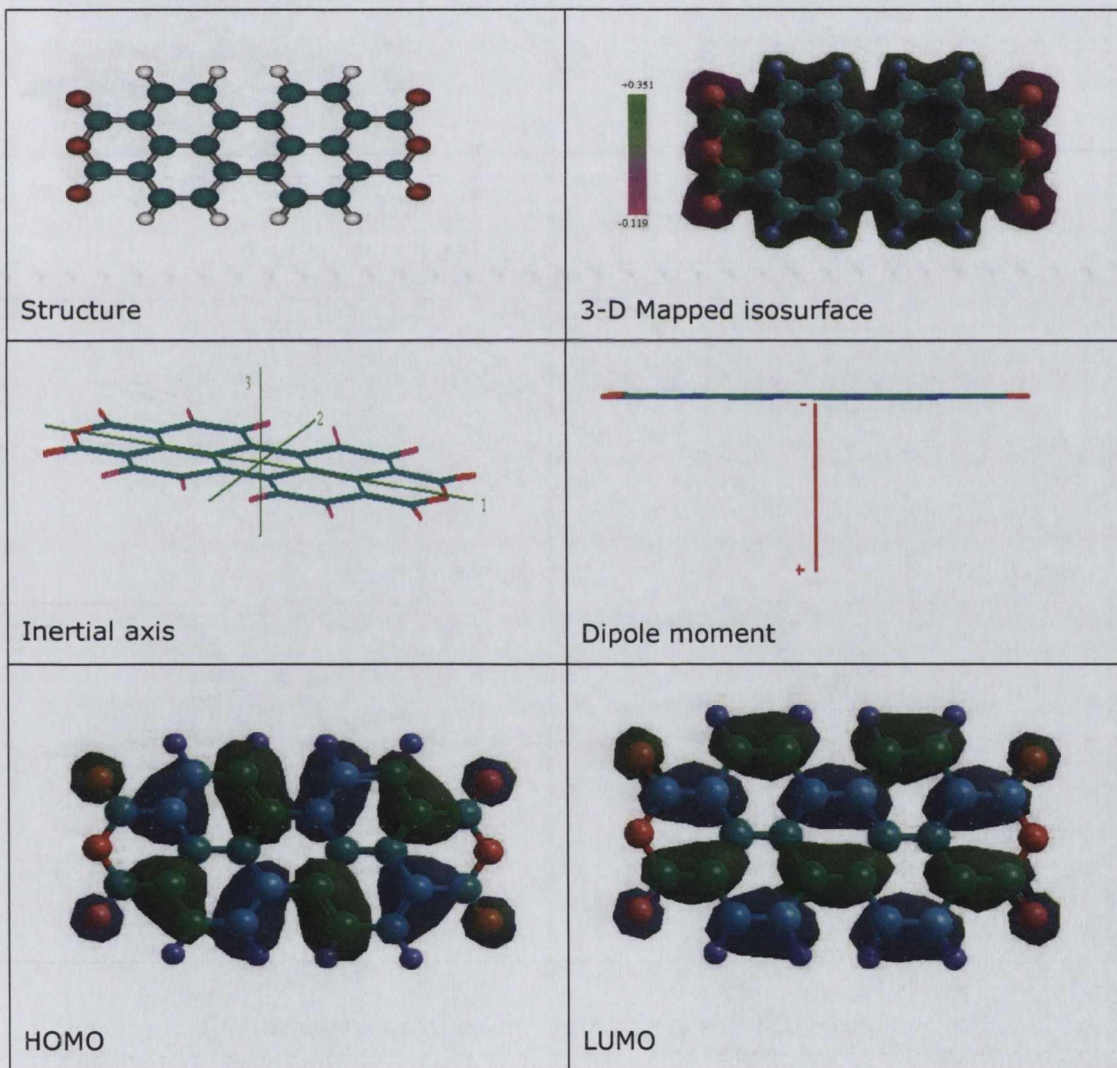


Figure 3.3 Geometry optimised properties for PTCDA

The geometrically optimised structures and properties of PTCDA obtained by the modelling are shown in Figure 3.3. The inertial axes reveal the already known planar structure whilst both the 3-D mapped isosurface and the dipole moment show symmetrical charge distribution(30). Hyperchem also confirmed the D2H molecular point group for perylene and even to allocate it to the C2V subgroup of the D2H. As in the case with perylene above, the HOMO and LUMO orbitals of PTCDA are similar to previously observed and reported in literature (31-34) except for values. Considering results for perylene and PTCDA, Hyperchem is thus a good modelling package for other perylene derivatives.

Non-planarity

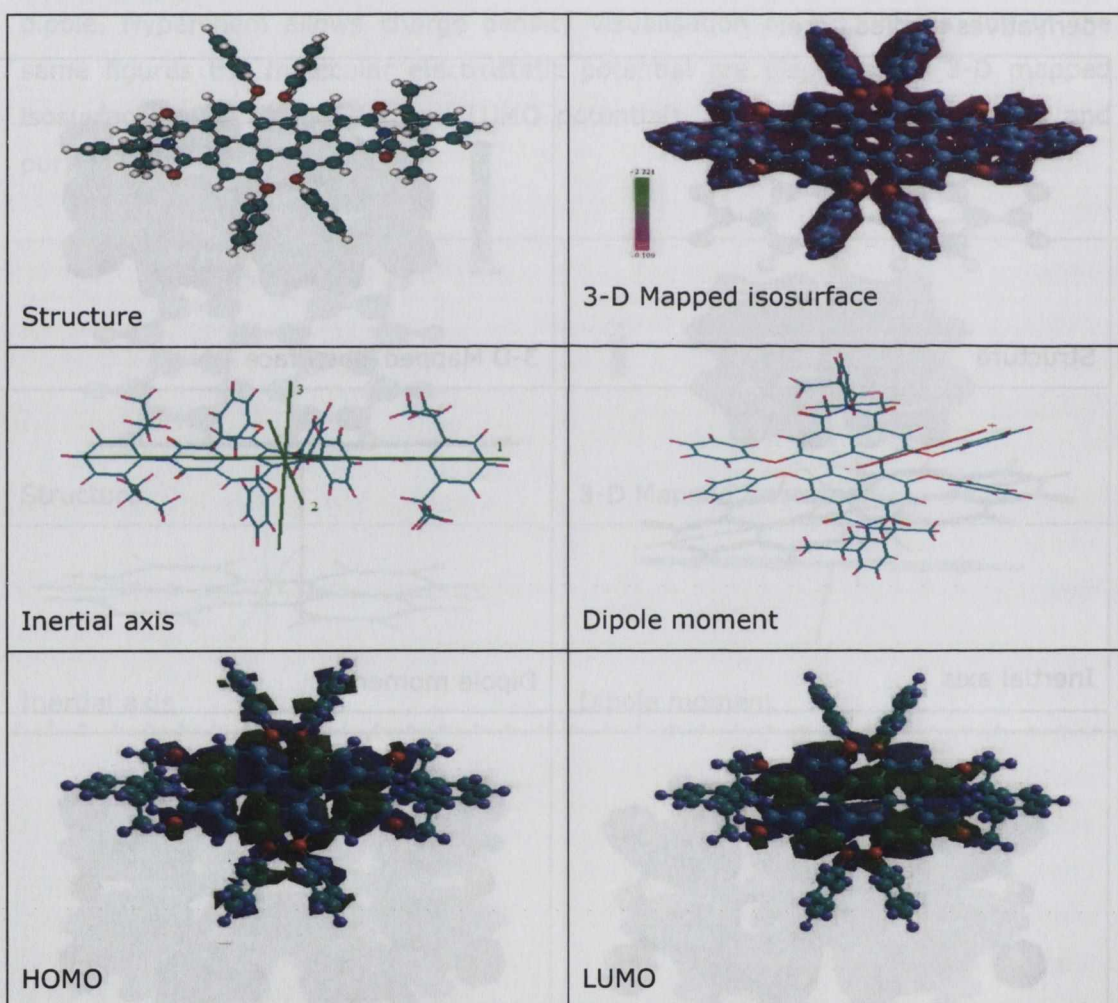


Figure 3.4 Geometry optimised properties for PR

The performed geometry optimisations for all the other perylene derivatives PR, PO, PB, PV, PY and TBPB show that the most stable structures of the respective molecules are associated with perpendicular position of all substituents to the

perylene core as shown in figures 3.4 to 3.9. This is referred to as the non-planar structure as opposed to the structures of perylene and PTCDA. The non-planarity feature is independent of the position of the substituents be they at the peri- or bay- positions or both. As evident from the results, all perylene derivatives reach optimisation by some form of twisting in relation to steric hindrance. However this is not so obvious in PV and PY. The twisting and turning away from each other of the substituents causes the dipole moments to be directed as shown in the individual cases and is a result of charge redistribution.

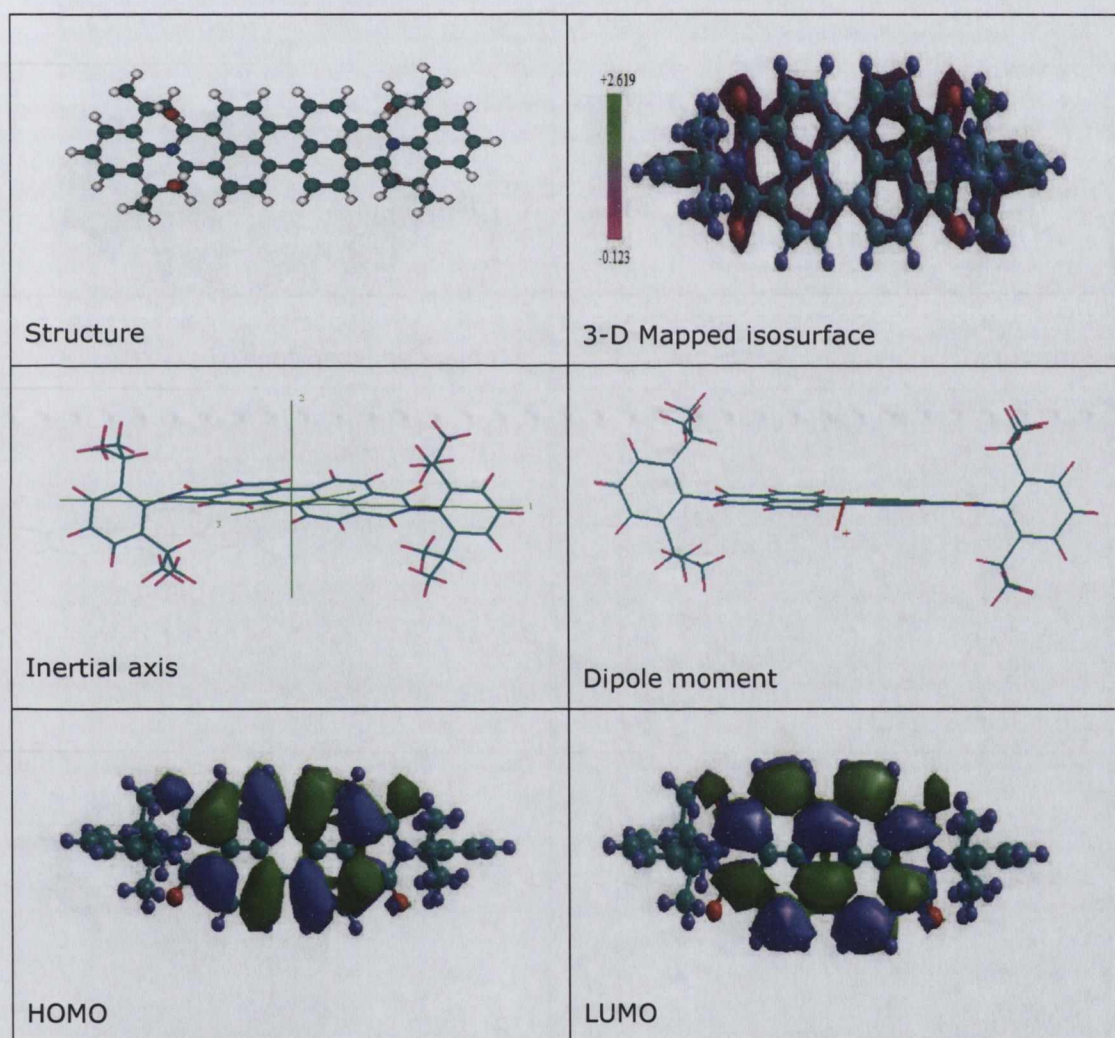


Figure 3.5 Geometry optimised properties for PO

The lack of both symmetry and planarity causes a structural behaviour which ensures that the dipole moments are not directed as in the cases of perylene and PTCDA in which they are perpendicular to the molecular plane(28, 29).

HOMO-LUMO

As in the case of perylene and PTCDA, the charge distribution for all the other perylene derivatives is concentrated at the peripheral atoms. The HOMO and LUMO orbitals potentials are also concentrated around the central perylene core for each derivative. The potential distributions for the HOMO and LUMO obtained for perylene and PTCDA were not consistent with previous findings, neither were the band gaps as shown in Table. 3.16. As a consequence, the HOMO and LUMO of all the other derivatives obtained here by Hyperchem are suspect. Whilst this may be considered a limitation of Hyperchem, there is no direct effect on other results. One

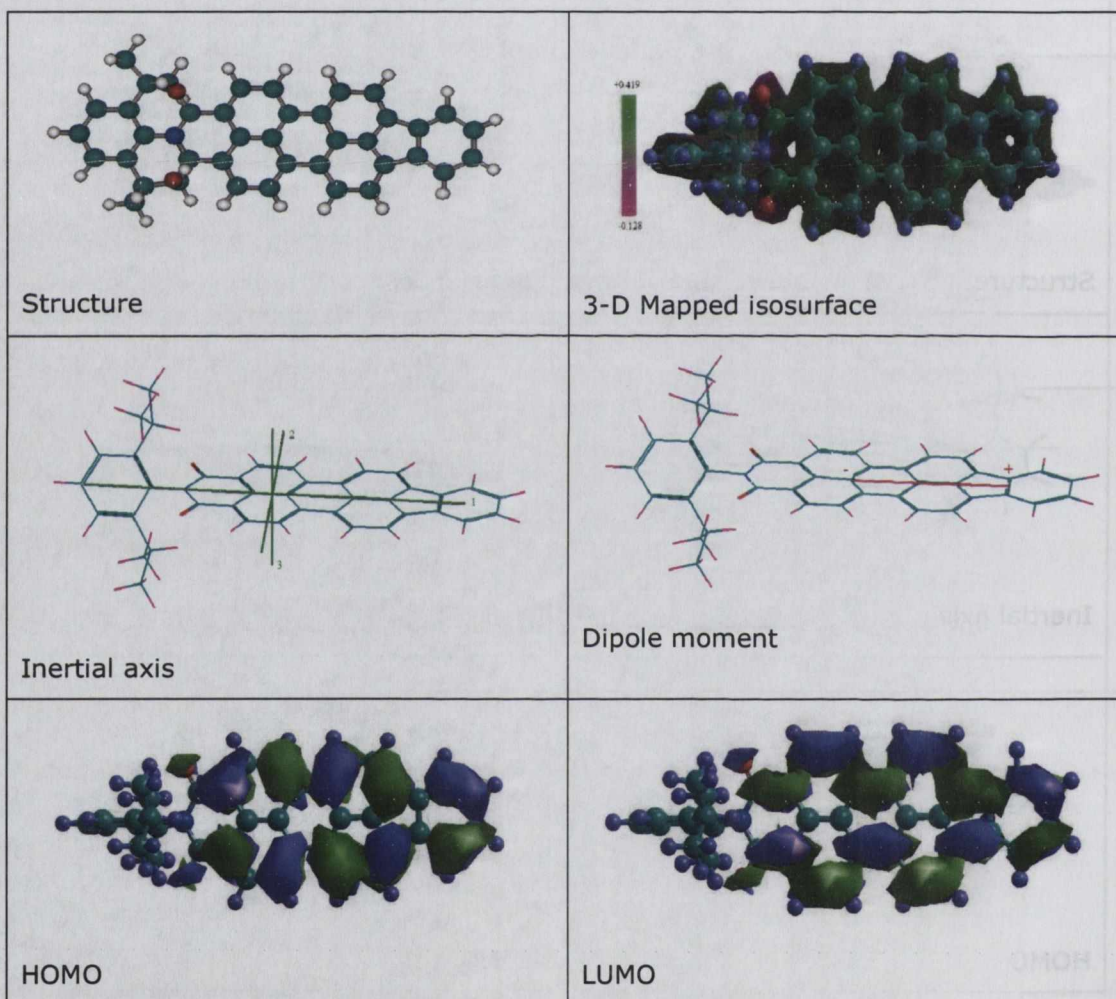


Figure 3.6 Geometry optimised properties for PV

of the reasons for this limitation is that most semi-empirical methods overestimate the energy level of the LUMO. Another reason is that in calculating the HOMO-LUMO bandgap, the modelling assumes ground state for the molecule. Removal of an electron from the HOMO or its addition to the LUMO would change the energy level due to Coulombic interactions which are not taken into effect. A better and more

accurate calculation of HOMO, LUMO and band gap can be arrived at by using density functional theory programs at the expense of time.

Symmetry and steric hindrance

Hyperchem predicts the molecular point group of PO, PV, PY, PB, PR and TBPB as C1. This group only contains one trivial symmetry operator E which is the identity operator. Therefore all the aforementioned molecules are asymmetrical or have molecular conformations. The results in the table confirm this and the molecules are therefore chiral. The lack of symmetry is attributed to the "repulsive"

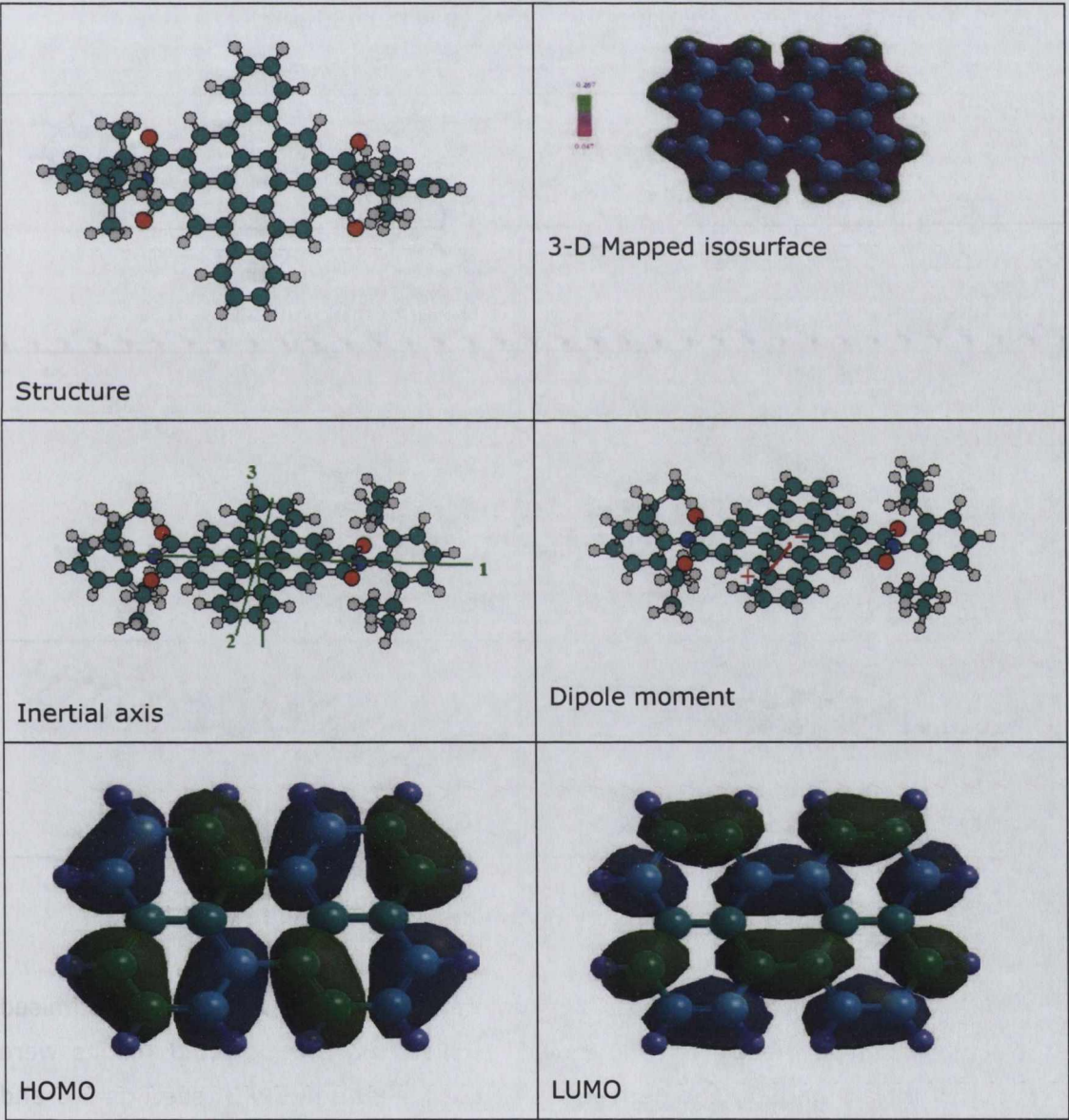


Figure 3.7 Geometry optimised properties for PY

effect the substituents have on each other at the various positions around the perylene core as they try to minimise energy in the ground state. This is commonly known as steric hindrance or steric effects and is a result of the associated cost in energy due to overlapping electron clouds (Pauli or Born repulsion) so affecting the molecule's preferred conformation and reactivity. It is the steric effects due to substituents which give the perylene derivatives studied here the asymmetric and hence chiral nature. In this research the geometry optimisation has also been used to predict the possibility of a synthesis of new derivatives. With the objective of studying the effects of bulky substituents on alkoxy perylene, the perylene derivatives PB, TBPB and BPPB with respective bulky groups of dodecane, tbutyl and 3,5 tbutyl phenoxy were modelled with a view to synthesis.

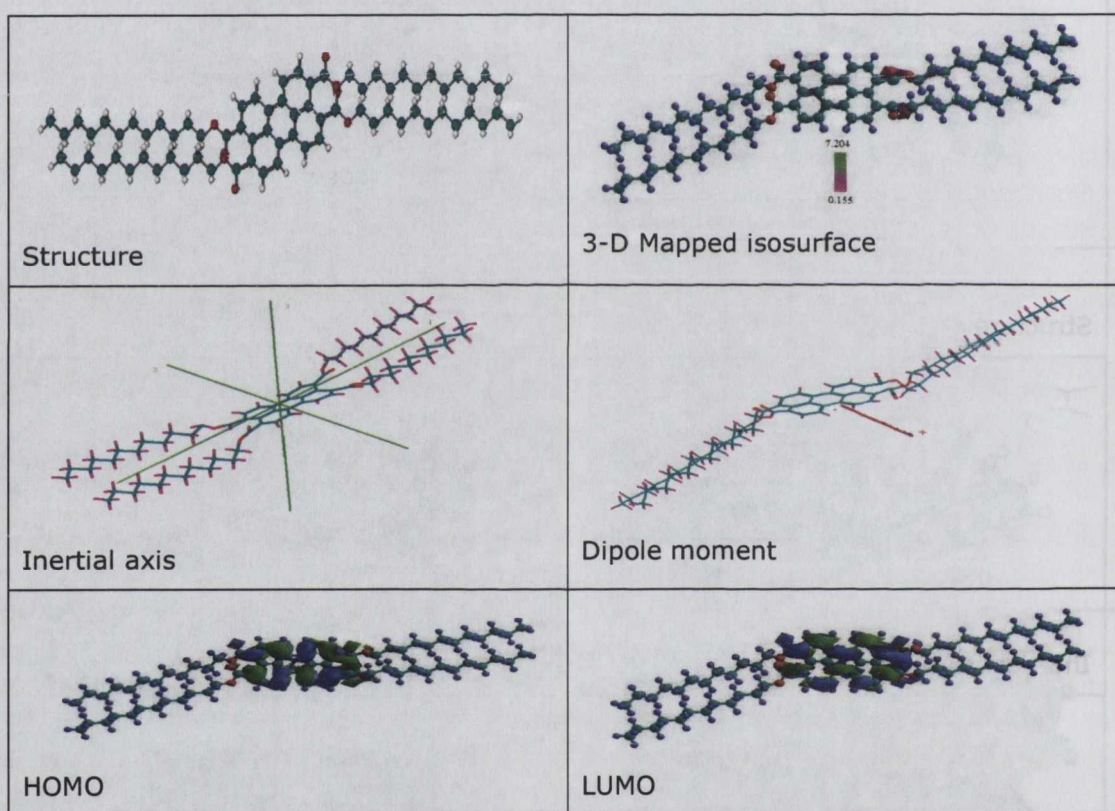


Figure 3.8 Geometry optimised properties for PB

Whilst predictions of possible conformations of geometrically optimised structures can be made from the molecular sketches, the expected results were obtained for all the perylene derivatives except for PB and BPPB (see figs 3.8 and 3.9). In PB, two of the oxygen molecules lie on the same side of the perylene core's plane, but from the Born or Pauli repulsion, one would expect that they be on either side of the perylene core's plane. As explained previously in section 3.2.1, there are

several possible minima and the one obtained by Hyperchem here, whilst “unexpected” is just one of them. One could be tempted to conclude that the molecule does not have geometrical conformation and would not exist, but as evident from Chapter 4, the molecule can be synthesised and was characterised to

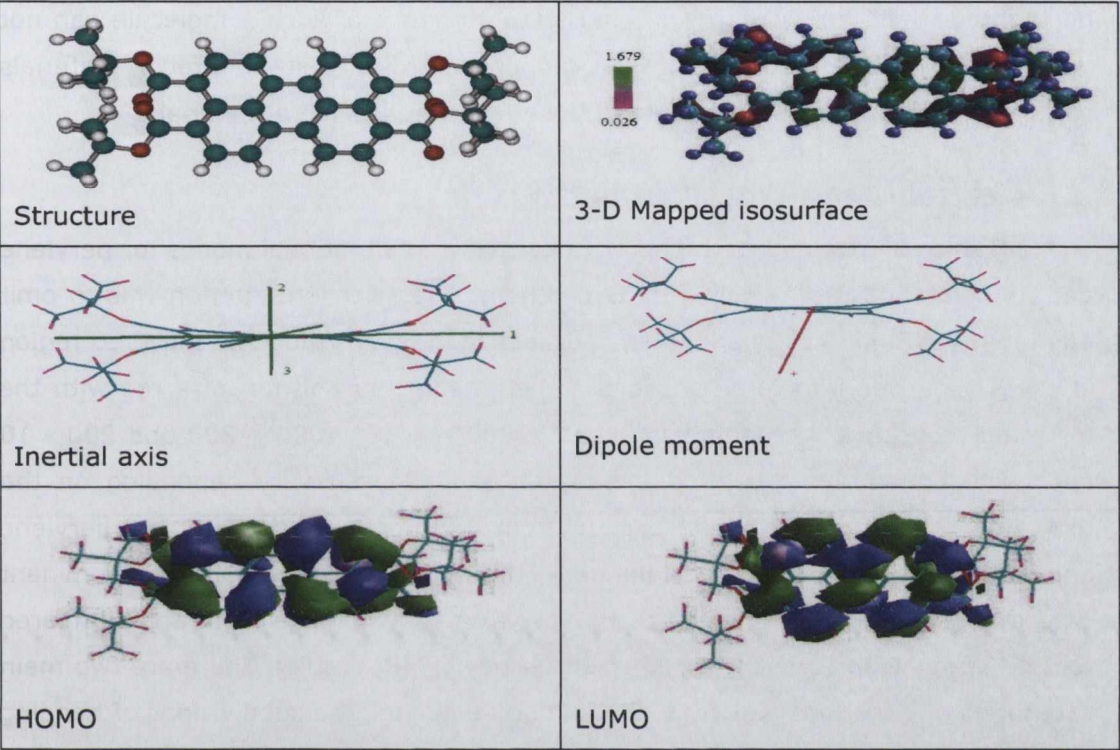


Figure 3.9 Geometry optimised properties for TBPB

prove evidence of steric hindrance and reduction of aggregation effects by bulky groups in small molecules. With TBPB, the substiutents are non-linear in comparison to PB and at the time of writing, the synthesis of TBPB was not effected. From the results obtained, it is possible that two tbutyl groups could be attached on opposite ends as well as opposite planes of the perylene core and the third and fourth group could not be attached due to strong steric hindrance. The continued attempt to synthesise and characterise TBPB is part of the future work.

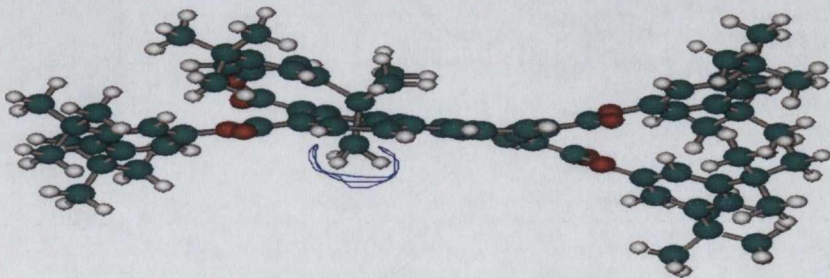


Figure 3.10 Geometry optimised structure for BPPB

Figure 3.10 shows the geometry optimised structure of BPPB. When compared to the chemical structure sketch in figure 3.1, the position of three of the four bulky 3,5 tbutyl phenoxy groups are as would be "expected" from symmetry theory, but the fourth group completely interferes with the whole structure as highlighted in Figure 3.10. The ground state structure of such a molecule can not be optimised and so such a molecule cannot exist due to steric effects. Materials science researchers would not be tempted to synthesise such a material.

3.4.2 Vibronic and electronic spectra

Tables 3.1 through to table 3.8 show selected vibrational modes for perylene and its derivatives as modelled by Hyperchem. The selection criterion was to omit any modes with infra red band intensities less than 50 km/mol. The infra red region is usefully divided into three sections namely near, mid and far infra red with the following respective wavenumber ranges 12800 – 4000, 4000 – 200 and 200 - 10 cm⁻¹. The boundaries are for didactic purposes and can vary depending on the experimental detector used. As evident from the aforementioned tables, perylene and its derivatives studied here absorb in the mid infra red region. The dominant type of vibration from modelling results are also shown in the table and compared to the Fourier Transform Infra Red spectroscopy (FTIR) results. There are two main categories of vibrations namely stretching and bending. The subdivisions of bending vibrations have been previously described in section 3.2.2. The actual vibrations are complicated as shown by the animations and only the "dominant" vibration is described in the tables.

Table 3.1. Selected vibrational modes for perylene.

NORMAL MODE	FREQUENCY (cm ⁻¹)	INFRARED INTENSITY (km/mol)
32	836	72.4
87	3006	50.7

Table 3.2 Selected vibrational modes for PTCDA.

NORMAL MODE	FREQUENCY (cm ⁻¹)	INFRARED INTENSITY (km/mol)
36	624	50.9
77	1576	68.3
78	1586	85.9
80	1660	50.3
81	1678	68.2
82	1716	229.2
84	1833	83.6
87	1894	71.2
88	1911	81.4
93	2038	107.8
97	2159	115.8
98	2176	124.8
99	2182	844.6
100	2198	218.9

Table 3.3. Selected vibrational modes for PV.

NORMAL MODE	FREQUENCY (cm ⁻¹)	INFRARED INTENSITY (km/mol)
130	1300	161.5
159	1658	298.6
160	1692	73.8
168	1870	63.8
174	1989	197.0
179	2142	153.4
180	2152	506.8
181	2170	54.7

Table 3.4. Selected vibrational modes for PO.

NORMAL MODE	FREQUENCY (cm ⁻¹)	INFRARED INTENSITY (km/mol)
176	1334	79.0
205	1423	54.1
206	1439	140.8
216	1579	331.8
219	1671	185.5
229	1814	148.0
233	1875	227.2
235	1907	430.5
237	2004	165.6
239	2144	431.4
240	2149	154.0
269	3011	58.8

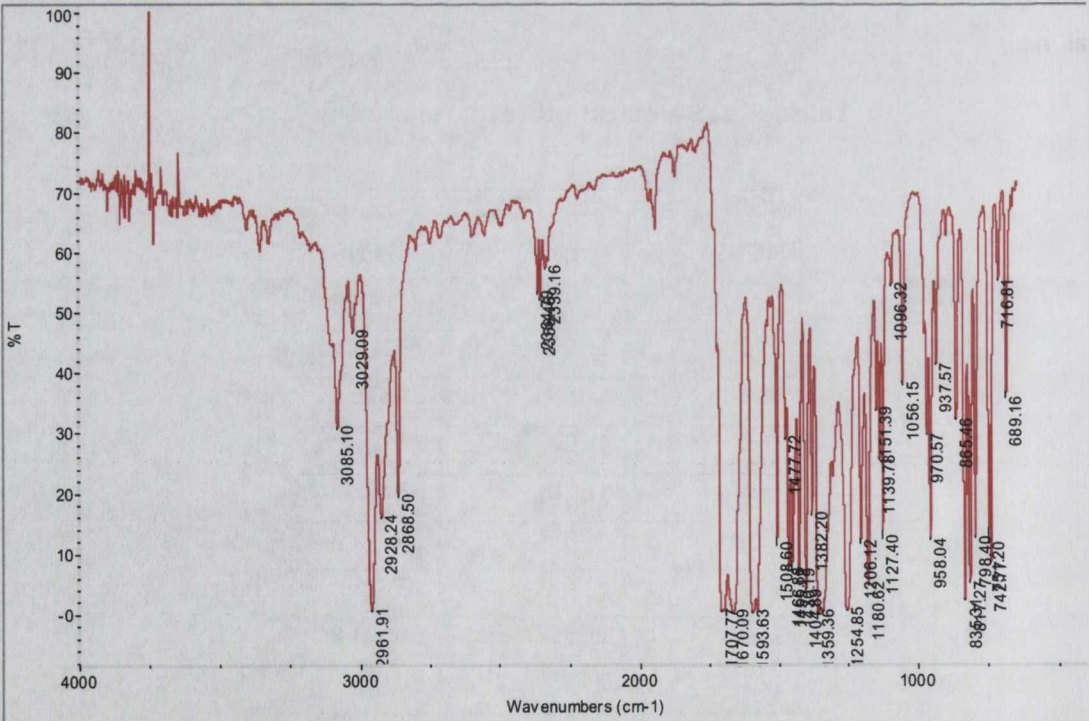


Figure 3.11 FTIR spectrum of perylene orange

Table 3.5. Selected vibrational modes for PR.

NORMAL MODE	FREQUENCY (cm ⁻¹)	INFRARED INTENSITY (km/mol)
147	800	62.8
268	1318	51.0
270	1328	85.5
299	1428	120.2
305	1474	98.8
321	1644	82.5
322	1646	64.4
325	1686	1058.5
328	1736	200.0
340	1785	60.0
348	1905	145.1
349	1919	296.1
351	1970	236.9
354	2144	208.1
355	2150	717.7

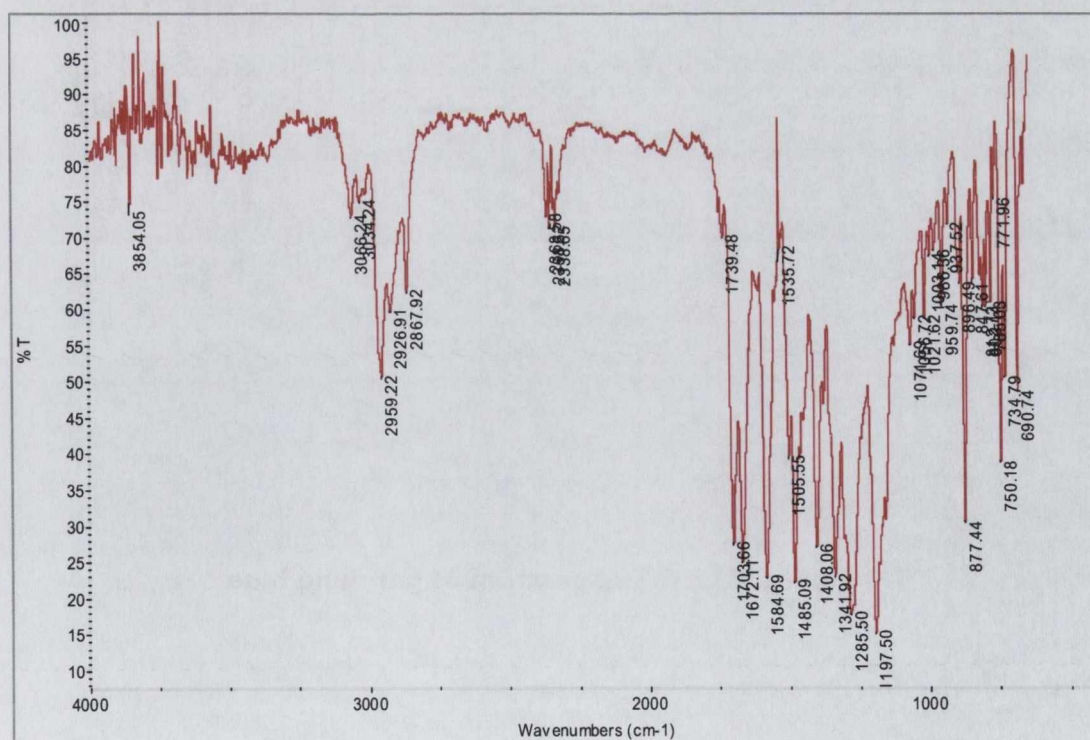


Figure 3.12 FTIR spectrum of perylene red

Table 3.6. Selected vibrational modes for PB.

NORMAL MODE	FREQUENCY (cm ⁻¹)	INFRARED INTENSITY (km/mol)
144	615.6	52.1
415	1405	63.8
422	1550	339.1
432	1832	68.7
436	1933	157.1
447	2094	227.0
448	2102	284.8
558	3158	103.4

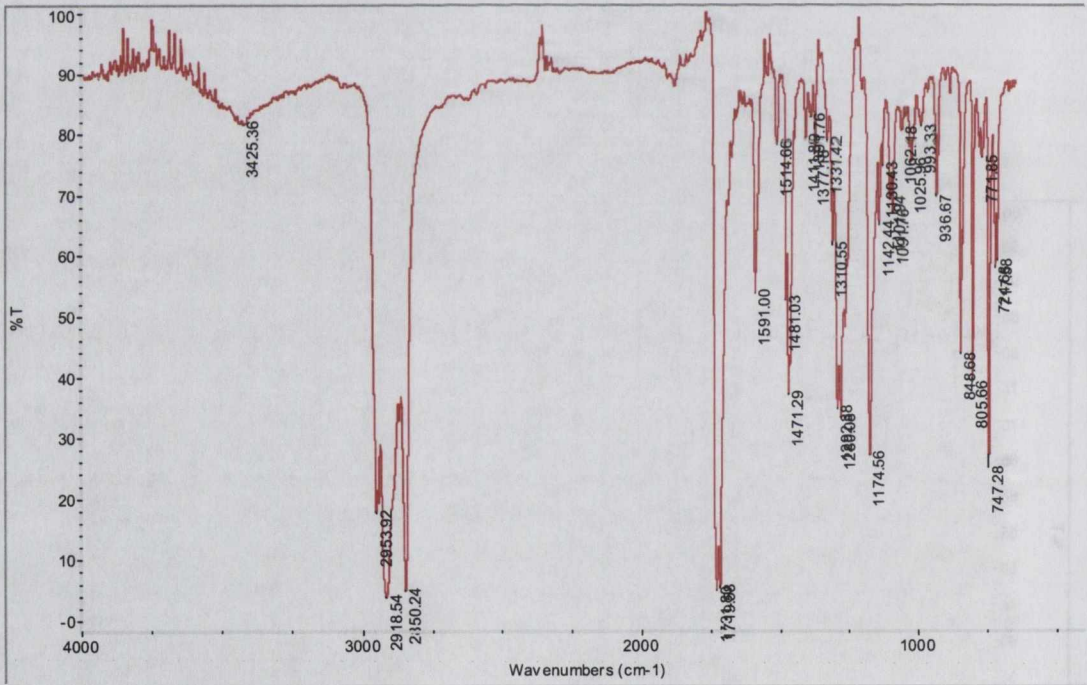


Figure 3.13 FTIR spectrum of perylene blue

Table 3.7. Selected vibrational modes for PY.

NORMAL MODE	FREQUENCY (cm ⁻¹)	INFRARED INTENSITY (km/mol)
198	1247	98.2
236	1422	84.1
252	1613	97.3
253	1628	178.7
254	1673	56.0
269	1804	233.1
275	1868	62.1
277	1885	64.0
279	1910	96.9
282	2071	82.2
283	2076	787.7

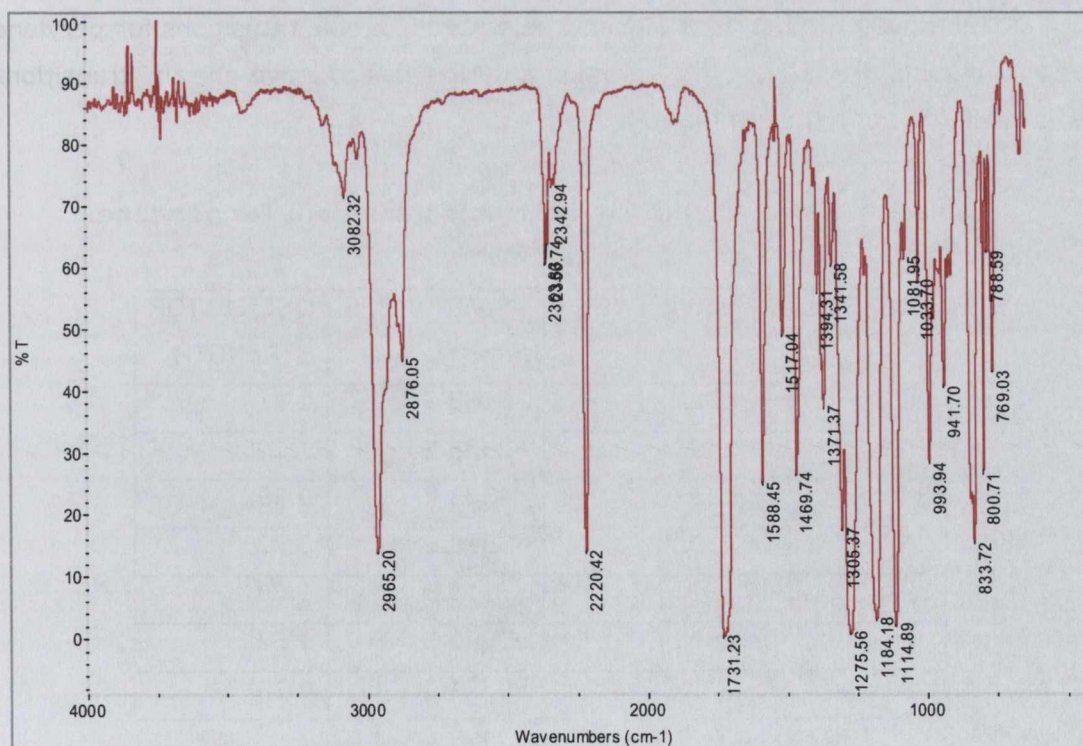


Figure 3.14 FTIR spectrum of perylene yellow.

Table 3.8. Selected vibrational modes for TBPB.

NORMAL MODE	FREQUENCY (cm ⁻¹)	INFRARED INTENSITY (km/mol)
239	1417	77.0
240	1428	167.3
243	1563	535.0
255	1904	362.3
262	2052	173.4
267	2170	553.7
269	2185.68	51.4
270	2186.35	73.0

The selected vibrational modes for perylene orange, perylene red, perylene yellow and perylene blue compare well with the FTIR spectra of the corresponding dyes.

Tables 3.9 through to 3.15 show selected electronic transitions for perylene and its studied derivatives. The selection criterion was to leave out any transitions with oscillator strength less than 0.1.

Table 3.9. Selected allowed electronic transitions for perylene.

TRANSITION	WAVELENGTH (nm)	WAVENUMBER (cm ⁻¹)	OSCILLATOR STRENGTH
2	431.6	23168.3	0.71
22	235.1	42533.5	1.10
24	225.6	44323.9	0.59
25	219.7	45518.5	0.73
39	194.1	51519.8	1.60
48	181.5	55091.5	1.82
49	181.1	55224.3	0.10

Table 3.10. Selected allowed electronic transitions for PTCDA.

TRANSITION	WAVELENGTH (nm)	WAVENUMBER (cm ⁻¹)	OSCILLATOR STRENGTH
2	478.8	20884.7	0.91
22	255.6	39116.8	0.75
24	237.6	42090.6	0.08
25	235.1	42534.9	0.36
28	231.1	43263.5	0.93
33	210.1	47588.7	0.31
35	207.4	48205.5	0.17
38	204.2	48966.8	1.72
41	199.9	50037.3	0.57
42	194.7	51360.4	0.14
50	180.4	55422.0	0.30

Table 3.11. Selected allowed electronic transitions for PV.

TRANSITION	WAVELENGTH (nm)	WAVENUMBER (cm ⁻¹)	OSCILLATOR STRENGTH
3	495.9	20167.3	1.29
11	317.9	31454.5	0.19
15	290.7	34405.3	0.13
24	260.5	38381.1	0.46
25	257.5	38835.7	0.58
27	245.3	40763.2	0.42
29	226.1	44227.4	0.80
33	211.3	47316.7	0.13
34	210.8	47427.3	0.70
36	207.0	48306.3	0.27
46	194.0	51539.2	0.22
62	177.6	56308.3	0.40

Table 3.12. Selected allowed electronic transitions for PO

TRANSITION	WAVELENGTH (nm)	WAVENUMBER (cm ⁻¹)	OSCILLATOR STRENGTH
2	446.9	22374.7	1.35
19	274.3	36452.1	0.34
20	261.6	38222.2	0.65

Table 3.13. Selected allowed electronic transitions for PR

TRANSITION	WAVELENGTH (nm)	WAVENUMBER (cm ⁻¹)	OSCILLATOR STRENGTH
2	486.9	20539.5	0.89
13	289.4	34556.6	0.13
14	276.0	36235.9	1.48
24	234.6	42634.0	0.10
28	226.4	44166.3	0.26
30	219.6	45541.5	0.13
32	214.6	46587.9	0.14

Table 3.14. Selected allowed electronic transitions PB

TRANSITION	WAVELENGTH (nm)	WAVENUMBER (cm ⁻¹)	OSCILLATOR STRENGTH
2	504.4	19823.7	0.95
26	257.4	38847.7	0.24
27	246.3	40602.9	0.13
29	239.1	41818.0	1.39
36	215.6	46385.0	1.16
40	210.7	47470.2	0.31
41	209.9	47633.3	0.37
43	207.8	48133.2	0.35
46	206.4	48444.6	0.32
54	189.7	52704.2	0.42
57	187.6	53314.5	0.13

Table 3.15. Selected allowed electronic transitions PY

TRANSITION	WAVELENGTH (nm)	WAVENUMBER (cm ⁻¹)	OSCILLATOR STRENGTH
3	425.2	23518.3	0.51
4	403.0	24813.9	0.23
13	289.7	34518.5	1.18
21	271.7	36805.3	1.90

Table 3.16. Selected allowed electronic transitions for TBPB

TRANSITION	WAVELENGTH (nm)	WAVENUMBER (cm ⁻¹)	OSCILLATOR STRENGTH
2	464.4	21535.1	0.80
21	260.6	38371.6	0.54
26	233.9	42747.4	0.52
28	228.4	43780.3	1.01
37	204.3	48954.3	0.11
38	202.3	49432.1	1.62
43	196.9	50785.6	0.64
44	192.3	52011.1	0.34
50	186.8	53547.2	0.34
52	184.2	54276.7	0.49
54	179.5	55710.5	0.14

3.4.3 QSAR

Tables 3.17 and 3.18 respectively show properties from geometry optimised structures and QSARs of the perylene derivatives studied. The properties in table 3.17 have been discussed under section 3.4.1. The HOMO and LUMO values for each molecule indicate the orbital symmetry. From table 3.17, the molecular weight obviously increases almost proportionally with the number of atoms for each molecule. It must be noted that all materials here have a common perylene core and substituents with additional O, H, C and N atoms. The type of building atoms for all molecules remain the same and the possibility of an almost linear

relationship between number of atoms and mass are high, but limited by the fact that the substituent groups at the peri-, bay- or both positions are different.

In table 3.18, two sets of values are given for each molecule's volume, grid surface area and approximate surface area. The first values are based on a solvent accessible surface where the solvent probe radius is 1.4 Å whereas the corresponding values in parenthesis are due to computations based on a Van der Waals surface approximation. The Van der Waals surface and molecular volume are conventional abstractions as they assume spherical atoms and only consider the external surface for area and the enclosed area for volume disregarding the intersections of the atoms. In table 3.18, the solvent accessible surface values are greater than the Van der Waals based ones for the sole reason that a fixed probe radius was used. Hyperchem allows this value to change between -1 and 10 and thus different results could be obtained. For volume and surface area calculations, Hyperchem outputs the individual atomic contributions to the total molecular quantity, the difference between approximate surface area and grid surface area is that in the later, the same atoms have different atomic contributions of the same property in this case area.

By recognising that molecular weight divided by density is molecular volume and applying that in equation (10), it is possible to calculate refractive indices for the perylene derivatives. Such indices are shown in table 3.18. By modelling all derivatives have an refractive index of 1.1. Hence light passing through such materials is not refracted significantly which makes these materials appropriate in applications where refraction of light will be a nuisance.

Table 3.17. Properties of perylene derivatives from geometry optimised structures.

MATERIAL	STRUCTURAL FORMULA	MOLECULAR WEIGHT (g)	NUMBER OF ATOMS	MOLECULAR POINT GROUP	DIPOLE MOMENT (Debye)	HOMO (eV)	LUMO (eV)	BAND GAP (eV)
Perylene	C ₂₀ H ₁₂	252.32	32	D2H	0.0003	-7.85 (2AU)	-1.49 (3B1G)	6.36
PTCDA	C ₂₄ H ₈ O ₆	392.33	38	D2H	0.1794	-9.16 (70A)	-3.42 (71A)	5.74
PR	C ₇₂ H ₅₈ N ₂ O ₈	1079.27	140	C1	0.5409	-8.12 (202A)	-2.47 (203A)	5.65
PO	C ₄₈ H ₄₂ N ₂ O ₄	710.88	96	C1	0.5325	-8.78 (134A)	-2.95 (135A)	5.83
PY	C ₆₀ H ₄₆ N ₂ O ₄	859.05	112	C1	2.2944	-8.80 (160A)	-2.99 (161A)	5.81
PV	C ₄₀ H ₂₉ NO ₂	555.68	72	C1	5.198	-8.21 (103A)	-2.65 (104A)	5.56
PB	C ₇₂ H ₁₀₈ O ₈	1101.66	188	C1	4.428	-8.15 (222A)	-2.46 (223A)	5.69
TBPB	C ₄₀ H ₄₄ O ₈	652.79	92	C1	0.3301	-8.48 (126A)	-2.47 (127A)	6.01

Table 3.18. QSAR properties of perylene derivatives.

MATERIAL	MASS (amu)	VOLUME (Å ³)	GRID SURFACE AREA (Å ²)	APPROXIMATE SURFACE AREA (Å ²)	LOG P	HYDRATION ENERGY (kcal/mol)	POLARISABILITY (Å ³)	MOLAR REFRACTIVITY (Å ³)	REFRACTIVE INDEX
Perylene	252.315	701.850 (228.323)	408.281 (243.148)	254.958 (223.188)	1.365	-2.469	31.684	93.425	1.14
PTCDA	392.324	863.712 (291.326)	488.319 (302.467)	336.630 (287.993)	1.273	-8.619	39.094	105.012	1.13
PR	1079.260	2706.968 (984.636)	1367.134 (1050.930)	1053.759 (1004.320)	17.118	-5.463	125.23	318.770	1.12
PO	710.872	1848.686 (659.146)	963.480 (712.542)	736.212 (717.082)	17.473	-0.926	81.862	205.295	1.13
PY	859.04	2129.39 (779.230)	1076.16 (811.51)	812.61 (810.23)	14.05	-1.960	106.160	262.24	1.13
PV	555.675	1444.333 (504.930)	783.592 (535.910)	552.204 (520.946)	8.237	-1.904	65.659	173.306	1.12
PB	1101.643	3219.690 (1137.880)	1693.793 (1331.964)	1609.521 (1366.723)	16.54	6.86	129.996	339.22	1.11
TBPB	652.784	1691.805 (593.602)	884.315 (659.716)	829.717 (694.268)	2.365	0.357	71.276	191.713	1.12

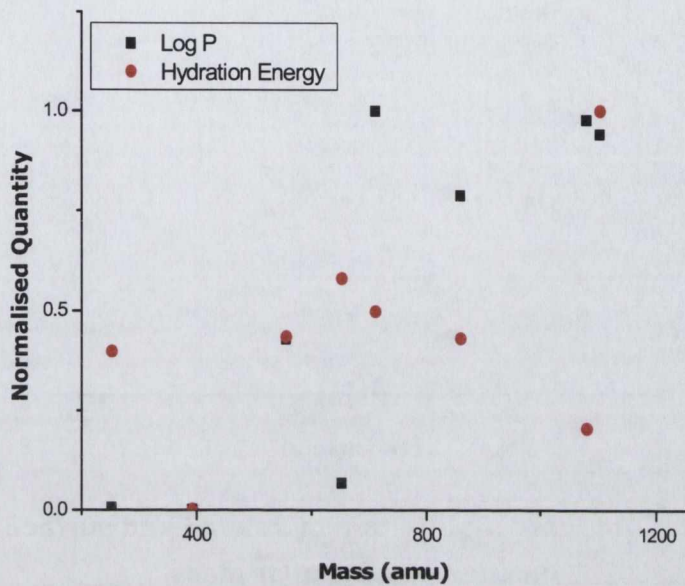


Figure 3.15. Distribution of normalised Log *P* and hydration energy with molecular mass.

Hydration energy is amount of energy released when one mole of the substance is dissolved in water. Log *P* has already been defined in equation (3.7). The variation of both of these two quantities for perylene and its derivatives seem to have no correlation to the molecular masses as shown in figure 3.15. In addition the hydration energies are on the high side (see table 3.18). This is because most perylene derivatives are hydrophobic. The few known hydrophilic exceptions also tend to aggregate(35) and efforts have been made to produce water soluble and less aggregate forming perylene derivatives(36, 37). The perylene derivatives studied in this research are not water soluble.

Volume and surface area

Figure 3.16 shows the normalised distribution of the volume and surface area of the perylene derivatives with molecular mass. Obviously the volume and grid surface area are superimposed due to reasons previously explained at the beginning of this section. A mathematical linear fitting analysis of grid surface area vesus volume gave a gradient of 1 with a zero standard error in the mean and an adjusted R-square of 1. On the same argument the approximate surface area has no correlation to the volume and grid surface area.

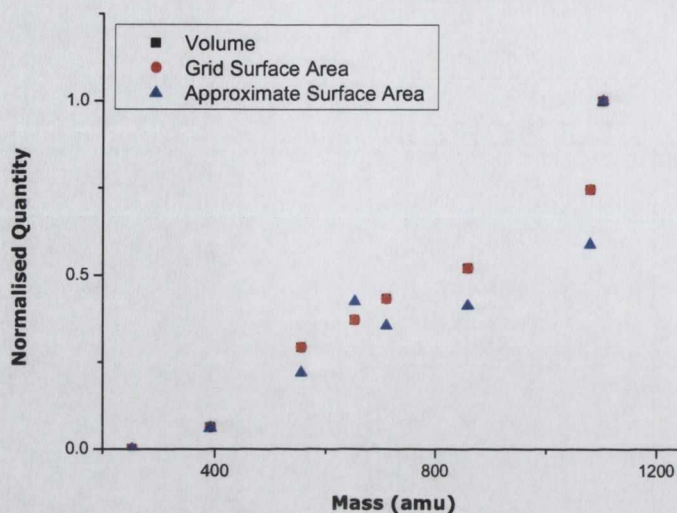


Figure 3.16. Normalised distribution of volume and surface area as a function of molecular mass.

Polarisability and molar refractivity

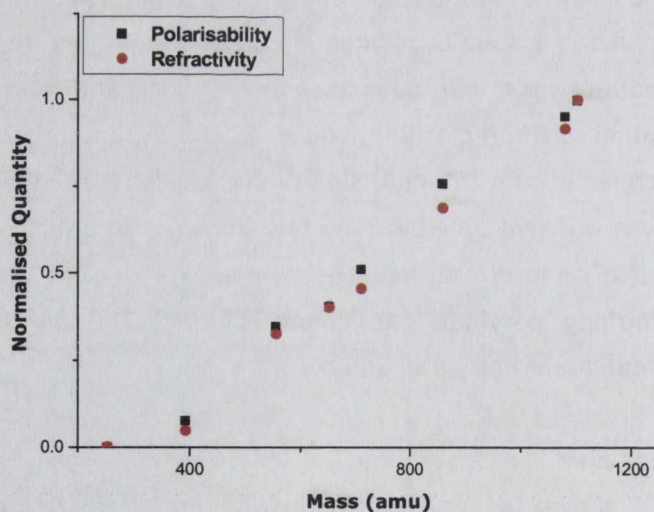


Figure 3.17. Normalised distribution of polarisability and refractivity with molecular mass.

Figure 3.17 shows the normalised distributions of polarisability and molar refractivity as a function of the molecular mass. Linear curve fitting of both parameters have shown them to be linear with respective gradients of $(0.104 \pm 0.003) \text{ \AA}^3/\text{amu}$ and $(0.301 \pm 0.005) \text{ \AA}^3/\text{amu}$ for polarisability and refractivity for

the molecules studied herein. The adjusted R-square values were 0.99 (2 d.p.) in both cases. Linear equations relating polarisability and refractivity to molecular mass for the perylene based molecules can therefore be given by equations (3.11) and (3.12) where MW is the molecular weight of the molecule.

$$\text{Polarisability (MW)} = 10 + 0.104\text{MW} \tag{3.11}$$

$$\text{Refractivity} = 0.301\text{MW} \tag{3.12}$$

With respect to the linear fitting relationship in equation (3.11), the value 10 would be that due to the environment in which the molecules are placed implying a minimum polarisability associated with perylene derivatives.

It can be noted from figure 3.17 to note that both polarisability and refractivity vary in the same manner with molecular weight which can be related to molecular volume through Hypercem derived QSAR properties. Mathematical based cubic polynomial fitting confirmed that both polarisability and refractivity are directly proportional to volume with adjusted R-square values of 0.98 each. This is consistent with theory as given in equations (3.9) and (3.10) as molecular weight divided by density is just molecular volume. Figure 3.18 shows the normalised distribution of polarisability with volume along with the fitting cubic polynomial.

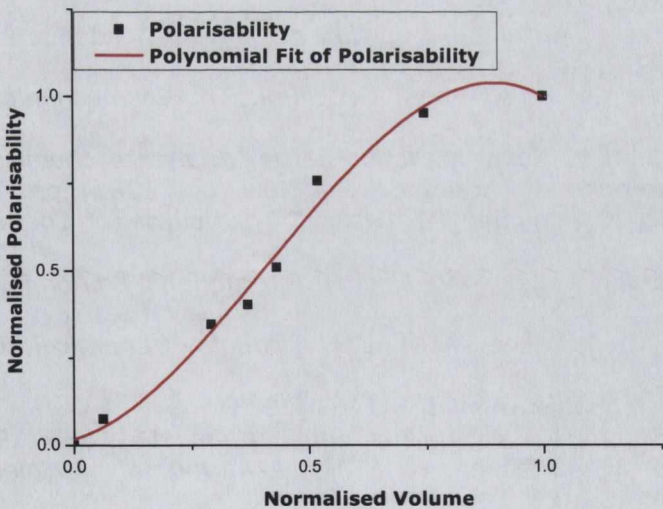


Figure 3.18 Normalised variation of polarisability with volume

From equation (3.10), the larger the molecular weight, the larger is the molecular volume and hence the higher also is the molar refractivity and so the more

pronounced are the steric effects. Thus the steric effects are higher in perylene derivatives with higher molecular weights.

3.5 Conclusions

Molecular modelling is a good technique for predicting properties of materials prior to synthesis. Geometry optimisation studies can be used to predict the possibility of success in the synthesis. Perylene derivatives with very bulky side groups are not conformationally stable and therefore very difficult to synthesis due to steric effects. The steric effects are higher in perylene derivatives with greater molecular weights.

The orientation of side groups attached to the N of imides in perylene derivatives is such that they are perpendicular to the plane of the perylene core. The angle however is controlled by the steric effects of the actual groups.

The perylene derivatives have C1 as their molecular point group.

Molecular modelling results are insufficient to predict possible applications of molecules, they need to be complimented with empirical results.

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Chapter 4

Synthesis, characterisation and optical limiting properties of 3,4,9,10-tetra-(12-alkoxycarbonyl)-perylene.

4.1 Introduction

Efforts are being made to produce soluble perylene derivatives as well as boosting their physical properties for improved device performance. The addition of alkyl chains to the peri- or bay- positions of the perylene aromatic core improves the solubility hence making it possible to process the derivatives in solution. The resulting alkoxycarbonyl groups diminish the electron density of the perylene aromatic system so enabling charge (electron) transport(1). Perylene derivatives are pi-conjugated systems so favour aggregation. Steric inhibition of aggregation is of interest in view of enhancing processability and increasing the quantum efficiency. The bulky functional alkyl groups are expected to reduce aggregation of the perylene derivatives as is the case in conjugated polymers(2). The successful synthesis of the 3,4,9,10-tetra-(12-alkoxycarbonyl)-perylene molecule reported here is a practical implementation of the aforementioned theories resulting in a product with improved solubility and reduced aggregation.

The two-photon-absorption (TPA) properties of derivatives of perylene have been scarcely investigated(3-6) and yet are extremely useful for potential applications in two-photon-pumped frequency up conversion lasers(4), TPA optical limiters(7), three-dimensional optical storage, three-dimensional photo polymerisation, photodynamic therapy, micro fabrication and microlithography(8-13). The synthesis of new nonlinear optical (NLO) materials is fundamental in the development of optoelectronic technologies(14). The open-aperture Z-scan is a convenient and quick experimental method for analysis of nonlinear optical properties of materials(15) and has been successfully applied in this research.

Here are presented the synthesis, characterisation and optical limiting properties of the novel 3,4,9,10-tetra-(12-alkoxycarbonyl)-perylene. The parent molecule was chosen as 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA) an archetypal molecule whose basic properties have been studied for more than a decade(16). In addition, the useful nonlinear optical property of this dye is demonstrated.

4.2 Theory

4.2.1 Solubility

The Hildebrand solubility parameter is chosen as a measure of solubility since its solvent spectrum includes the complete solvent range and most solubility scales can be easily related to it. The Hildebrand solubility parameter, δ , of a material is given by the square root of the cohesive energy density as in equation 4.1(17, 18).

$$\delta = \sqrt{\left(\frac{\Delta E}{V}\right)} \quad (4.1)$$

The cohesive energy density is the energy ΔE needed to remove a molecule from its nearest neighbours per unit volume V of the moved molecule. The enthalpy of mixing of a solution, ΔH_{mix} , can then be calculated from equation 4.2,

$$\Delta H_{mix} = V_{mix}(\delta_1 - \delta_2)\phi_1\phi_2 \quad (4.2)$$

where V_{mix} is the total volume of mixing, δ_1 is the Hildebrand solubility parameter of the solvent, δ_2 is the Hildebrand solubility parameter of the solute, ϕ_1 and ϕ_2 are the respective solvent and solute volume fractions(18). A good solution is formed at zero enthalpy of mixing and this occurs when the solute and solvent Hildebrand solubility parameters are the same, hence the chemistry adage "Like dissolves like". In this thesis, the theory is practically applied to compare the solubility of the parent molecule to the product.

4.2.2 Exciton binding energy

An exciton is a bound state of an electron and a hole in an insulator or semiconductor bound by a Coulombic force. In current research, the bound hole and electron pairs transport energy without transporting net charge. An exciton is created by energy absorption as when a photon enters a semiconductor exciting an electron from the valence band into the conduction band. The hole left behind by the electron is attracted to the electron by the Coulomb force. The exciton results from the binding of the electron with its hole. Thus the exciton has slightly less energy than the unbound electron and hole. The exciton binding energy can be used to classify excitons. For materials with large dielectric constants, screening

reduces the Coulombic interaction between holes and electrons resulting in Mott-Wannier excitons which have a radius much larger than the lattice spacing. The binding energies for Mott-wannier excitons are typically of the order of ~ 0.1 eV. When the dielectric constant of the material is small, the Coulombic interaction is strong, the excitons tend to be smaller and of the same order as the unit cell. Such are called Frenkel excitons and the order of the binding energy is ~ 1.0 eV. Excitons are annihilated through recombination.

It is possible to determine the binding energy of an exciton from the absorbance of a thin film of the material deposited onto a transparent substrate. The optical band gap of an organic semiconductor can be determined by applying the Tauc relation (19, 20), given in equation (4.3), to the optical absorption edge of the thin film of the organic semiconducting material,

$$A h\nu = (h\nu - E_g)^n \quad (4.3)$$

where A is the absorbance, E_g is the optical band gap corresponding to a specific absorption in the thin film, $h\nu$ is the photon energy and n has the values $1/2$, 2 , $3/2$ and 3 respectively for allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions materials. An extrapolation of absorbance squared versus photon energy, (as shown in Fig.4.5. for 3,4,9,10-tetra-(12-alkoxycarbonyl)-perylene) can be used to determine the optical band gap. The exciton energy in electron volts, $E_{ex}(\text{eV})$, is determined from equation (4.4)

$$E_{ex} = (1240)/\lambda_{max} \quad (4.4)$$

where λ_{max} is the maximum absorption wavelength of the thin film. The exciton binding energy, E_{be} , can then be calculated from both the optical band gap and the exciton energy from equation (4.5)

$$E_{be} = E_g - E_{ex} \quad (4.5)$$

From the binding energy, the exciton can be classified and conclusions on the material's properties can be drawn.

4.2.3 Z-scan theory

With reference to the open aperture Z-scan in Chapter 2 Section 2.3.6, the normalised transmittance $T_N(z)$ is a function of position z (see Fig.2.9) and is given by equation (4.6)(14),

$$T_N(z) = \frac{\log_e[1+q_o(z)]}{q_o(z)} \quad (4.6)$$

where $q_o(z)$ is given by

$$q_o(z) = \frac{q_{oo}}{1+(z/z_o)^2} \quad (4.7)$$

where z_o is the optical beam's diffraction length and q_{oo} is given by

$$q_{oo} = \beta_{eff} I_o L_{eff} \quad (4.8)$$

where β_{eff} is the effective intensity-dependent non-linear absorption coefficient and I_o is the light intensity at focus, i.e. $z = 0$, and L_{eff} is the sample's effective length defined in terms of the true optical sample path length L and the linear absorption coefficient α_o as given in equation (4.9)

$$L_{eff} = [1 - e^{(-\alpha_o L)}] / \alpha_o \quad (4.9)$$

The imaginary third-order optical susceptibility, $Im\{\chi^{(3)}\}$, directly varies with the intensity-dependent absorption coefficient β_I as

$$Im\{\chi^{(3)}\} = \frac{\eta_o^2 \epsilon_o c \lambda \beta_I}{2\pi} \quad (4.10)$$

where η_o is the linear refractive index of the sample, ϵ_o is the permittivity of free space, c is the speed of light and λ is the wavelength of the incident light. The imaginary second order molecular hyperpolarisability, $I_m\{\gamma\}$, is defined in terms of $Im\{\chi^{(2)}\}$ as

$$I_m\{\gamma\} = \frac{I_m\{\chi^{(2)}\}}{f^4 c_{mol} N_A} \quad (4.11)$$

where f is the Lorentz-focal length-field enhancement factor defined as

$$f = \frac{\eta_{sp}^{2+2}}{3} \quad (4.12)$$

c_{mol} is the sample molar concentration and N_A is Avogadro's number. In this research, these equations were incorporated into a computer code and a least-squares regression algorithm was employed to fit this to experimental data. Apart from characterising the product reported in this chapter, this theory is applied again in Chapter 6 when compared to other families of perylene derivatives.

4.3 Experimental

4.3.1. Synthesis

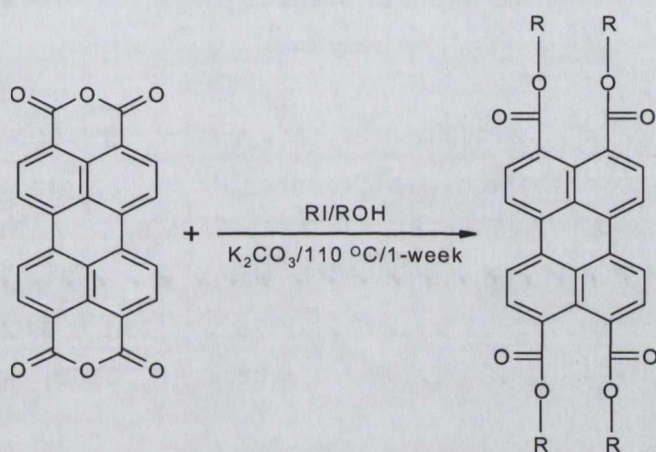


Figure 4.1. Synthesis of 3,4,9,10-tetra-(12-alkoxycarbonyl)-perylene from PTCDA; R = CH₃(CH₂)₁₁.

A 95% yield of 3,4,9,10-tetra-(12-alkoxycarbonyl)-perylene was produced by refluxing 1 g of PTCDA in a 5:1 1-iodododecane (CH₃(CH₂)₁₁I) and 1-dodecanol (CH₃(CH₂)₁₁OH) mix over 5 g of potassium carbonate (K₂CO₃) at 110 °C for 7 days. (see Fig.4.1.). The product was dissolved in spectro-photometric grade chloroform and the K₂CO₃ filtered out. The chloroform was extracted, followed by a filtration yielding a golden yellow product which was dried in a vacuum oven at 60 °C. The compound was characterised by ¹HNMR, ¹³CNMR, FTIR, mass spectroscopy and chemical analysis to confirm the product. The sharp ¹HNMR peaks obtained are indicative of very high material purity (see Fig.4.2.)

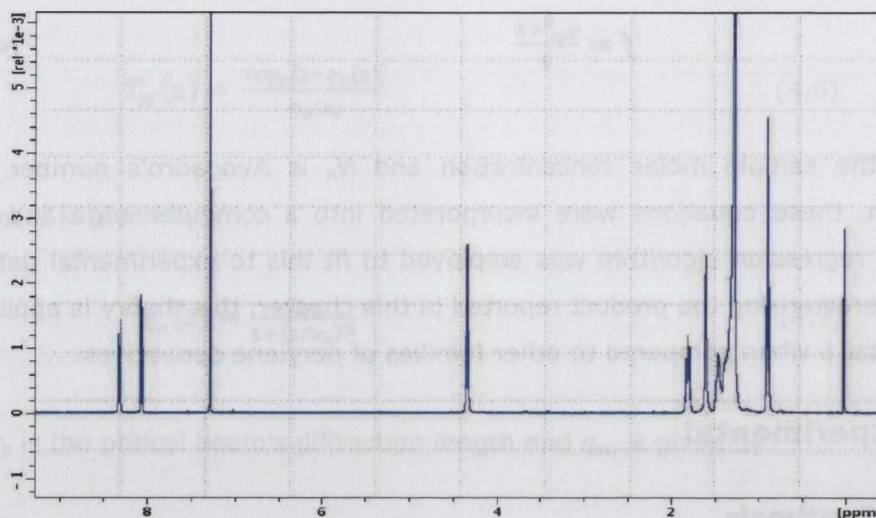


Figure 4.2. ^1H NMR Spectrum of 3,4,9,10-tetra-(12-alkoxycarbonyl)-perylene.

^1H NMR (400 MHz, CDCl_3): δ 0.89 (t, 12H, CH_3), 1.44(m, 72H, 9(CH_2)), 1.50 (m, 8H, O-C- CH_2), 4.33(t, 8H, O-C- CH_2), 8.05(d, 4H, CH), 8.30(d, 4H, CH). ^{13}C NMR (100 MHz, CDCl_3) 14.2, 22.7, 26.0, 28.6, 29.3, 29.5, 29.6, 29.7, 31.9, 66.6, 121.4, 128.9, 1129.1, 130.4, 133.1, 168.5. FTIR (NaCl): ν = 2954.0, 2919.4, 2850.3, 1731.9, 1719.6, 1584.5, 1471.9, 1292.2, 1279.5, 1173.5, 747.2 cm^{-1} . MS 1100. Anal. Calc. for $\text{C}_{72}\text{H}_{108}\text{O}_8$: C 78.50%, H 9.88%, (M, 1100) Found: 77.54.0%, 9.81%, (M^+ , 1100)].

4.3.2. Characterisation

The ^1H NMR spectra were recorded on a Bruker Avance III 400 spectrometer with a proton resonance of 400.23 MHz. ^{13}C NMR were recorded on a Bruker Avance III 400 spectrometer with a carbon resonance of 100.65 MHz, tip angle of 30° , an acquisition time of 0.5 s and a relaxation delay of 1 s. Tetramethoxysilane (TMS) was used as the internal reference with deuterated chloroform (CDCl_3) as the NMR solvent. A Micromass LCT Orthogonal Acceleration TOF Electrospray mass spectrometer was used to determine the molecular weight of the compound. The FTIR spectra were taken on a Nicolet NEXUS FTIR spectrometer in the transmission mode. UV-Vis absorption was recorded on a CARY 6000i UV-Vis-NIR spectrophotometer. The fluorescence spectra were obtained using a PerkinElmer LS55 Luminescence Spectrometer. Thermal responses were studied using PerkinElmer Thermo gravimetric Analyser Pyris TGA and PerkinElmer Pyris Diamond DSC. Structural studies were carried out on a Nanoscope 111a AFM machine, a

Hitachi S-4300 Field Emission microscope operating in high vacuum mode for HRSEM images and a Jeol 2100 Transmission Electron Microscope.

4.3.3 Nonlinear optical measurement

The Z-scan technique is a well-known method applicable to study the NLO properties of materials, including nonlinear absorption, scattering or refraction(15). A standard open-aperture Z-scan system (14, 21) was used to measure the nonlinear extinction (NLE including non-linear absorption and scattering) coefficients, as well as the optical limiting properties of 3,4,9,10-tetra-(12-alkoxycarbonyl)-perylene at 1 g cm^{-3} concentration in spectro-photometric grade chloroform. The experiment was performed using 6 ns pulses from a Q-switched Nd:YAG laser. The laser, operating at its second harmonic, 532 nm, with a pulse repetition rate of 10 Hz, was spatially filtered to remove higher-order modes, and tightly focused with a 9 cm focal length lens. In order to enhance NLO response, all samples were tested in 1 cm quartz cells(21, 22). Simultaneously, a focusing lens setup was arranged at 30° to direct the incident beam to monitor the scattered light from the perylene solutions.

4.4 Experimental results and discussion

4.4.1 Solubility

At room temperature, the parent molecule in the synthesis PTCDA, was found to be best soluble in NMP, $\delta=23.1 \text{ (MPa)}^{1/2}$ and partially soluble in both pyridine $\delta=21.7 \text{ (MPa)}^{1/2}$ and DMSO $\delta=26.4 \text{ (MPa)}^{1/2}$ (23). These results suggest a Hildebrand solubility parameter for PTCDA as $\delta=(23\pm2) \text{ (MPa)}^{1/2}$. PTCDA is therefore best soluble in polar aprotic solvents. Previous studies have shown that PTCDA is insoluble or poorly soluble in organic solvents(24). The solvents which minimize the enthalpy of mixing for PTCDA are generally very harsh and toxic therefore not preferred for use in device fabrication. Due to the inherently low solubility, the production of PTCDA based devices is therefore mostly by thermal evaporation with extremely high expenses. The synthesis of 3,4,9,10-tetra-(12-alkoxycarbonyl)-perylene from PTCDA adds 12-C chain alkyl groups to the peri-positions of the perylene core making it easily soluble at room temperature in most common organic solvents like chloroform $\delta=18.7 \text{ (MPa)}^{1/2}$, dichloromethane $\delta=20.2 \text{ (MPa)}^{1/2}$, tetrahydrofuran $\delta=18.5 \text{ (MPa)}^{1/2}$ and toluene $\delta=18.3 \text{ (MPa)}^{1/2}$ (23). These

results suggest a Hildebrand solubility parameter of (19 ± 1) (MPa)^{1/2} for the molecule. This marked improvement in solubility makes device fabrication in solution possible by such methods as spin coating, dipping, stamping, doctor blading, ink-jet printing or casting which are less expensive relative to thermo sublimation as highlighted in Chapter 1. The soluble product can also be easily blended with polymers in such cases as the production of optoelectronic devices where bulky heterojunctions are made from intimate mixtures of donors and acceptors, as is the case in organic photovoltaic cells, so reducing the chance of exciton recombination. The improvement in solubility can be attributed to the introduction of the alkoxycarbonyl groups which reduce the interaction between the perylene rings.

4.4.2 Linear optical properties

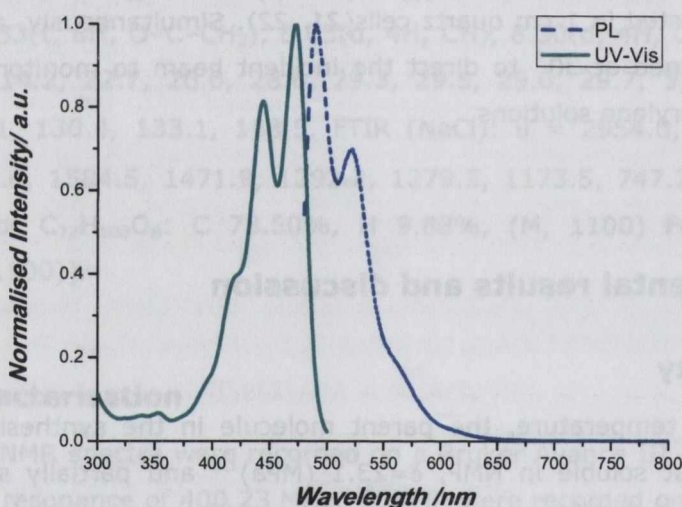


Figure 4.3. Normalised absorption and fluorescence spectra of 3,4,9,10-tetra-(12-alkoxycarbonyl)-perylene in spectro-photometric grade chloroform.

Dilute solutions of 3,4,9,10-tetra-(12-alkoxycarbonyl)-perylene have an intense yellowish-green colour and show a bright emission when exposed to ordinary light. Fig. 4.3 shows the normalized absorption and fluorescence spectra of 3,4,9,10-tetra-(12-alkoxycarbonyl)-perylene in chloroform. The spectra are strongly structured with peak wavelengths for absorption and fluorescence at 472 and 489 nm, respectively, resulting in a narrow Stokes's shift of 17 nm. A second absorption peak occurs at 444 nm with a shoulder occurring at 417 nm. This structure is similar to the perylene ring progression of $\pi\text{-}\pi^*$ $S_0\text{-}S_1$ or $S_1\text{-}S_0$

transitions (25). The fluorescence spectrum is a close mirror image of the absorption spectra but with different relative intensities. Previous studies on similar materials of the form 3,4,9,10-tetra-(*n*-alkoxycarbonyl)-perylene where $2 \leq n \leq 10$ showed similar spectra confirming that the perylene core has a greater influence on the absorption and emission than the alkyl chain length(25-27). In fact, this observation is consistent independently of the position of substitution in all perylene derivatives, be it peri-, bay- or at the N-atom in perylene imides(26, 28). The absorption and emission peaks remain the same independent of solvent, as is the case for relative peak intensities, but the actual intensities decrease in the order dichloromethane, chloroform, toluene and tetrahydrofuran for the same concentration. The peak integrals for absorption increased linearly with wavelength and were proportional to the concentration. The energy difference between peaks is 0.16 eV, about the same (0.15 eV) as that of the benzene ring stretch oscillation of perylene(29). This suggests that the dilute series absorbances are controlled by monomeric absorption. No shift in the peak wavelengths was observed for concentration dependent UV-Vis in the individual solvents. The photoluminescence excitation spectra resembled the absorption spectra in solution.

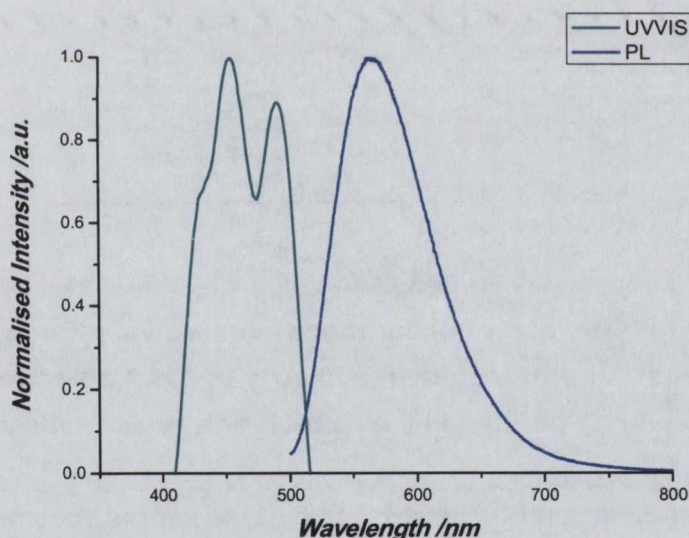


Figure 4.4. Normalized absorption and fluorescence spectra of 3,4,9,10-tetra-(12 alkoxy carbonyl) perylene spin cast onto glass from a 1 g cm⁻³ spectro-photometric grade chloroform solution.

Fig. 4.4. shows the normalized absorption and fluorescence spectra of a spin cast film of the compound from a chloroform solution. Both spectra are very broad, unstructured and bathochromically shifted compared to the spectra of the monomeric solution. This red shift and broadening are due to fluorescence

emanating from excimers owing to the different energetic environments(30). For absorption, the trend is attributed to additional interactions between individual molecules and their surroundings, much stronger in the solid phase than in monomeric solution. Evidence of aggregation in thin films of perylene derivatives usually occurs in the form of an additional absorption peak around 570 nm(31). The absence of this absorption peak in the case of 3,4,9,10-tetra-(12-alkoxycarbonyl)-perylene is possibly due to lack of dimers or higher aggregates as a result of steric hindrance by the bulky alkyl chains. For the emission spectra, there is no corresponding band in the absorption spectra thus the mirror symmetry exhibited in solution is lost. The formation of excimers in thin films is highly likely as the distance between adjacent molecules is much shorter than in solution.

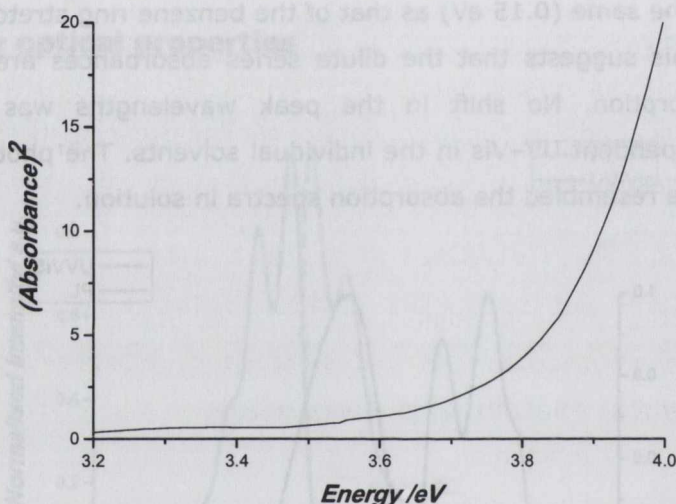


Figure 4.5. Van-Tauc plot of absorbance squared vs. photon energy for determination of the band gap energy of 3,4,9,10-tetra-(12-alkoxycarbonyl)-perylene by extrapolation to zero absorbance.

The optical band gap was determined by applying the Tauc relation(19, 20), given in equation (4.3) to the optical absorption edge of the thin film of 3,4,9,10-tetra-(12-alkoxycarbonyl)-perylene. As explained under Section 2.2.2, an extrapolation of absorbance to zero on the straight line section of the plot of absorbance squared versus photon energy, (Fig.4.5.) was used to determine the optical band gap as 3.81 eV. Application of equation (4.4) resulted in an exciton energy of 2.63 eV. Hence by equation (4.5), the exciton binding energy for the 3,4,9,10-tetra-(12-alkoxycarbonyl)-perylene is predicted at 1.2 eV. This suggests Frenkel type excitons and consequently a small dielectric constant for the material. Further evidence of the small dielectric constant is supported the solvents in which

it readily dissolves as listed in the first paragraph of this section. This result is consistent with previous findings on the exciton binding energies of small molecule or oligomeric organic semiconductors(32).

The results of a concentration dependence fluorescence study are shown in Fig.4.6. on a logarithmic scale. An initial study using a 10 mm x 10 mm cuvette revealed a deviation from linearity at high concentrations. This would normally be attributed to some complex processes like aggregation or some equivalent effect. Rickard et al. have shown that the deviation is due to the inner filter effect and re-absorption(33). The inner filter effect is attributed to the instrument, where light absorbed by the cuvette's edge will fluoresce but the detector is not able to detect the fluorescence. Re-absorption occurs where the fluorescence emission and absorption spectra overlap as shown in the region just below 500 nm in Fig.4.3.

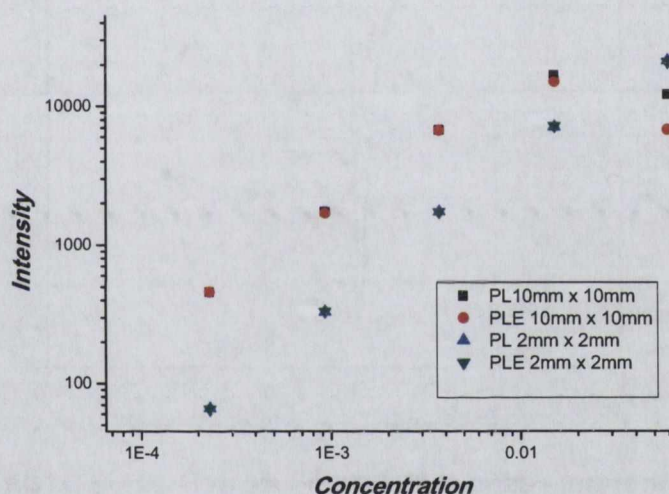


Figure 4.6. Concentration dependent photoluminescence, (PL) and photoluminescence excitation, (PLE) results of 3,4,9,10-tetra-(12-alkoxycarbonyl)-perylene in spectro-photometric grade chloroform, showing the response to cuvette path length.

The use of a smaller path length cuvette reduces the two effects and more so re-absorption. A second study using a 2 mm x 2 mm micro-cuvette showed linearity over the whole range of concentrations, suggesting absence of or reduced aggregation or equivalent effects.

4.4.3 Thermal responses

Fig.4.7. shows the TGA and its first derivative (DTGA) curves for 3,4,9,10-tetra-(12-alkoxycarbonyl)-perylene performed in an air environment at a scan rate of 10 °C/min. The 3,4,9,10-tetra-(12-alkoxycarbonyl)-perylene is thermally stable up to 300 °C in air which is very good for normal everyday operations. The onset of the weight loss begins around 300 °C and is completed at 557 °C with 100% weight loss. This trend is similar to that of perylene, the aromatic core for 3,4,9,10-tetra-(12-alkoxycarbonyl)-perylene. The first and second endothermic peaks at 370 °C and 450 °C, respectively can therefore be attributed to the destruction of the perylene core, the third endothermic peak at 521 °C corresponds to the burn off of

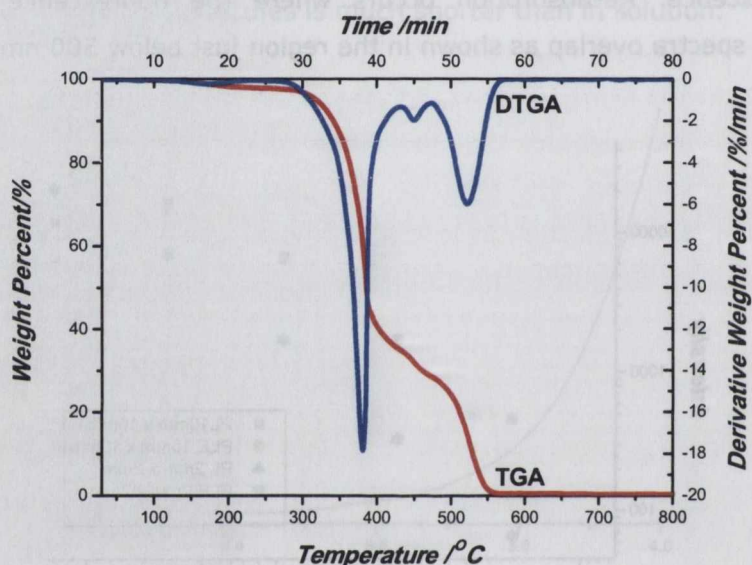


Figure 4.7. The thermal response TGA and its derivative DTGA of 3,4,9,10-tetra-(12-alkoxycarbonyl) perylene at 10 °C/min in air.

any remaining organics. In some perylene imides, the alkyl group on the diimide nitrogen is lost between 416 °C and 513 °C (28, 34).

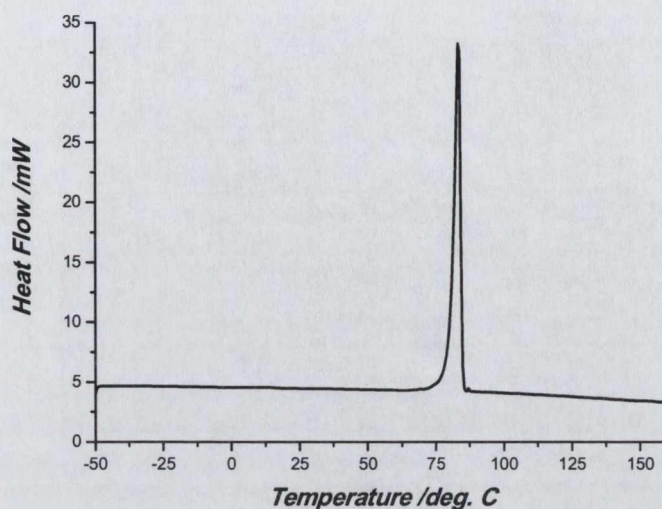


Figure 4.8. A DSC trace of 3,4,9,10-tetra-(12-alkoxycarbonyl)-perylene

The melting point for 3,4,9,10-tetra-(12-alkoxycarbonyl)-perylene was determined using DSC to be at 80 °C (Fig.4.8). This is much lower than that of the parent molecules PTCDA which is above 200 °C. Introduction of alkyl chains to the aromatic perylene core lowers the melting temperature independent of the position to which the chain is added(25, 28). The low melting point implies that boiling water can be used to achieve melting. The liquid crystalline phase, normally present in similar 3,4,9,10-tetra-(*n*-alkoxycarbonyl)-perylenes for $2 \leq n \leq 9$, is absent in the DSC trace. Previous studies(25) have shown that these 3,4,9,10-tetra-(*n*-alkoxycarbonyl) perylenes form liquid crystals for $n = 2$ to $n = 9$ with the $n = 10$ showing no liquid crystalline phase just like the $n = 12$ being reported here. This gives partial support for the reduced aggregation behavior. The molecular volume is much smaller for shorter C-chains than for longer ones, thus the higher molecular volume due to long chains is unfavorable for stacking.

4.4.4 Morphology

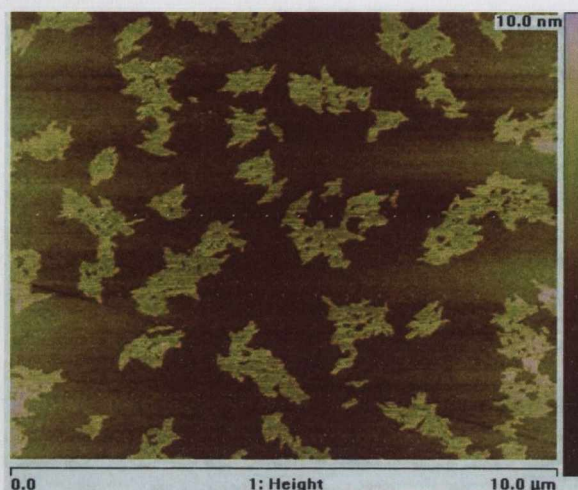


Figure 4.9. An AFM micrograph of 3,4,9,10-tetra-(12-alkoxycarbonyl)-perylene spin cast from a chloroform solution at 4500rpm for 30s onto a Si wafer.

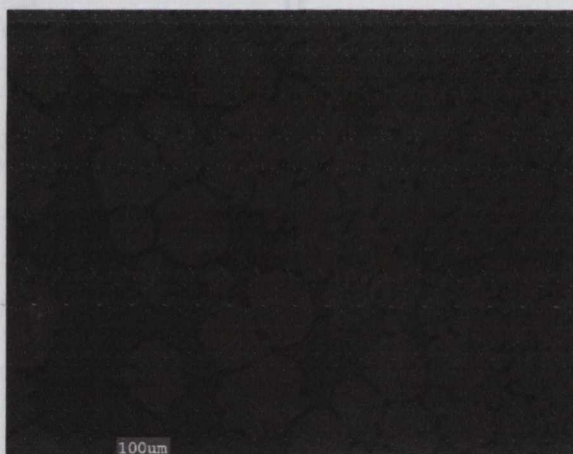


Figure 4.10. An SEM micrograph of 3,4,9,10-tetra-(12-alkoxycarbonyl)-perylene spin cast from a chloroform solution at 4500rpm for 30s onto a Si wafer.

Solutions of 3,4,9,10-tetra-(12-alkoxycarbonyl)-perylene in chloroform were spin cast and drop cast onto glass, ITO and Si(111) substrates for structural studies using scanning electron microscopy (SEM) and contact mode atomic force microscopy (AFM). As shown in Fig.4.9, the AFM micrographs of spin cast solutions on respective substrates indicate clusters less than 7 nm in height, suggesting lack of higher aggregates. Compared to drop cast samples, the clusters in the spin cast films are less coalescent whereas extended coalescence is observed in drop cast

films. This trend was also confirmed by SEM as shown in Fig.4.10. In drop cast films, the coalescence increases with concentration as does the height of the clusters. Two possibilities are pertinent to the formation of clusters, they are either formed dynamically during film formation or they already exist in solution. Transmission electron microscopy (TEM) studies have revealed nanoparticles less than 100 nm in diameter as source of the clusters (see Fig.4.11).

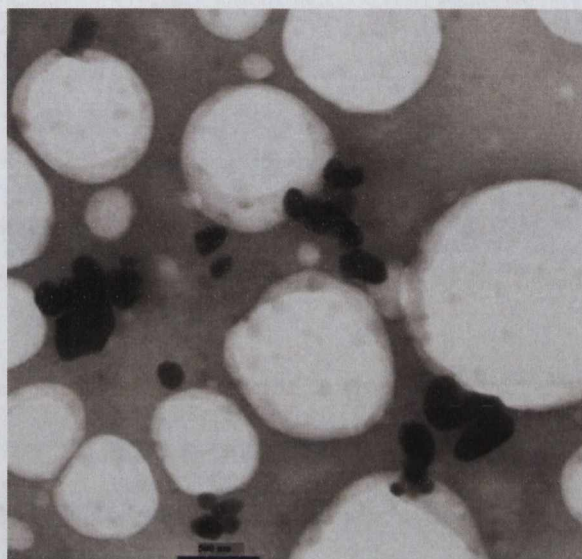


Figure 4.11. A TEM micrograph of 3,4,9,10-tetra-(12-alkoxycarbonyl) perylene drop cast from a chloroform solution onto a silicon nitride TEM grid.

4.4.5 Optical limiting

The NLE coefficient, β_{eff} , for the 3,4,9,10-tetra-(12-alkoxycarbonyl)-peryene solution in chloroform was measured by the open aperture Z-scan method at 532 nm. The incident laser pulsed energy used in the Z-scan measurement was altered from 0.10 to 0.32 mJ. The corresponding on-focus beam intensity varied from 0.68 to 1.91 GW cm⁻². All Z-scans performed in this experiment showed a reduction in the transmission about the focus of the lens, indicating the optical limiting property. As evident in the Z-scan trace shown in Fig.4.12, the depth of reduction changes along with the variation of the on-focus intensity. The β_{eff} were deduced from the Z-scan data by curve fitting theory based on an intensity dependent extinction coefficient(15). The linear and NLO results for the 3,4,9,10-tetra-(12-alkoxycarbonyl)-peryene solution are summarized in Table 1.

Table 4.1. Summary of typical linear and NLO results for 3,4,9,10-tetra-(12-alkoxycarbonyl) perylene.

Conc. [mg/mL]	Transmission [%]	α_0 [cm ⁻¹]	β_{eff} [cm W ⁻¹]	$\text{Im}\{\chi^{(3)}\}$ [esu]
1	95.6	0.045	$(3.0\pm0.6)e^{-10}$	$(11\pm2)e^{-14}$

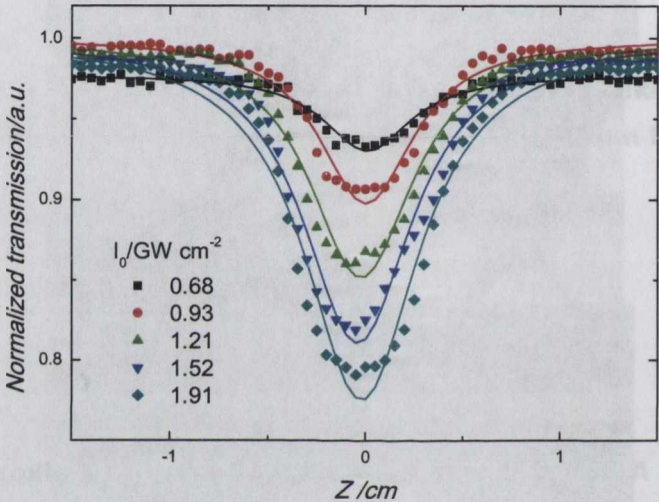


Figure 4.12. A Z-scan signature of a 1g cm⁻³ chloroform solution of 3,4,9,10-tetra-(12-alkoxycarbonyl)-perylene.

As shown in figure 4.13, the nonlinear transmission has an apparent discontinuity, corresponding to the limiting threshold. The transmission keeps roughly constant when the energy fluence is below the threshold. When the incident fluence exceeds the threshold, the transmission reduces significantly. The optical limiting trace of the 3,4,9,10-tetra-(12-alkoxycarbonyl)-perylene solutions is analogous to that of single-walled carbon nanotube (SWNT) dispersions, resulting from the thermally-induced nonlinear scattering(21, 22). Therefore, it is believable that the optical limiting for the 3,4,9,10-tetra-(12-alkoxycarbonyl)-perylene solutions is largely due to the nonlinear scattering, as is implied by both the evident limiting threshold and the strong scattering signal observed at 532 nm whose response is shown in Fig.4.13.

Referring to the nonlinear scattering mechanism of SWNT dispersions (21, 22, 35, 36), the scattering centres in the perylene solutions may arise from the formation of the solvent bubbles and/or the vapor bubbles, resulting from the

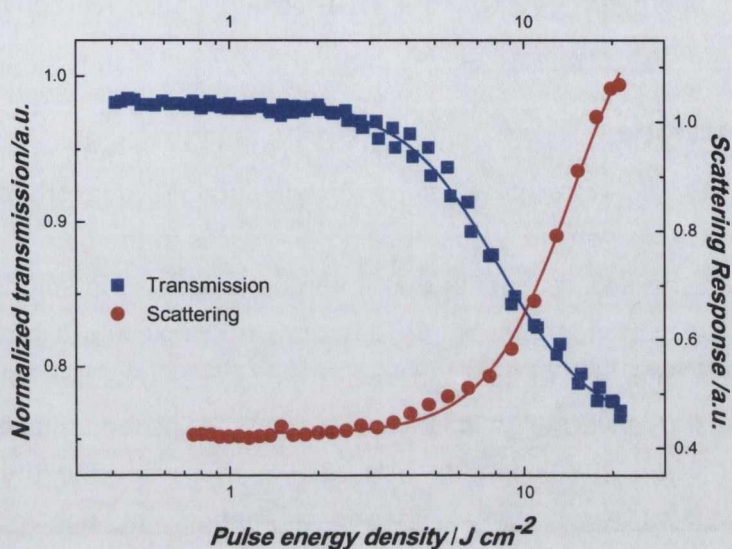


Figure 4.13. Evidence of limiting threshold from optical limiting trace and the scattering response of 3,4,9,10-tetra-(12-alkoxycarbonyl)-perylene.

sublimation of the nanoparticles by the aggregation of the 3,4,9,10-tetra-(12-alkoxycarbonyl)-perylene molecules (see Fig.4.11). Nevertheless, we cannot rule out the contribution of TPA to the optical limiting response, but the contribution should be very restricted since (1) the wavelength of the incident beam 532 nm is far away from the TPA resonant wavelength of the perylene solutions (5, 7) and (2) the nanosecond incident pulses are inferior for the TPA-induced optical limiting(37, 38). In addition, the excited state absorption, such as reverse saturable absorption or saturable absorption could have influence on the nonlinear responses of the perylene solutions. However, such nonlinear absorption effects can be suppressed when nonlinear scattering becomes significant since the increased scattering cross section results in the reduced absorption cross section(39, 40). Although, the optical limiting efficiency of the 3,4,9,10-tetra-(12-alkoxycarbonyl)-perylene solutions is lower to the present laser source, it is expected that the perylene solutions would be effective to attenuate the laser beam with picosecond or femtosecond pulses and suitable wavelength in the near infrared(37, 41).

4.4.6 Chemical Stability

The reproducibility of all results from fresh samples to samples aged up to 24 months in all experiments described in this chapter are evidence of both the chemical and photostability of the 3,4,9,10-tetra-(12-alkoxycarbonyl)-perylene.

4.5 Conclusions

The 3,4,9,10-tetra-(12-alkoxycarbonyl)-perylene dye offers both chemical and thermal stability, strongly absorbs and fluoresces in the blue section of the UV-Vis range with the added benefits that it can be processed in solution and its bulky alkyl chains hamper aggregation. In addition, the molecule exhibits good optical limiting with a high absorption and/or scattering cross section. The solubilisation exhibited by the molecule is due to the alkyl chains and makes the molecule desirable for polymer blending or film casting thus reducing the cost of device fabrication. These results have opened a window for ongoing investigations regarding a wide variety of possible optoelectronic applications.

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Chapter 5

Thermal stability and photophysics of perylene derivatives

5.1 Introduction

Our advances in the ability to control and design at molecular and atomic level have seen materials science develop rapidly as evidenced by nanotechnology, previously defined in Chapter 1. Nanotechnology is seen as a new frontier in materials, with the promise of performance and end functionality far exceeding even current standards. The ability to characterise and better understand the behaviour of even the so termed "conventional" materials has lead to incremental performance enhancements. To meet current demands, as well as aim for future demands, characterisation and its techniques have kept pace with the development of new materials. The definition of materials characterisation as given in the ASM-International Materials Characterization Handbook (1) relates to "those features of composition and structure (including defects) of a material that are significant for a particular preparation, study of properties, or use, and suffice for reproduction of the material." This definition excludes those methods that yield information primarily related to materials properties, such as thermal, electrical, and mechanical properties. A very important component of materials science engineering involves knowledge of the properties, behaviour and structure of materials.

In most cases, the characterisation of complex behaviour is made indirectly by complementing models with empirical data. In this thesis, modelling has been reported in chapter 3 and this current chapter presents findings on the thermal stability and photophysics of selected perylene derivatives. The spectroscopic characterisation and optical properties of organic semiconductors aims at understanding and control of energy transfer and emission properties of the same(2). Derivatives of perylene have high extinction coefficients(3), are usable as energy donors in thin film devices, are also mainly n-type semiconductors(4) offering both thermal and photochemical stability for a wide range of optoelectronic applications as outlined in chapter 4. In order to make maximum use of this class of π -conjugated organic chromophores, an extensive knowledge of their properties is required. This chapter presents results from UV-vis absorption, emission, quantum yield, lifetimes and variable angle spectroscopy along with

associated parameters, and relates the same to the functionality of the perylene derivatives.

5.2 Experimental

5.2.1 Thermal stability

The thermal stability of the perylene derivatives were studied using a PerkinElmer Thermo gravimetric Analyser Pyris TGA by heating approximately 6 mg of each material from room temperature to 800 °C in an air atmosphere at a heating rate of 10 °C per minute. Subsequent TGA runs were performed from room temperature to just above each loss event's temperature and FTIR spectra of the residue were taken on a Nicolet NEXUS FTIR spectrometer in the transmission mode against a sodium chloride plate.

5.2.2 Photophysics

Stock solutions of each perylene derivative were prepared at a concentration of 1 g/l in spectrophotometric grade chloroform and diluted down in 1/3 and/or 1/4 steps to 12 times. Thin films of each perylene derivative were prepared by thermo-sublimation at a vacuum pressure of about 1×10^{-5} bar in 30 nm thickness steps from 30 nm to 150 nm. Room temperature UV-vis absorption spectra for each sample were taken on a CARY 6000i UV-Vis-NIR spectrophotometer. Room temperature emission and excitation spectra were recorded on a PerkinElmer LS55 Luminescence Spectrometer. Temperature dependent UV-Vis absorption spectra were recorded on a Cary 300 Scan dual beam, 6'6 Multicell Block Peltier Temperature Controlled spectrophotometer for fresh samples of the perylene derivatives at high and low concentrations of about 0.05g/l and 0.005g/l respectively in spectrophotometric grade isopropyl alcohol.

The photoluminescence quantum yield (PLQY) of each derivative was determined from absorption and emission spectra taken on a CARY 6000i UV-Vis-NIR spectrophotometer and a PerkinElmer LS55 Luminescence Spectrometer respectively for solutions at 10^{-6} M concentration by employing the one point method. Coumarin 500 in spectrophotometric grade chloroform was used as the standard for the determination of PLQY for solutions of perylene violet, perylene blue and perylene yellow in the same solvent. The excitation wavelengths used were 374 nm for perylene violet and 410 nm for both perylene blue and perylene yellow. Cresyl violet in spectrophotometric grade methanol was used for one point determination of the PLQY of solutions of perylene orange and perylene red in the same solvent at excitation wavelengths of 523 nm and 570 nm respectively.

The average fluorescent lifetimes were taken on a Horiba Jobin-Yvon Time Correlated Single Photon Counting (TCSPC) Flourog Lifetime Spectrometer for spectrograde chloroform and toluene solution samples at 0.005g/l and on a PicoQuant Microtime200 time-resolved confocal microscope system with 150 ps resolution for 100 nm thermally sublimated thin film samples of the perylene derivatives. Only perylene blue was spin cast from a 0.005g/l spectrophotometric grade chloroform solution.

Variable angle spectroscopic ellipsometry (VASE) was employed to determine the thickness and refractive indices of selected perylene derivatives thermally-sublimated 100nm thin films on glass substrates. A SOPRA GES 5 Variable Angle Spectroscopic Ellipsometer was used to scan a wavelength range of 250 nm to 850 nm (1.45 eV to 4.95 eV) in 5 nm steps and varying the angle between 54° and 60° in 3° steps.

5.3 Results and discussion

5.3.1 Thermogravimetric analysis

The thermogravimetric (TG) curves for the perylene derivatives studied are shown in Fig. 5.1.

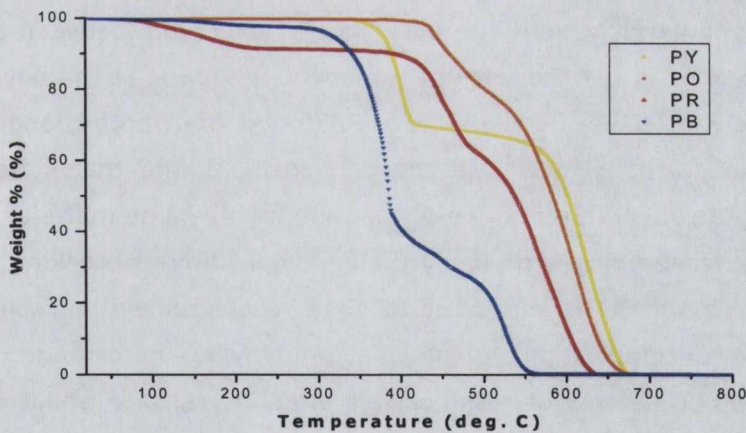


Figure 5.1. Thermogravimetric curves for perylene derivatives.

From the derivatives of the thermogravimetric curves (DTG) in Fig.5.2, it is evident that all the perylene derivatives studied are thermally stable in air up to 300 °C, and therefore suitable for normal everyday operations and environments. The DTG curves also clearly display the events or decomposition temperatures. Perylene orange is the most stable with the first event's onset temperature occurring at 450 °C losing 20% of its original weight. The first event onset temperature for perylene red is 440 °C making it the second thermally stable molecule of the perylene

derivatives studied with a loss of 40% of the material. Perylene yellow is the third stable with an onset first event temperature pegged at 400 °C and a loss of 35% of the starting weight. Perylene blue first loses 65% of the original weight at 380 °C whilst 100% of perylene violet is lost at 330 °C. Three of the perylene derivatives,

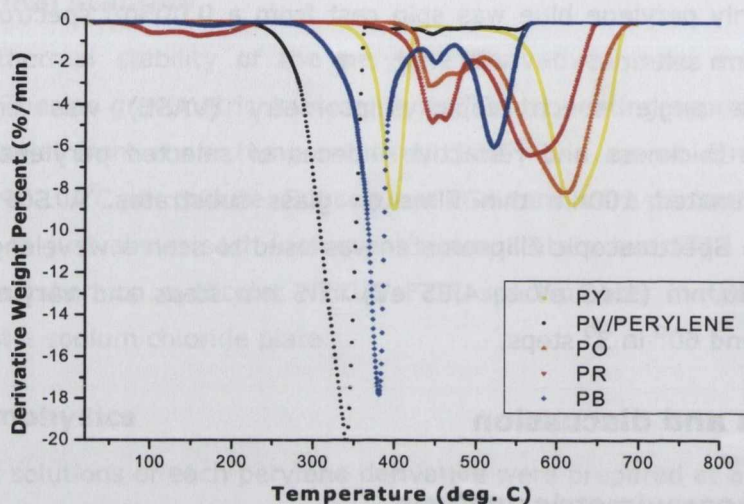


Figure 5.2. Thermogravimetric curves for perylene derivatives.

namely blue, orange and red, have a common loss event at about 450 °C. Whilst this is the first loss event for perylene orange, it is the second loss event for perylene blue and perylene red. The difference in structures between perylene red and perylene orange is the presence of the phenoxy groups at the bay positions in the perylene red molecule. Perylene blue is different from both orange and red in that it has alkoxycarbonyl chains at the peri positions and that it has no amine groups (see Figure 2.17). This suggests that almost the same material constituents are lost at this event which is probably the decomposition or breaking down of the perylene core. This result is supported by FTIR results shown in Table 5.1, which summarises the decomposition events, accompanying percentage losses and compares the FTIR spectra of residues left after TG runs to about few degrees centigrade above each event at the same rate of 10°C/minute under the same starting conditions as the original ones.

The FTIR spectra of the three materials, PO, PR and PB show common and similar trends about 450 °C. At this temperature, the original material fingerprint is lost and becomes broadened towards the high wavenumber (2000cm^{-1}). In addition common new vibrations in the range ($3000 - 3700$) cm^{-1} are observed. This suggests that common materials are formed at this temperature for the three materials. The burn off of remaining organics for the three materials occurs in the order perylene blue at 500 °C with 35%, perylene red at 570 °C with 60% and

perylene orange at 620 °C with 80%, which is consistent with their ranking in thermal stability.

Table 5.1 Summary of events, losses and changes in FTIR spectra of perylene derivatives from TG analysis.

ATERIAL	EVENT/LOSS TEMPERATURE (deg. C)	% LOSS WEIGHT (%)	FTIR FINGERPRINT REGION	FTIR LOSS GROUPS (cm ⁻¹)	FTIR NEW GROUPS (cm ⁻¹)
PR	200	10	As in pure PR	None	None
PR	450	30	Different from pure PR	All fingerprint	3200-3700
PR	575	60	-	-	-
PB	200	5	As in pure PB	None	None
PB	420	60	As in pure PB	Fingerprint broadened	3050-3140
PB	500	35	Different from pure PB	2850-3140 and fingerprint	3000- 3670
PY	400	35	Different from pure PY	Fingerprint broadened	3161, 3500-3650
PY	630	65	-	-	-
PO	450	20	As in pure PO	Fingerprint broadened	3200-3680
PO	620	80	-	-	-
PV	330	100	-	-	-

The TG trends in perylene yellow and perylene violet do not have any similarities to those of the orange, blue and red derivatives. This suggests completely different decomposition mechanisms. The results show that perylene violet completely burns off at the first event whilst perylene yellow is lost in two steps. The TG trend for perylene violet is exactly the same as that of perylene.

The FTIR results summarised in table 5.1 confirm that for all the perylene derivatives, the starting material is still available after heating up to 400 °C and so is a consistent result with the thermal stability displayed in the DTG curves in figure 5.2. These perylene derivatives fulfil the requirements of high temperatutre stability for optoelectronic thin layer devices.

5.3.2 Photophysics

UV-vis absorption and solvent effects

The solubility of perylene derivatives in different solvents was tested at 0.05g/l concentration for all derivatives, except perylene violet at 0.1g/l, in each of dimethylformamide (DMF), 2-propanol (IPA), trichloroethane (TCE), chloroform, dichloromethane (DCM), tetrahydrofuran (THF), ethanol, acetone and toluene. These solvents were chosen on the basis of the solubility findings for perylene blue(5) reported in Chapter 4 as regards its suggested Hildebrand solubility parameter as well as allowing solution aggregation studies to be carried out. In addition, boiling points were also considered in solvent selection so as to allow a wide range of temperature for temperature dependence solubility studies.

All the derivatives dissolved straightaway without agitation in chloroform, THF and toluene. The average Hildebrand solubility parameter and refractive index for these solvents are $18.5 \text{ (MPa)}^{1/2}$ and 0.57 respectively (see table 2.2). Perylene blue would not dissolve in DMF, IPA, ethanol and acetone even after agitation by shaking vigorously or using the sonic bath. Longer times in the sonic bath only revealed cloudy solutions which settled down to suspensions after setting. Perylene violet dissolved in DMF when taken through the sonic bath as did perylene orange, perylene blue and perylene yellow in TCE. All perylene derivatives remained in solution in TCE and DCM after sonication in a water bath. This suggests that the perylene derivatives are generally soluble in chlorinated solvents as well as other solvents with both low Hildebrand solubility parameters and low refractive indices.

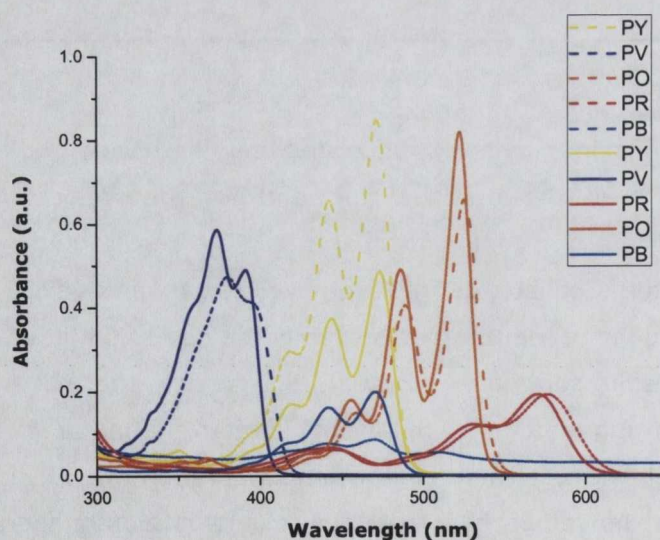


Figure 5.3 Comparison of UV-vis absorption peaks and intensities in IPA(dashed lines) and TCE (solid lines)

The absorption spectra do not suggest general patterns or trends for individual perylene derivatives as regards absorption intensities and peak absorption wavelengths in individual solvents. Figure 5.3 shows the absorption spectra for all the derivatives in each of two extremes of high and low Hildebrand solubility parameter solvents of $24.5 \text{ (MPa)}^{1/2}$ (IPA) and $15.8 \text{ (MPa)}^{1/2}$ (TCE) respectively. There is a very small bathochromic shift in the absorption maximum peak wavelength for perylene violet, perylene red and perylene orange in changing solvent from TCE to DCM whilst the peak absorption wavelengths for perylene yellow and perylene blue remain constant. It is evident that there is no regular pattern in the absorption intensities. Where they exist, the shifts of UV-vis absorbance depending on polarity of the environment can be used as empirical means of quantifying solvent polarity one application of which can be solvent selection for organic synthesis.

With the exception of perylene violet, all the other molecules are symmetrically substituted. The absorption spectra of such perylene based molecules are strongly structured and are little influenced by the solvents effect and in the case of imides may not be influenced by substituents at the imide position (6, 7). Whilst not practically affecting the spectral properties of the perylene derivative, the type of substituent at the imide nitrogen plays a role in the organisation of the molecule as shown in Chapter 3, particularly to produce PL in the solid phase(8).

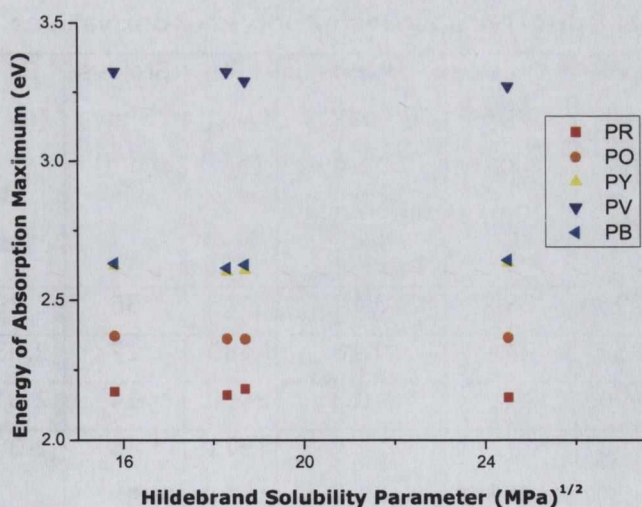


Figure 5.4 Independence of maximum absorption energy from solvent parameter for each perylene derivative

However, the absorption spectral patterns' change in wavelength fall within a 3nm range over all tested solvents for each perylene derivative.

Figure 5.4 also shows the independence of the absorption maximum energy from the solvent for each perylene derivative. The solvents used here are chloroform, TCE, toluene and IPA whose Hildebrand solubility parameters and other properties are shown in table 2.2. The solubility of each derivative in individual solvents therefore depends solely on the interaction of the molecule with the solvent. All molecules have the same building block of a perylene core, suggesting that the molecule-solvent interaction is controlled by the groups (chromophores) attached at different positions of the perylene core. Whilst other solvent parameters like refractive index and solvent parameter may make insignificant contributions, the above results suggest that the chromophores are a major contributing factor to the maximum absorption peak and thus the final colour of the molecule. This allows material scientists to chemically “tune” the colour of perylene derivatives for specific optoelectronic applications.

Room temperature UV-Vis absorption and photoluminescence

Table 5.2 shows optical properties obtained from UV-Vis absorption and photoluminescence of the perylene derivatives studied. The absorption and photoluminescence results were obtained from 1g/l spectrophotometric grade chloroform solutions whilst the binding energies (E_{be}) were deduced from the exciton energies (E_{ex}) and optical gap energies (E_g) as explained under theory in Chapter 4 (see equations 4.3, 4.4 and 4.5).

Table 5.2. Optical properties of perylene derivatives.

MATERIAL	UV-Vis λ_{max} (nm)	UV-Vis $\epsilon_{\lambda_{max}}$ (L/mol)	Other UV-Vis maxima (nm)	UV-Vis Peak Energy differences (eV)	PL λ_{max} (nm)	Stoke's Shift (nm)	E_{ex} (eV)	E_g (eV)	E_{be} (eV)
PV	377	64093	394	0.14	413	36	3.29	4.23	0.94
PB	472	21152	444	0.16	489	17	2.63	3.81	1.18
PY	476	64093	445	0.18	490	14	2.61	3.62	1.01
PO	525	41293	490, 459	0.17, 0.17	571	46	2.36	3.33	0.96
PR	568	18732	532, 443	0.15, 0.47	613	45	2.18	3.30	1.12
PERYLENE	434	38494	411, 391	0.16, 0.15	441	7	2.85	-	-

The chloroform solution based absorption spectra are strongly structured and contain absorption peaks of the $\pi\text{-}\pi^*$ electronic transitions and their vibronic progressions including shoulders as shown in table 5.2. This trend is characteristic of the perylene ring progression of $\pi\text{-}\pi^*$ $S_0\text{-}S_1$ or $S_1\text{-}S_0$ transitions (2, 5, 9, 10). The corresponding photoluminescence or emission spectra for each perylene derivative are mirror images of the $S_0\text{-}S_1$ absorption and not of the total spectrum (see Figure 5.5). This occurs due to the involvement in both absorption and emission of the same transitions as well as the similarities of the vibrational levels of S_1 and S_0 . Kasha's rule (11, 12), which states that photon emission occurs only from the lowest-energy excited electronic state of a molecule, explains this mirror image behaviour.

The average energy difference between the solution absorption peaks for each perylene derivative is 0.16eV. (see table 5.2 and note that perylene red's 443nm shoulder's difference from its 532 nm peak has been excluded from the calculation of the average energy difference). The 0.16 eV energy difference is almost the same as the 0.15 eV benzene ring stretch oscillation of perylene(13, 14) thus suggesting that the solution absorbances are controlled by monomeric absorption.

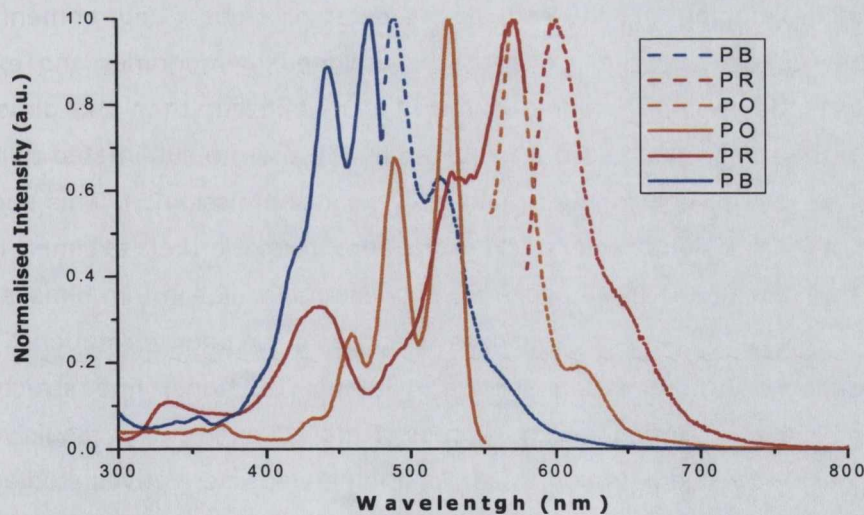


Figure 5.5. Normalised absorption (solid lines) and fluorescence spectra (dashed lines) for selected perylene derivatives in 1g/l spectrophotometric grade chloroform solution

The energy associated with fluorescence emission transitions (see Figures 2.10) is typically less than that of absorption, the resulting emitted photons have less energy and are shifted to longer wavelengths. As explained in section 2.3.7,

this phenomenon is termed Stokes Shift and is typical of almost all flourophores involved in solution investigations(15). Stokes shifts for the individual perylene derivatives are tabulated in table 5.2. The size of the Stokes shift depends chiefly on the molecular structure but in no particular trend. Since the chromophores in the case of perylene derivatives control the maximum absorption peak, they are also responsible for the Stokes shift. It is also evident that both the absorption and emission spectra of the perylene derivatives are bathochromically shifted spectra of perylene except for perylene violet which is blue shifted. When compared to perylene, the Stokes shifts of the studied perylene derivatives are larger and therefore more influenced by the existence of additional oscillations in each molecule connected with the chains attached to the perylene core. Other additional contributing factors include energy losses associated with relaxation to the ground vibrational states, solvent effects, excited state reactions, complex formation and energy transfer. The perylene derivatives' Stokes shift ranges from double to more than six times greater than that of perylene. The existence of Stokes shift is critical to the extremely high sensitivity of fluorescence imaging measurements and so makes these perylene derivatives prospective candidates for such applications.

The thin film absorption and emission spectra for the perylene derivatives are broad and unstructured consisting of overlapping "double" peaks in most cases. In addition, they are bathochromically shifted with respect to solution spectra. The red shift and broadening is enhanced by the different energy environments(16). These results suggest that the peaks can be assigned to monomer and excimer emitters. Since the excimer channel is much more efficient than the dimer and monomer(2), the strong fluorescence exhibited by the thermo sublimated thin films of perylene derivatives is attributed mainly to excimer emission(3). This suggests that any three-dimensional self stacking favours formation of excimer in the evaporated thin films(17, 18). The distance between molecules in thin films is much shorter than in solution and so enhances chances of excimer formation(5). The structurelessness of the emission spectra, without vibrational fine structure is because of excimer emission which process leads to a strongly repulsive and dissociative geometry in the ground state. For the perylene derivatives studied here, Kasha's rule does not apply any more to the thin film samples and so the mirror symmetry exhibited in solution is lost.

The exciton binding energies are calculated by application of the Van Tauc equation to the absorption edge of the thin film spectra. The average exciton binding energy for the perylene derivatives calculated from Table 5.2 is 1.04 eV. This is typical of Frenkel type excitons (19-21). This also makes the perylene derivatives studied here attractive candidates amongst aromatic molecules for

applications where energy can be transferred without the actual transfer of net charge. Generally the dielectric constants for the materials with Frenkel type excitons are small. This is confirmed earlier in this chapter by the type of solvents in which the perylene derivatives readily dissolve, all are of low dielectric constants.

Concentration dependent room temperature UV-vis absorption was performed in chloroform solutions from 10^{-3}M down to 10^{-9}M . For all the perylene derivatives, there is no observed peak wavelength shift with concentration. Figure 5.6 shows the linear section of a plot of absorbance versus concentration for all the perylene derivatives. This allows the molar extinction coefficient ϵ to be evaluated from the gradient of the graph based on Beer-Lambert's law explained previously in section 2.3.7 (see equation 2.1). This parameter shown in table 5.2 for each perylene derivative is evaluated from figure 5.6 at each molecule's maximum absorption wavelength in chloroform.

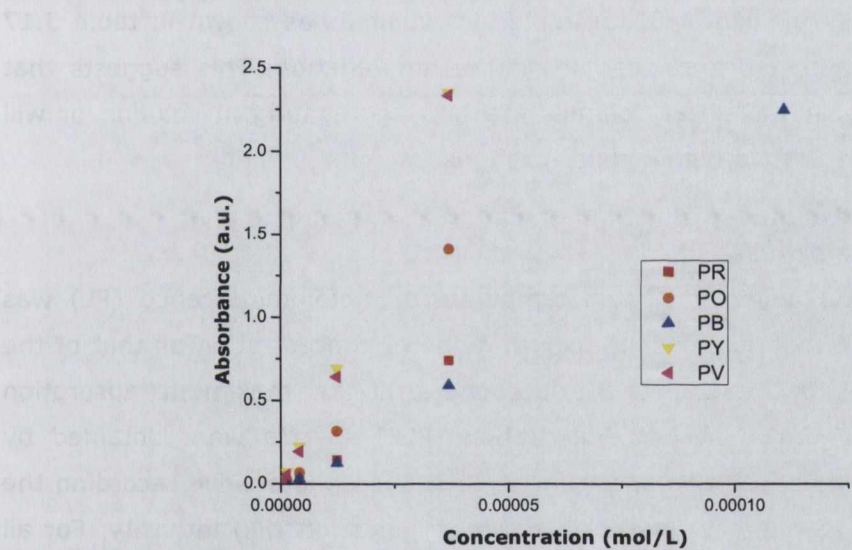


Figure 5.6. The linear section of the variation of absorbance with concentration for perylene derivative solutions in chloroform for the determination of the molar extinction coefficients.

Perylene violet and perylene yellow have the highest molar extinction coefficients at their maximum absorption wavelengths. From the definition of the extinction coefficient, this suggests that the two molecules have the highest fraction of light lost to scattering and absorption per unit distance in the participating medium. Perylene orange has the second highest followed by perylene red whilst perylene blue has the lowest of the five derivatives. Since the optical properties of materials are controlled by their interaction with the electric field component of the electromagnetic spectrum, the extinction coefficient can be regarded as the decay of the incident electric field's oscillation amplitude. Thus damping of electric fields

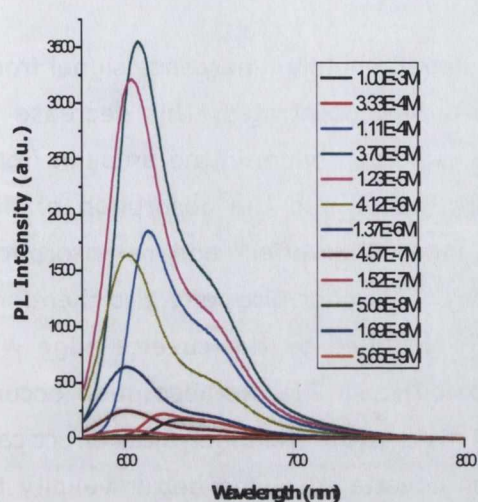
decreases in the order perylene violet and perylene yellow, perylene orange, perylene red and perylene blue. The major factor that controls the extinction coefficient appears to be the molecule's side groups interaction with the medium.

The limit of proportionality for Beer-Lambert's law signifies the onset of either aggregation or some other effect. From figure 5.6, perylene blue would be the molecule with aggregation effects occurring at the highest concentration, above 1×10^{-4} mol/L, compared to the other molecules. This is consistent with the report given in Chapter 4 Section 4.1 where this molecule was synthesised with a view to control aggregation. All the other perylene derivatives studied here have aggregation effects occurring at a much lower concentrations than 1×10^{-4} mol/L. In fact, perylene violet and perylene yellow would tend to form aggregates at low concentrations, followed by perylene orange at a higher concentration, then perylene red and then perylene blue. Comparing parameters deduced from molecular modelling in Chapter 3, the molecular volumes as shown in table 3.17 almost rank the same order as that of reduced aggregation. This suggests that molecules with higher molecular volumes are less aggregating in solution or will begin to form aggregates at higher concentrations.

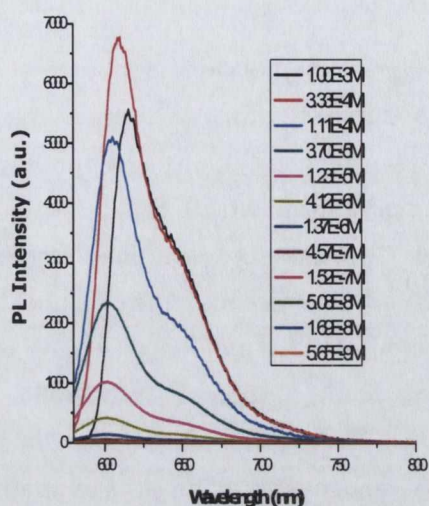
Concentration dependent PL/PLE

Concentration dependent room temperature photoluminescence (PL) was carried out on each molecule over the same range of concentration as that of the UV-vis absorption by exciting each fluorophore at its maximum absorption wavelength. The photoluminescence excitation (PLE) spectra were obtained by scanning through the absorption spectrum of each fluorophore while recording the emission intensity at the wavelength of maximum emission (PL) intensity. For all the perylene derivatives studied herein, the PLE spectra are identical to the room temperature UV-Vis absorption spectra for each concentration. When these PL/PLE spectra were obtained using 10 mm x 10 mm cuvettes, deviations from linearity for both PL and PLE were observed for all molecules. The deviations in the case of PLE spectra were exactly the same as observed in the Uv-Vis absorption spectra reported earlier. This is in compliance with the Beer-Lambert's law up to the limit of proportionality. These deviations would be associated with some complex process like aggregation or some equivalent effect.

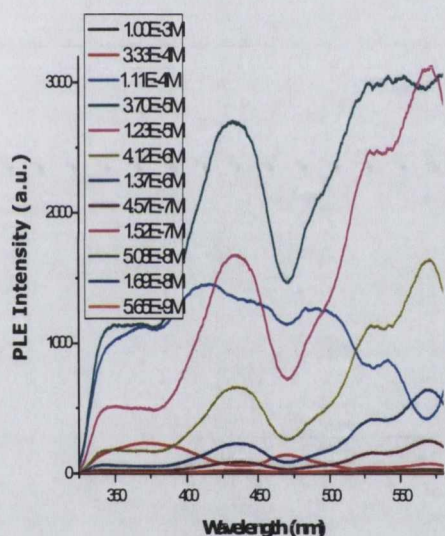
Figure 5.7 shows the cuvette path length response of PL/PLE spectra for perylene red measured in two sizes of 10 mm x 10 mm and 2 mm x 2mm cuvettes. It is evident from these results that fluorescence emission spectra excited in regions of high absorbance are suppressed in the 10 mm x 10 mm cuvettes and are



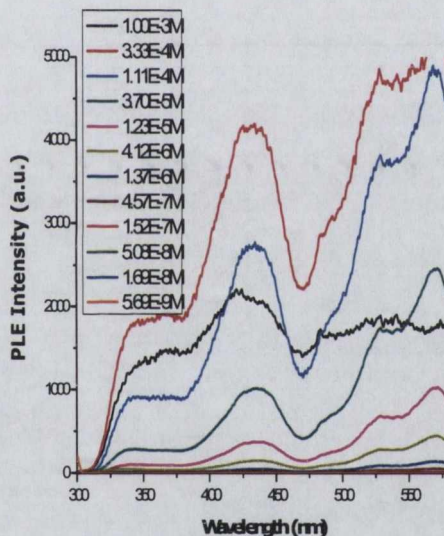
(a)



(b)



(c)



(d)

Figure 5.7. Concentration dependent photoluminescence, (PL) and photoluminescence excitation, (PLE) results of perylene red in spectro-photometric grade chloroform, (a) and (c) measured in 10 mm x 10mm cuvette, (b) and (d) measured in 2 mm x 2 mm cuvette.

enhanced in the smaller paths length cuvette. As the concentration of the molecule is increased, the initial linear growth of photoluminescence with concentration falls away in the larger path length cuvette and less so in the 2 mm x 2 mm cuvette. Considering the several bands differing in amplitude present in the molecule's absorption spectra, the bands with relatively higher absorption coefficients are depressed in the 10 mm x 10 mm cuvettes relative to those with lower ones in the PLE spectra except at low concentrations. This effect is greatly reduced in the 2 mm

x 2 mm cuvette. These effects are evident in all the perylene derivatives studied herein.

For all the perylene derivatives, the observed photoluminescence signal from solution decreases as the solution becomes more concentrated. This decrease is due to two main facts; the attenuation of the excitation beam in the areas in front of the point from which the detector collects the PL and the absorption of the emitted PL within the solution, termed the inner filter effect and re-absorption respectively (Ref standards in PL spectroscopy). The inner filter effect is therefore attributed to the instrument, where the light absorbed by the cuvette edge will fluoresce but the detector is not able to detect the PL(22). Re-absorption occurs where the PL emission and absorption spectra overlap(5). The inner-filter effect can thus be reduced by using smaller path length cuvette so giving better validity to results interpretation as regards aggregation and/or other complex effects.

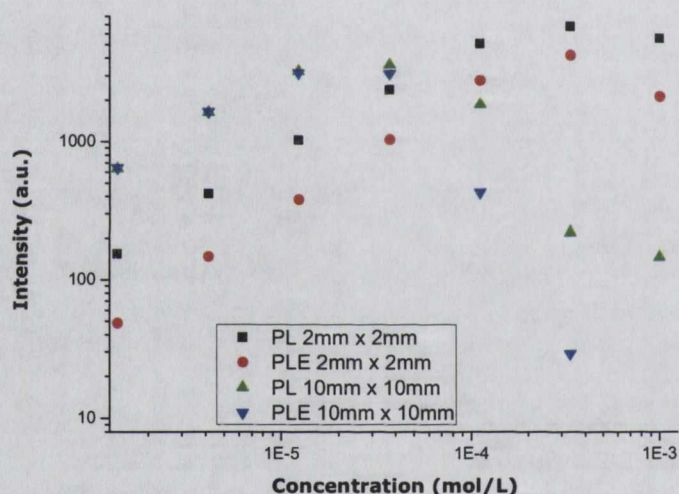


Figure 5.8 Concentration dependent photoluminescence, (PL) and photoluminescence excitation, (PLE) results of perylene red in spectro-photometric grade chloroform, showing the response to cuvette path length.

Figure 5.8 shows the logarithmic plot of the variation of PL and PLE maximum wavelength peak intensity with concentration for the perylene red molecule in spectro-photometric grade chloroform in cuvettes of different path lengths. The linear response range is greater in the smaller path length cuvette. This trend has been previously reported for perylene blue(5) in Chapter 4 (see Figure 4.6) showing complete linearity for spectra taken in the 2 mm x 2 mm cuvette. The same order as shown in Figure 5.6 is displayed also by the effect of reducing the cuvette path length so supporting that aggregation effects are less

pronounced in perylene blue, followed by perylene red, then perylene orange, and perylene violet and perylene yellow.

Fluorescence quantum yields and lifetimes

Table 5.3 shows the quantum yields and average lifetimes of the perylene derivatives. The relative quantum yields were obtained by comparing the PL integrals of very dilute solutions of the perylene derivatives against those of fluorescent quantum yield standards. The absorption peak values for all solutions in

Table 5.3 Fluorescence quantum yields and average lifetimes

MATERIAL	PLQY (%)	CHCl ₃ τ_{av} (ns)	Toluene τ_{av} (ns)	Thin film τ_{av} (ns)
PV	75	5.02	4.47	6.09
PB	89	3.92	3.81	4.25
PY	91	4.03	4.01	6.97
PO	99	3.94	3.70	4.15
PR	98	6.00	5.52	3.38

the PLQY determination were below absorbances of 0.2 arbitrary units so ensuring that re-absorption along the fluorescent path did not play a relevant role(23). Perylene orange has the highest PLQY of 0.99 closely followed by perylene red at 0.98 and perylene yellow at 0.91. The new perylene blue dye has a PLQY of 0.89 whilst perylene violet is fifth placed for the dyes studied here at 0.75. As previously noted in Chapter 2, materials with a PLQY of 0.1 are considered quite luminescent. Porphyrins and phtythalocyanines have average PLQY of that order (24, 25). With respect to that, the perylene derivatives are highly luminescent and thus become superior their counterparts in suitable optoelectronic applications especially OLEDs. PLQY was previously defined in Chapter 2 as the fraction of flourophores that decay via emission of a photon compared to all other processes, i.e. the fraction of excited molecules which become de-excited by fluorescence, hence can be considered as the probability that a molecule will fluoresce. Thus molecules with higher PLQY value exhibit stronger fluorescence. However, PLQY are solvent polarity dependent as well as concentration dependent. Less polar solvents generally offer higher PLQY. For fluorescent molecules, the PLQY is a sensitive function of the environment. The solvent used here was spectrophotometric grade chloroform.

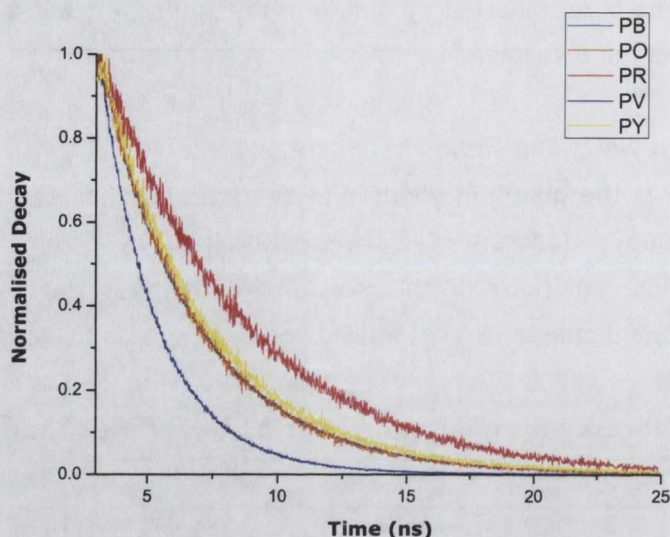


Figure 5.9 Fluorescence decay profiles for perylene derivatives in drop cast from spectrophotometric grade toluene solutions

Chloroform has 3 bonds with chlorine, (two of them symmetrical) and one with hydrogen. Chlorine is very electronegative and it pulls electrons towards its nucleus. Thus, it is a polar bond. The two symmetrical chlorine-carbon bonds "balance out" this pulling, so that no net pull occurs. The remaining chlorine-carbon bond is not "balanced out" by the less-polar hydrogen-carbon bond, resulting in a net polarity, with the "negative" end towards the chlorine.

This PLQY dependence on solvent polarity is mirrored by a similar trend in the fluorescent lifetimes. The fluorescence lifetime is the time required by a population of N excited states to decrease exponentially to N/e by losing excitation energy through fluorescence and other deactivation pathways. Results from table 5.3, based on single exponential fits of equation 2.5, show that the average fluorescent times are higher in chloroform than in toluene. Chloroform is more polar than toluene(26). The values of the lifetimes are all less than that of the unfunctionalised perylene in toluene solution(27) suggesting that the chromophores lower the lifetimes. However, it is not the size of the chromophore which determines the lifetime. It is the molecule's structure as well as dipole moment's interaction with the solvent that determine the PLQY and the average lifetimes in solution. In this study, the toluene based lifetimes are determined from drop cast toluene solutions and are higher possibly due to the existence of aggregates much higher than monomers. Typical solution and thin film based fluorescent decay profiles are shown in figs. 5.9 and 5.10 respectively. There is a possibly a higher degree of aggregate formation in the thin films as suggested by the results. The

thin film lifetimes are generally higher than solution lifetimes and are independent of thickness of film over the range 30 nm to 150nm.

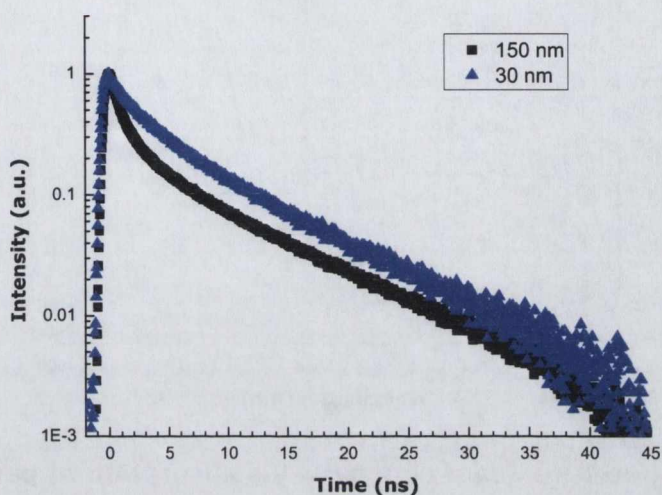


Figure 5.10 Fluorescence decay profiles for thermo-sublimated perylene red thin films on a glass substrate.

Fluorescence of excimers is often observed in solid state and in highly concentrated solutions of aromatic molecules (9, 28, 29). Larger aggregates, probably dimers (30) exist under high concentration conditions. In cases where the lifetimes are higher in thin films than in solution, it is also possible that defects are taking an active role. Fluorescence lifetimes of molecules are not only determined by their structure and photochemistry, but also by the geometry of the surrounding media.

Temperature dependent absorption

For all the perylene derivatives, temperature dependence UV-Vis absorption shows the existence of isosbestic points before and after each peak wavelength and shoulder. Usually isosbestic points are associated with the interaction of different species, but in the case at hand they arise as a result of the variation of a single parameter specifically temperature. At the isosbestic points, the absorption coefficients are the same. For all the perylene derivatives studied here, there is a very small shift in wavelength of about $\pm 5\text{nm}$ between the highest and lowest temperature where there is a hypsochromic shift from low to high temperature. When aggregates form in this fashion, they will be J-type aggregates(31). The difference in absorption intensities for the same peak is also very small with the lowest temperature having the highest intensity and vice versa.

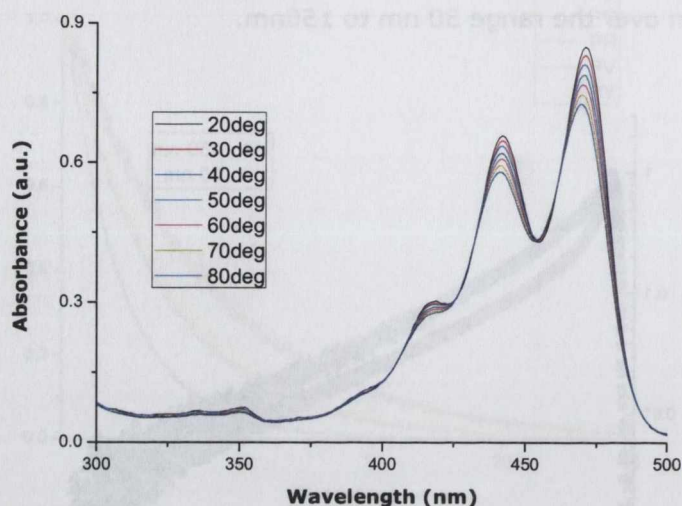


Figure 5.11 Temperature dependence UV-Vis absorption of perylene yellow 10^{-6} M in spectrophotometric grade isopropanol showing isosbestic points.

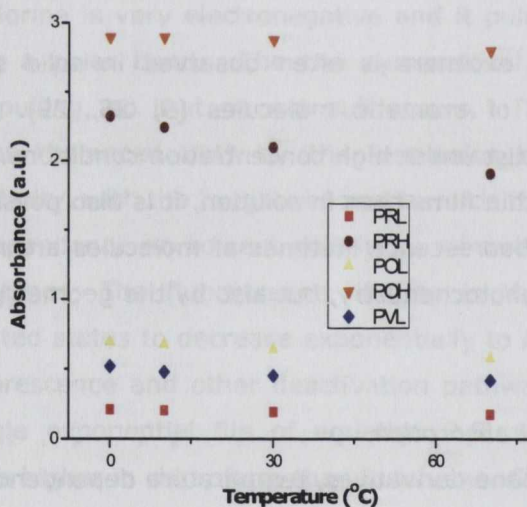


Figure 5.12 Temperature dependence UV-Vis absorption of perylene orange, perylene violet and perylene red at low and high concentration in spectrophotometric grade isopropanol.

Figures 5.12 and 5.13 shows the variation of absorption intensities with temperature for all the perylene derivatives studied here at both low and high concentration. Only perylene violet at high concentration is not shown as it saturated. The linear dependence of maximum absorption peak intensity with temperature is evident at low concentration for perylene orange, perylene violet,

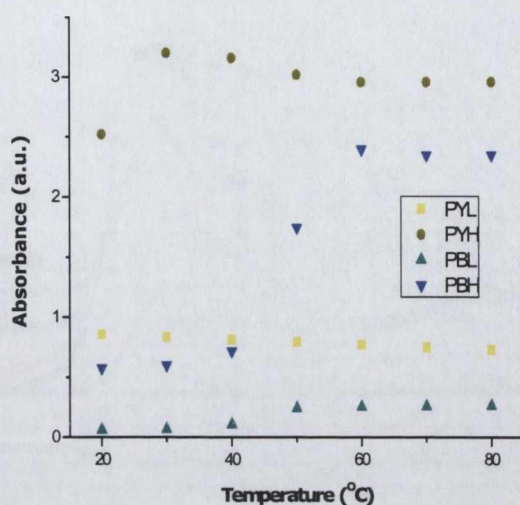


Figure 5.13 Temperature dependence UV-Vis absorption of selected perylene blue and perylene yellow at low (L) and high (H) concentration in spectrophotometric grade isopropanol.

perylene red and perylene yellow. This is further evidence of monomeric behaviour in solution. Hence Beer-Lambert's law and linear dependence of absorption spectra known to be valid for dilute solutions(32) are also validated for perylene derivatives here as evidenced through isosbistics. For monomeric solution as herein for the perylene derivatives, it is easy to locate corresponding vibrational levels in the excited state when isosbestic points are observed in the temperature dependent electronic absorption spectra. The change in shape with temperature can only be caused by the change in population of the vibrational levels of the electronic ground state(33). The likelihood of a single species isosbestic arises from the fact that fluctuations modulating a solute's transition frequency are very microscopic. Conclusions regarding distinct solvation structures require more detailed dynamical information in one-dimensional spectra(34). The linear relation for spectra is more useful than to show that spectra have isosbestic points(35).

However for perylene blue, this linear dependence is lacking at low temperature. It has been previously mentioned that perylene blue would not dissolve in isopropanol so making it a "good" solvent for studying aggregation effects of the same molecule. At high concentration, perylene orange remains linear, perylene red is almost linear but not as much as perylene orange. However perylene blue and perylene yellow show no linearity at all with absorption intensities varying from low to high and low again through low, medium and high temperatures respectively. Furthermore, an additional peak exists at about

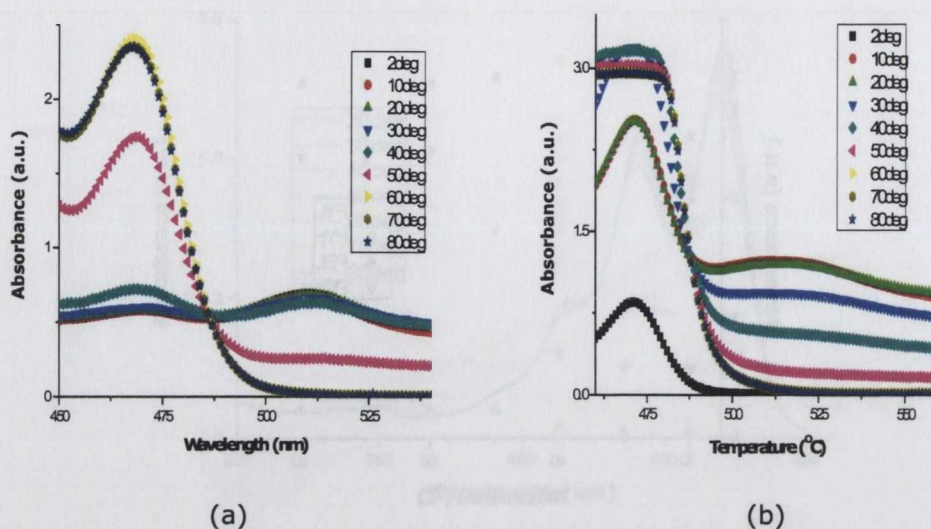


Figure 5.14 Isosbestic near maximum absorption peaks for PB (a) and perylene yellow (b) at high concentration showing the low temperature peak at around 510 nm wavelength.

510 nm for both perylene blue and perylene yellow at low temperatures (see figure 5.14). This peak is nonexistent in the other derivatives. This is further evidence of the tendency of perylene blue and perylene yellow to form higher aggregates at low temperature and high concentration. The aggregates formed here are J-type aggregates as there is a red shift in the UV-Vis absorption upon cooling (31, 36).

5.3.3 Variable angle spectroscopic ellipsometry

Variable angle spectroscopic ellipsometry (VASE) is one of the few techniques which addresses both optical properties and morphology of thin films. This is done by measuring the change in polarisation of polarised light reflected from a sample at an oblique angle of incidence(37) as described both in the experimental section of this chapter and also in Chapter 2 of this thesis. The actual sample characteristics is then coupled to the measured VASE data through an optical model in which parameters describing the thin film morphology, film thickness and complex index of refraction for each wavelength is fitted to the experimental data in a linear regression data analysis. The components of refractive index and extinction coefficient, well known as the n and k values respectively, as well as their dependence on wavelength or energy and the film thickness were determined for selected perylene derivatives.

In this research, global regression was applied using the Levenberg-Marquardt method. The Standard dielectric function / Sellmeier 3 dispersion law was used to fit the data and produce the n and k values. The phases were chosen as void (phase 1), isotropic material for the thin film (phase 2) on a glass substrate (phase 3). These results are compared to the bulk system of film plus glass.

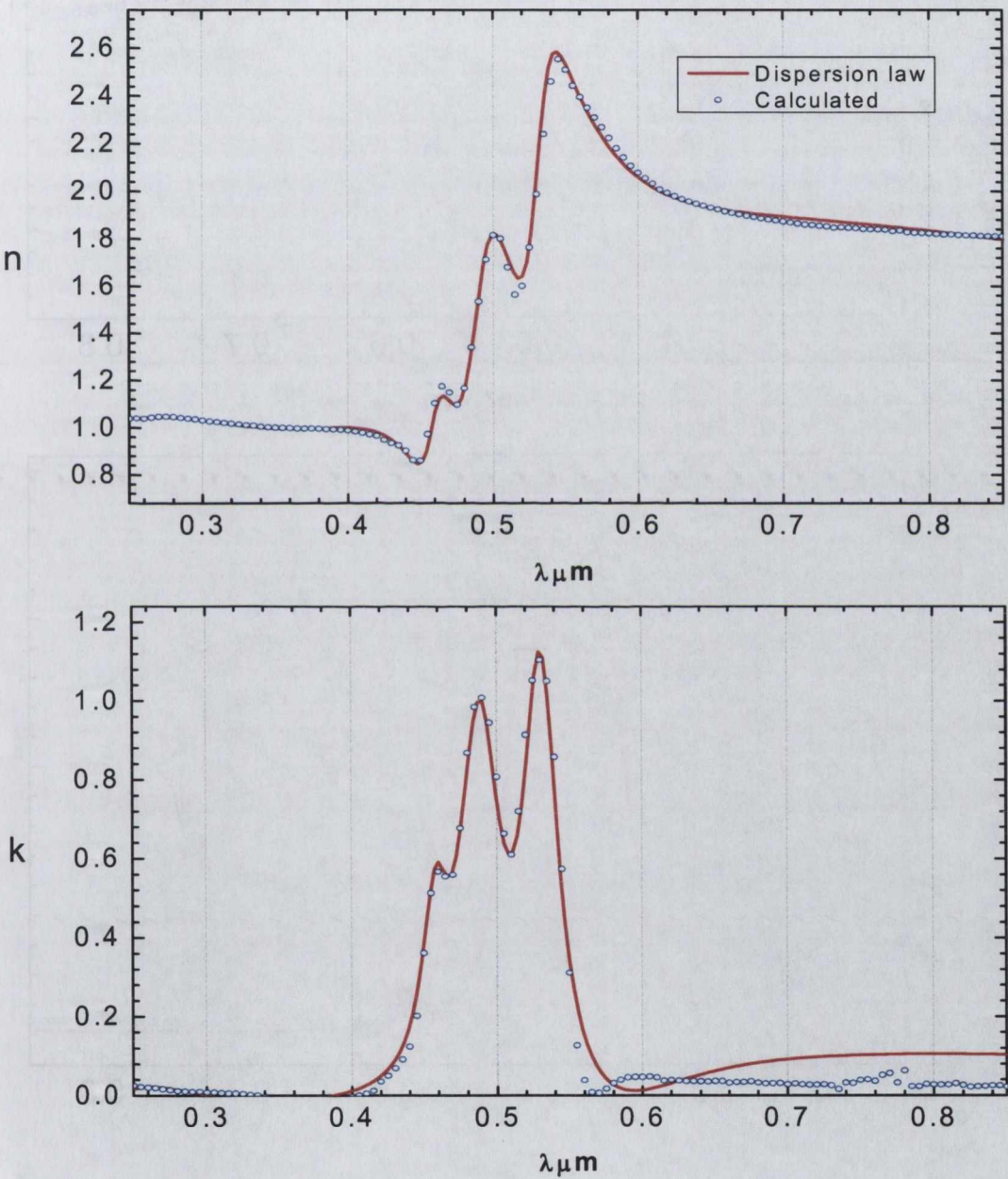


Figure 5.15 Complex Refractive index n and extinction coefficient k derived from the Dispersion model and that calculated point to point for perylene orange

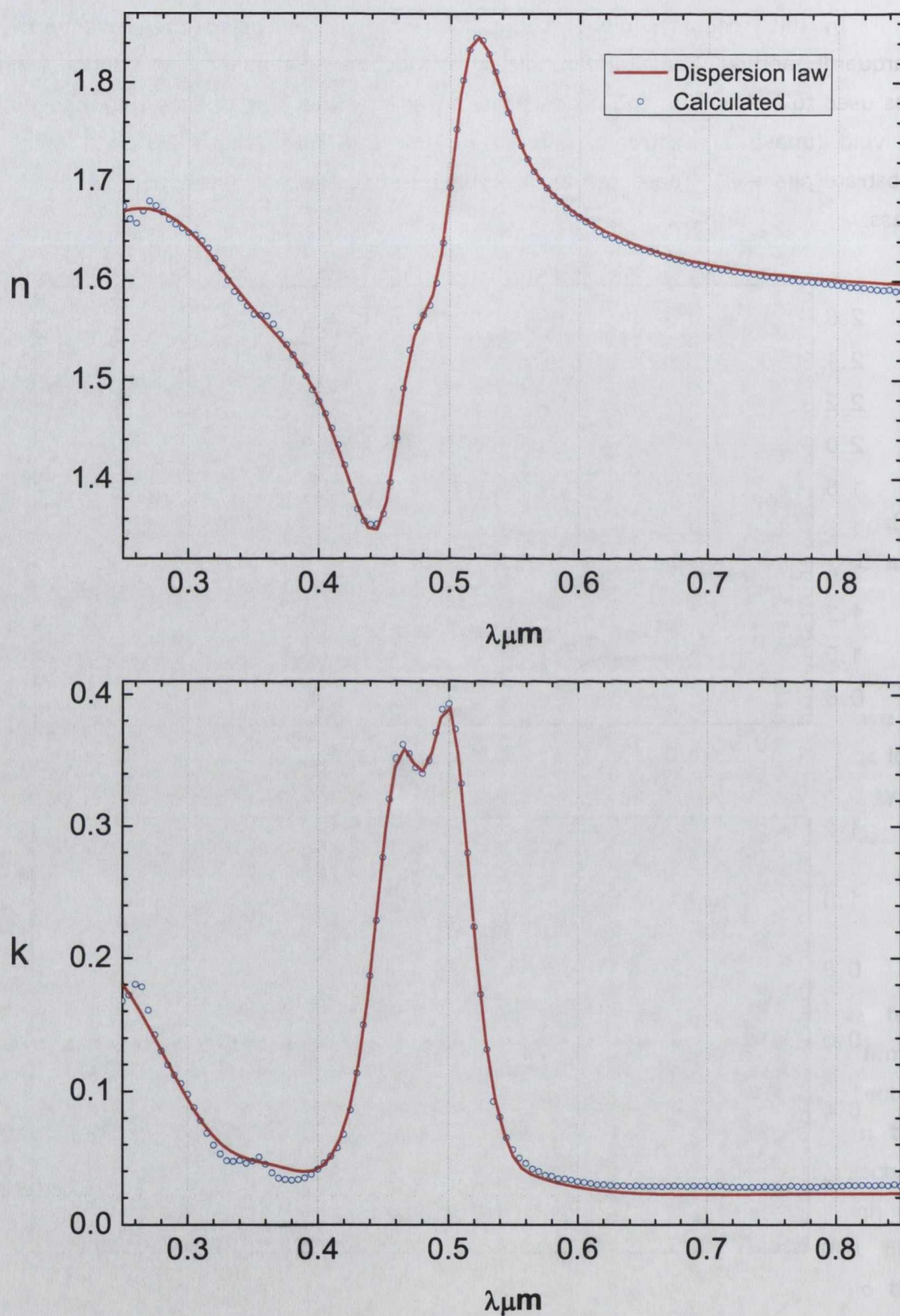


Figure 5.16 Complex Refractive index n and extinction coefficient k derived from the Dispersion model and that calculated point to point for perylene yellow.

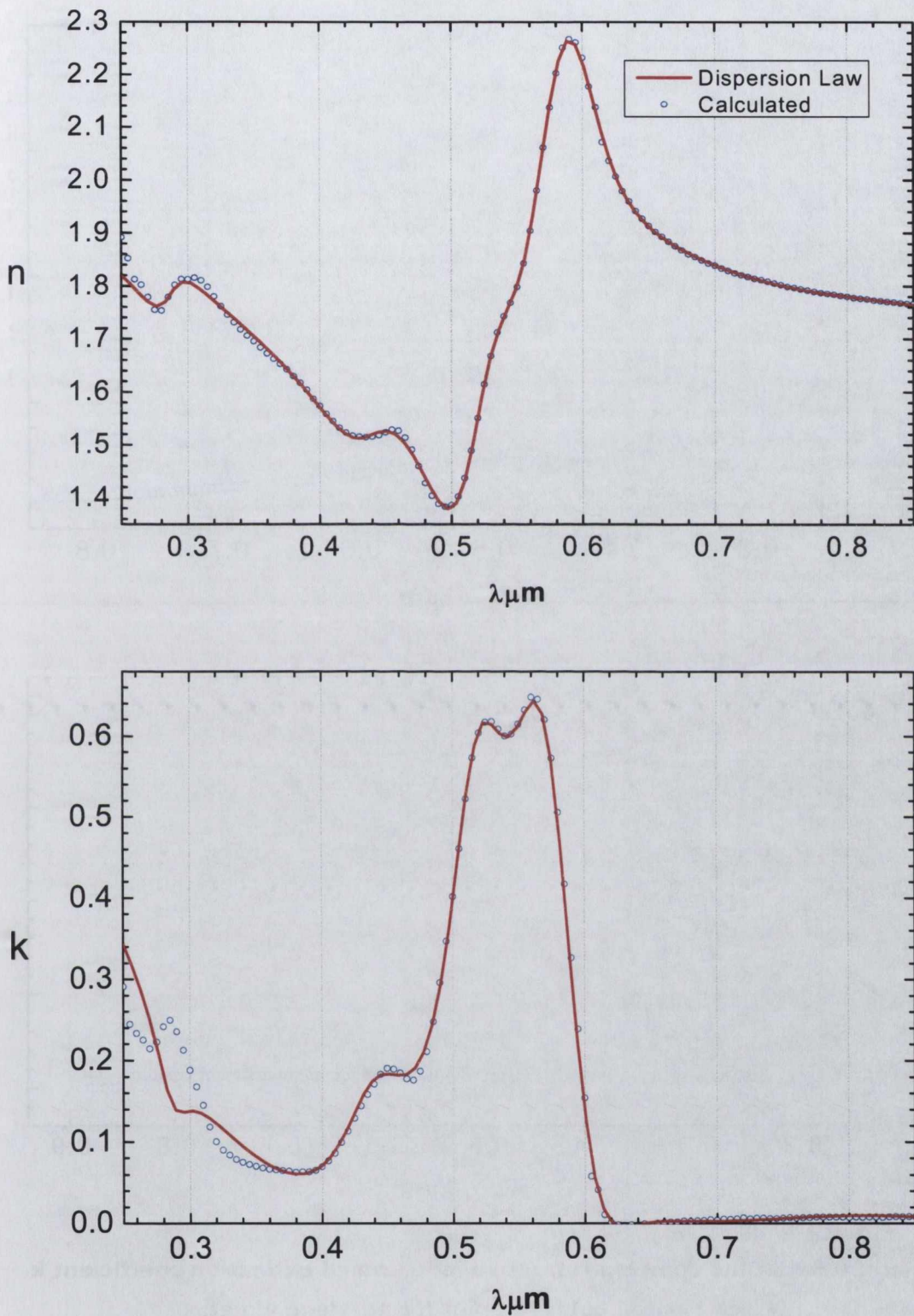


Figure 5.17 Complex Refractive index n and extinction coefficient k derived from the Dispersion model and that calculated point to point for perylene red.

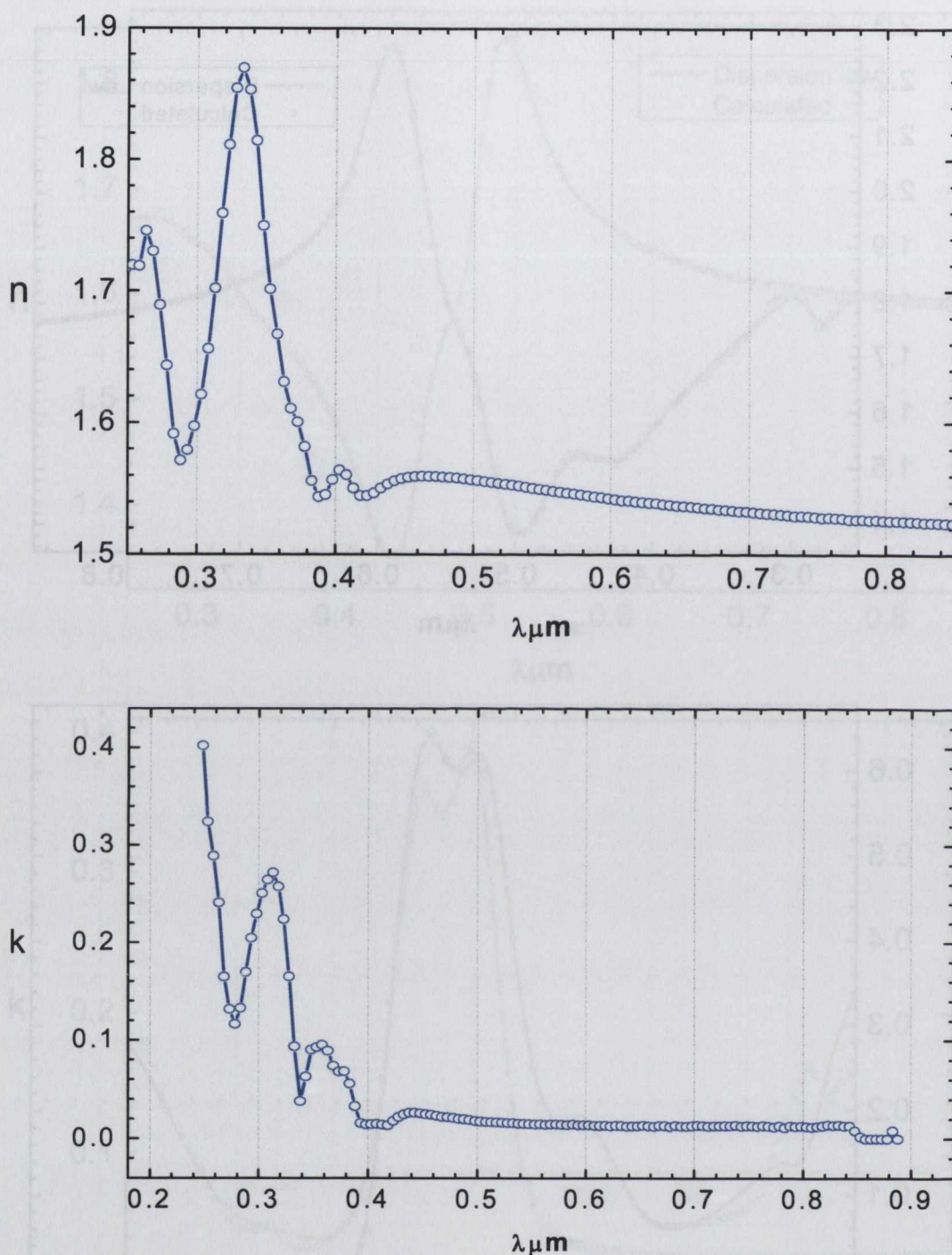


Figure 5.18 Bulk complex refractive index n and extinction coefficient k calculated point to point for perylene violet.

Figures 5.15 through to 5.18 show the complex refractive indices and extinction coefficient variation with wavelength for all the perylene derivatives studied here. Comparisons are made between the dispersion law fit and calculated data. For all the perylene derivatives, the overall shape of the imaginary part of the

dielectric function which is the extinction coefficient k is very much alike with the absorption spectra of each derivative's thin film thermo-sublimated onto the glass substrate (see figure 5.20). In some cases, the HOMO and LUMO can easily be identified. For these derivatives with C2 symmetry, anisotropy, i.e the property of directional dependence, in physical properties is expected and is evident in the results.

Perylene orange has the highest n and k values for peak wavelengths followed by perylene red, then perylene yellow. Perylene violet has the lowest.. Similar trends are shown by the direct inversion of raw data giving pseudo-refractive indices for the bulk system of film plus glass as shown in figure 5.19.

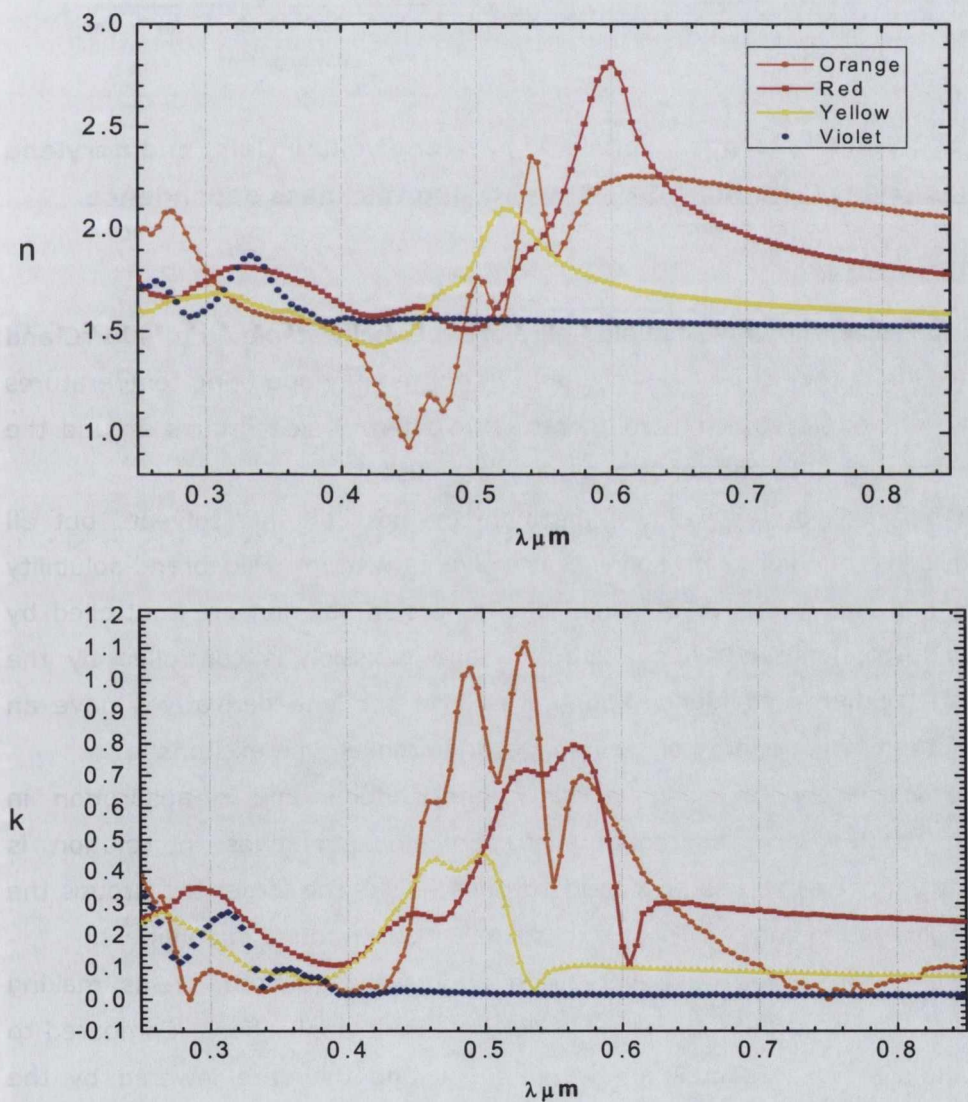


Figure 5.19 Direct inversion of the raw data giving the pseudo- refractive index and extinction coefficient for the bulk system of film plus glass.

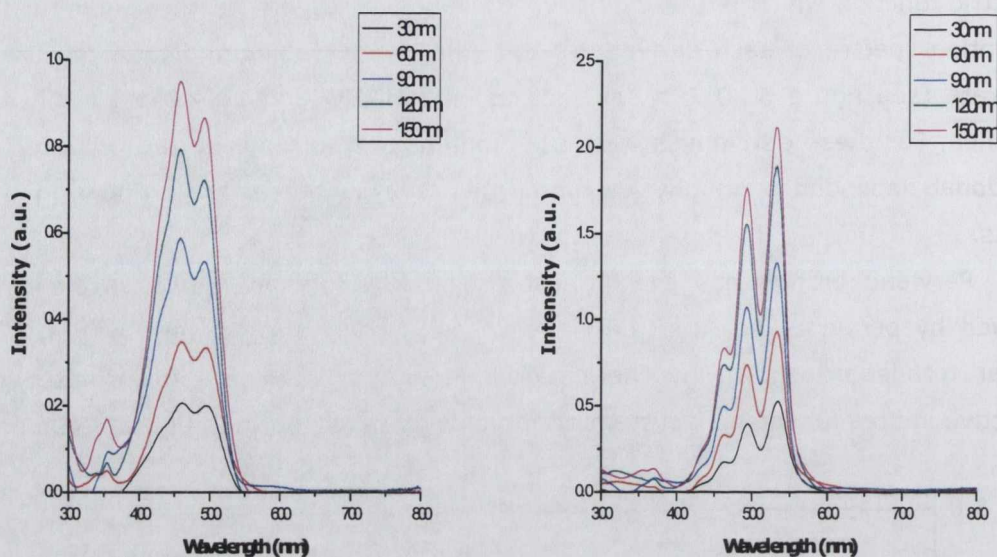


Figure 5.20 UV-vis absorption curves of perylene yellow (left) and perylene orange (right) thin films on glass showing thickness dependence.

5.4 Conclusions

The perylene derivatives studied here are thermally stable up to 400 °C and can then be used in optoelectronic devices both in normal day operating temperatures as well as high temperature environments. The different side groups around the perylene core cause different decomposition mechanisms.

The perylene derivatives are insoluble in most organic solvents but all generally dissolve in chlorinated solvents or solvents with low Hildebrand solubility parameters and low refractive indices. Absorbances in solution are controlled by monomeric absorption. Thin film absorption and emission is controlled by the existence of excimers and higher aggregates. The perylene derivatives have an average exciton binding energy of 1 eV suggesting Frenkel type excitons.

It is necessary to eliminate inner filter effects and re-absorption in aggregation studies. The aggregation of perylene derivatives in solution is controlled strongly by the size of the side group chains. The larger the groups the better the aggregation control. This trend is similar to that found in polymers.

Perylene derivatives have very high fluorescent quantum yields making them very attractive in fluorescent based optoelectronic applications. Compared to perylene, the average lifetimes are lower suggesting they are lowered by the additional side groups.

The perylene derivatives showed high anisotropy in the physical properties.

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Chapter 6

Structural and optical limiting properties of perylene derivatives

6.1 Introduction

Molecular modelling predicts the behaviour of molecules. Once synthesized, the bulk behaviour of the molecule can then be proved empirically by such characterisation techniques such as thermogravimetric analysis and photophysical studies. Information about molecular properties is useful but insufficient for designing actual devices because device performance is often controlled by properties that arise from aggregation of molecules(1). The aggregation of molecules depend mostly on the structural properties which are controlled by the environment i.e. whether in solution (concentration, solvent and temperature dependent) or in solid state (substrate dependent). Structural magnification and internal visualization are normally done in a type of microscope, such as Optical Microscope, Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), Field Ion Microscope (FIM), Scanning Tunneling Microscope (STM), Atomic Force Microscope (AFM). A combination of a few such microscopy methods can yield a lot of information as regards properties of materials and is useful in materials science. An intensive characterization of this nature encompassing molecular modelling, synthesis, bulk characterisation and optical microscopy gives a better understanding of the behaviour of molecules and so enables prediction of possible applications which can then be tested.

Perylene derivatives are small organic molecules with very good thermal and photochemical stabilities as well as high absorption and fluorescence quantum yields(2). As such they have prospects in optoelectronic applications including photovoltaic devices(3, 4), artificial light harvesting complexes(5, 6) and light emitting diodes (7). Their strong emission and absorption in the visible range make them prime candidates for applications as organic semiconductors, photoconductors, laser materials, thin film transistors as well as flat panel displays(8). The range of applications of perylene derivatives is thus almost limitless due to their functionalities. A relatively surprising new application of this family of molecules has arisen in their optical limiting capabilities as recently as 2003(9). This has been due to the discovery of large two photon absorption (TPA) cross sections in perylene derivatives. Materials exhibiting large TPA can find applications in three dimensional optical storage memory(10), two photon microscopy(11), up

conversion lasers(12-14), optical power limiting(15, 16) and photodynamic therapy(8). For this relatively new possible application, a materials science study is thus necessary to understand especially the structural properties and then relate them to the possible application as listed. Practical TPA materials are limited as of to date and thus exploration of new materials is urgent(8). Perylene derivatives are flat aromatic molecules with flexible side chains or functional chromophores. A quintessential property of such molecules is their ability to self organise and form aggregates with conjugated molecular cores stacked on top of each other and the branched chains or chromophores surrounding the columns.

This chapter reports on structural studies using AFM, SEM and TEM performed on selected perylene derivatives as well as on their optical limiting properties. Deposition of the derivatives on selected substrates by a variety of methods allows the recommendation of the best method for device fabrication. The structural studies also assist in the determination of the aggregation properties of the molecules, which are difficult to evaluate by computational techniques.

6.2 Experimental

Stock solutions of perylene derivatives were prepared in spectrophotometric grade chloroform and acetone at 1×10^{-3} M concentration. The stock solution was diluted down to 10^{-9} M concentration order in one third and one quarter steps. The cleaning procedure for silicon(111) wafers was as follows; successive rinsing in acetone and isopropyl alcohol followed by de-ionised water, boiling in base piranha for 30 minutes, washing each die in de-ionised water and drying gently with air duster or argon gas. The indium tin oxide and glass substrates were cleaned by sonicating in a de-con 90 and de-ionised water mix for one hour, rinsed successively and thoroughly with de-ionised water followed by isopropyl alcohol, boiled in isopropyl alcohol for 15 minutes and blow dried by an air duster or argon gas.

The dilution series were drop cast and spin cast at different high and low revolutions per minute onto the Si (111), ITO and glass substrates for AFM and SEM imaging. Some Si (111) wafers were left standing in the diluted solutions for 2-3 hrs prior to AFM and SEM imaging and allowed to dry out in air due to volatile solvents used. Thin films of perylene derivatives were prepared by thermo sublimation at 1×10^{-6} torr onto the substrates for AFM and SEM imaging. Samples for TEM imaging were prepared in two ways; solid state by simply dropping the dye molecules onto TEM grids and solution samples by drop casting onto SiN TEM grids prior to imaging.

The structural studies were carried out on Nanoscope 111a and Nanosurf Easyscan 2 AFM machines, a Hitachi S-4300 Field Emission microscope operating in high vacuum mode for HRSEM images and a Jeol 2100 Transmission Electron Microscope for TEM. The optical limiting properties for each perylene derivative were performed as described in section 4.3.3.

6.3 Results and discussion

6.3.1 Structural studies

General summary

The structure and aggregate morphology of the perylene derivatives was studied using AFM. SEM and TEM provided measurements and data of the structures. Images taken at different positions for each sample yielded similar results for each sample. All SEM and TEM micrographs show evidence of a large quantity of nanoparticles. The perylene derivatives showed different nanostructures. The morphology of the nanostructures depends strongly on the chemical structures of the perylene derivatives. Since all the perylene derivatives studied here have a perylene core, the nanostructures are strongly controlled by the side groups attached to the perylene core.

However similar trends exist in the morphology and distributions of each family's nanostructure as regards variation of parameters like concentration, spin rate, thickness and method of sample preparation for the structural studies. Concentration does not appear to affect the "grain" size the nanostructures but rather affects the heights of the nanostructures. In the perylene derivatives where thin films were produced by spin coating, the highest spin rates produced the thinnest film with the roughest surface, while the lowest spin rate produced the thickest films with the smoothest surface.

Where spin coating did not produce a thin film but nanostructures, higher spin rates had higher roughness than lower ones. The nanostructures and patterns produced by drop casting were the same as those produced by spin casting and only differed in the distribution of the nanostructures over the substrate.

For thermo sublimated films of the perylene derivatives, there was an increase in surface roughness with increased thickness independent of the substrate type whether glass or ITO. However, for the same thickness and same perylene derivative, the surface roughness was slightly lower for films on glass than that on ITO. Overall, the thermo sublimated thin films on both glass and ITO are very smooth with an average roughness of less than 2nm.

Figure 6.1 shows the AFM micrographs of plain substrates used in this study. The roughness figures are 0.12 nm, 0.61nm and 1.5 nm for silicon, glass and ITO respectively.

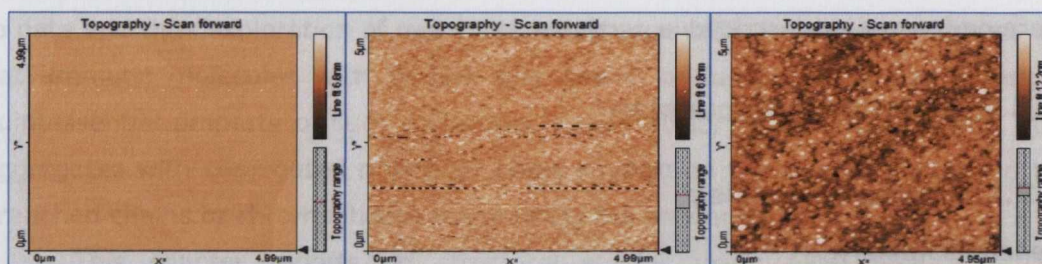


Figure 6.1 AFM micrographs of plain substrates used in this research. From L to R: Si (111), Glass and Indium Tin Oxide (ITO)

An individual perylene derivative structural analysis is provided below.

Perylene Red

Figures 6.2 and 6.3 shows typical AFM images of perylene red solutions from Si(111) wafers dipped into 4.12×10^{-6} M chloroform and drop cast from 3.33×10^{-4} M acetone solutions respectively. In both cases, AFM data show distinct cylindrical nanopillars. The nanopillars have an almost constant height of 10 nm but varying diameters for the chloroform solution whereas the heights are about 30nm and almost the same diameter for the acetone solution. The constancy of the height is reflected in the image roughness values r_a . The difference in heights is attributed to differences in concentration where the higher concentration has more of the molecules than the lower concentration.

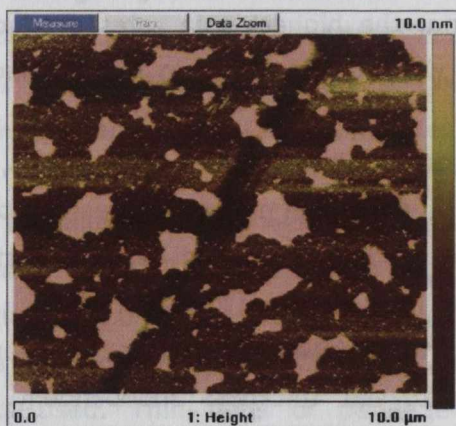


Figure 6.2 Planar and 3D AFM micrographs of perylene red prepared by "dipping" silicon (111) wafers into a spectrophotometric grade chloroform solution ($r_a = 3.45$ nm).

The agglomeration of the molecules in the different solvents is evident and could be attributed to solvent polarity, solubility of the molecule in the solvent as well as the rate of evaporation of the solvents. Chloroform evaporates almost twice as fast as acetone.

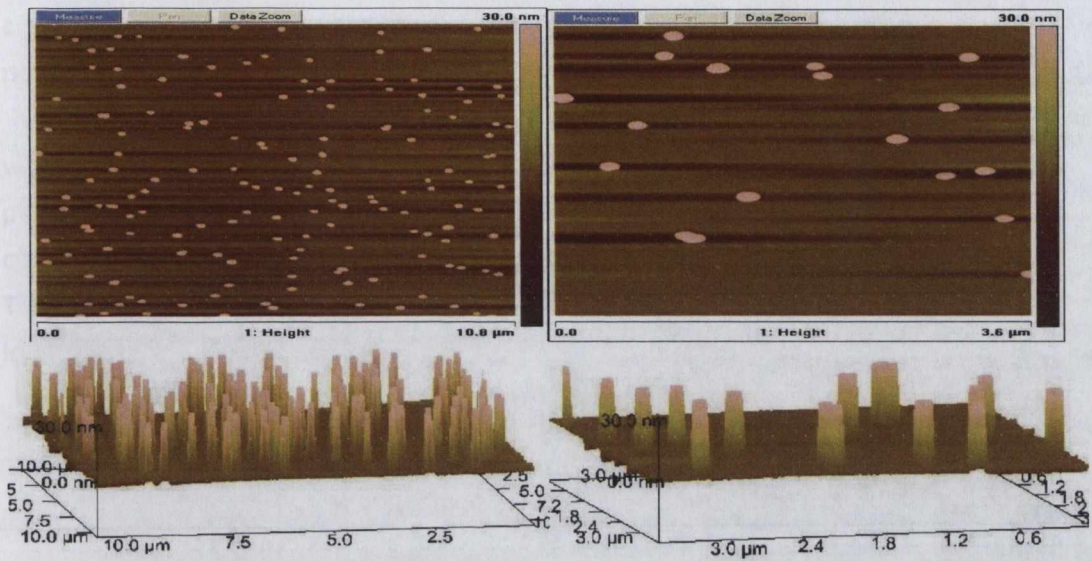


Figure 6.3 Planar and 3D AFM micrographs of perylene red drop cast onto silicon (111) wafers from a spectrophotometric grade acetone solution ($r_a = 2.36$ nm for left images and $r_a=1.79$ nm for the images on the right).

The diameter distributions of the cylindrical nanopillars are evident from both the gold coated SEM image and the TEM image in figure 6.4. The TEM image also shows the agglomeration of the perylene red nanoparticles. The average diameters of the nanoparticles and nanopillars are in the range 50 – 100 nm. The area number density of particles with the mean height is 1.5×10^{12} per m^2 .



Figure 6.4 SEM (left) and TEM(right) micrographs of perylene red drop cast onto silicon (111) wafer and SiN grid respectively from a spectrophotometric grade chloroform solution

Such distinct cylindrical nanopillars whose heights can be controlled by concentration can be very useful in optoelectronic applications where they can form part of an electric circuit or even as a photo luminescent nanostructure in either case activated by a current via an STM tip.

Perylene Orange

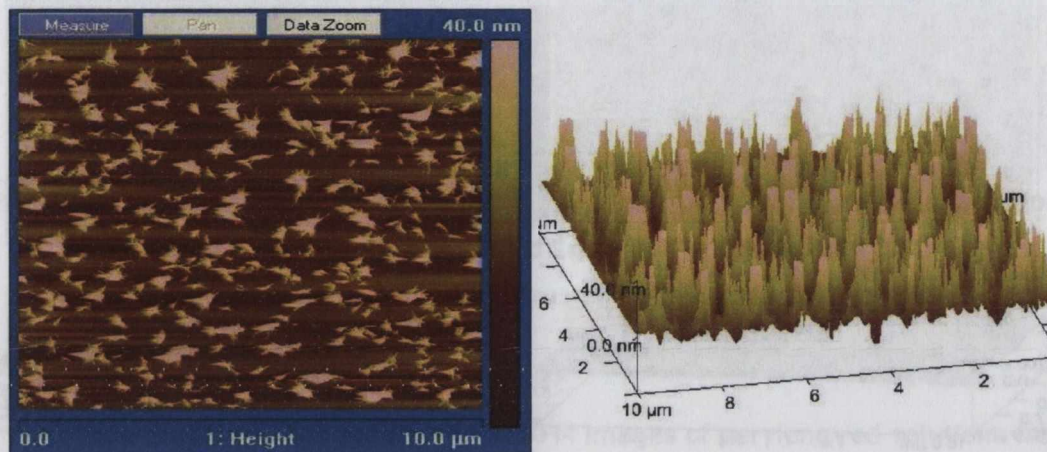


Figure 6.5 Planar and 3D AFM micrographs of perylene orange drop cast onto silicon (111) wafers from a spectrophotometric grade acetone solution ($r_a = 1.29$ nm)

The planar and 3D AFM micrographs of perylene orange Si(111) wafers dipped into 3.33×10^{-4} M spectrophotometric grade acetone solution are shown in figure 6.5 and display near conical nanospikes of 40nm heights. Just as in the case of perylene red, the agglomeration of perylene orange is an activity whose function is dependent on parameters like solvent polarity, solubility of the molecules in the

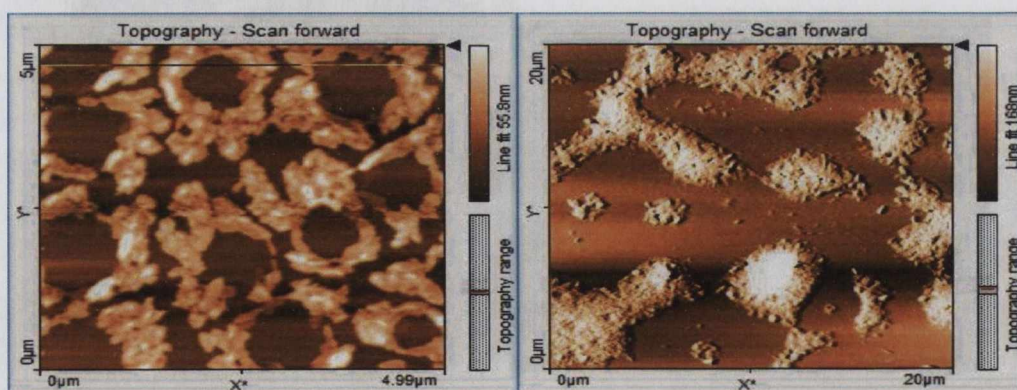


Figure 6.6 AFM micrographs of perylene orange drop cast onto silicon (111) wafers from a spectrophotometric grade acetone solution (left) and chloroform (right).

solvent, rate of evaporation of the solvent as well as the substituted chromophores onto the perylene core. This is also evident from the AFM micrographs of drop cast solutions of the same molecule from acetone and chloroform as shown in figure 6.6. It would appear that same grains of the nanostructures are evident but the agglomeration is different. The bigger structures are made of aggregated smaller nanoparticles.

However, when the same chloroform solution is spin cast onto the silicon wafers, the resulting structures are almost similar to the cylindrical nanopillars produced in the case of perylene red reported above. The nanopillars are more cylindrical with higher spin rates but have smaller heights as shown in Figure 6.7. The nanopillars have higher heights and larger diameters at low concentration and low spin rate.

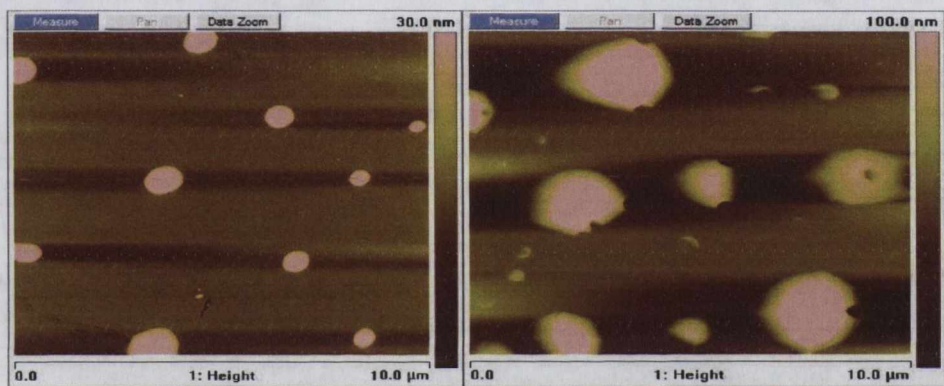


Figure 6.7 AFM micrographs of perylene orange spin cast onto silicon (111) wafer at 4500rpm (left) ($r_s=2$ nm) and 500rpm(right)($r_s= 17.5$ nm) from spectrophotometric grade chloroform solutions.

The TEM image in figure 6.8 shows the diameter distributions of the perylene orange nanoparticles which range between 50 and 100 nm.

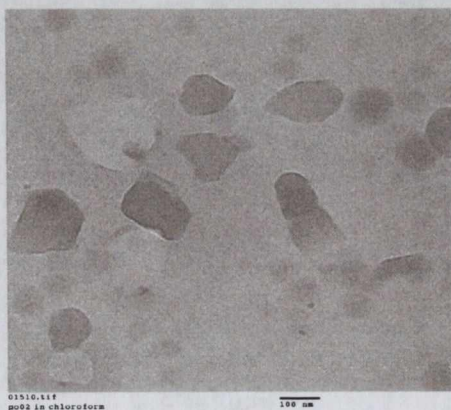


Figure 6.8 TEM micrograph of perylene orange drop cast onto SiN grid from a spectrophotometric grade chloroform solution.

Perylene blue

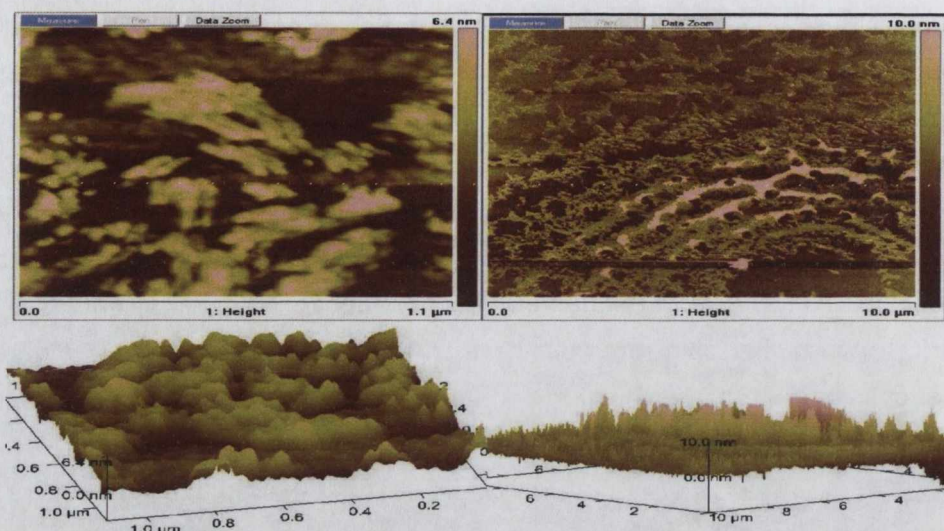


Figure 6.9 Planar (top) and 3D(bottom) AFM micrographs of perylene blue drop cast (left) and spin cast (right) onto silicon (111) wafers from a spectrophotometric grade acetone solution ($r_a = 1.17$ nm for drop cast image and $r_a=3.94$ nm for the spin cast images)



Figure 6.10 SEM (left) and TEM (right) micrographs of perylene blue spin cast and drop cast respectively onto Si (111) and SiN wafers from a spectrophotometric grade solution.

Figure 6.9 shows results of structures formed by drop casting and spin casting perylene blue onto Si (111) wafers. The results are consistent with findings reported above for perylene red and perylene orange. Structural reports on perylene blue have been provided in Chapter 4.

Perylene yellow

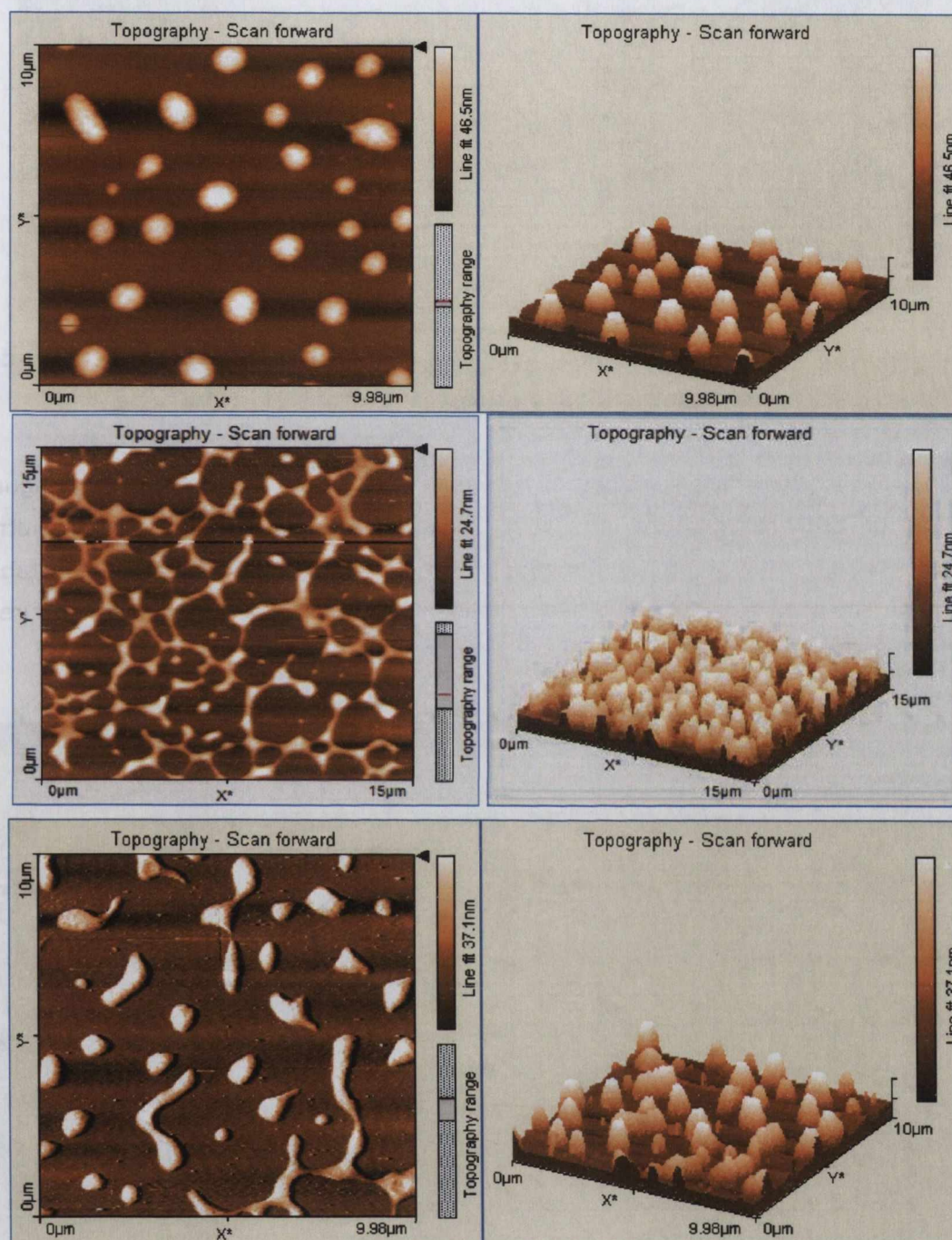


Figure 6.11 Planar (L) and 3D (R) AFM micrographs of spin cast perylene yellow spectrophotometric grade chloroform solution onto Si(111) wafers.

Figure 6.11 shows AFM micrographs of perylene orange spin cast at different rates onto Si wafers. Conical nanostructures or nanocones are formed and become more conical with increased spin rate. Most of the nanocones have a height of 40 nm and have an area number density of 2.1×10^{11} nanocones per m^2 . The roughness of the nanostructures is 5.2 nm.

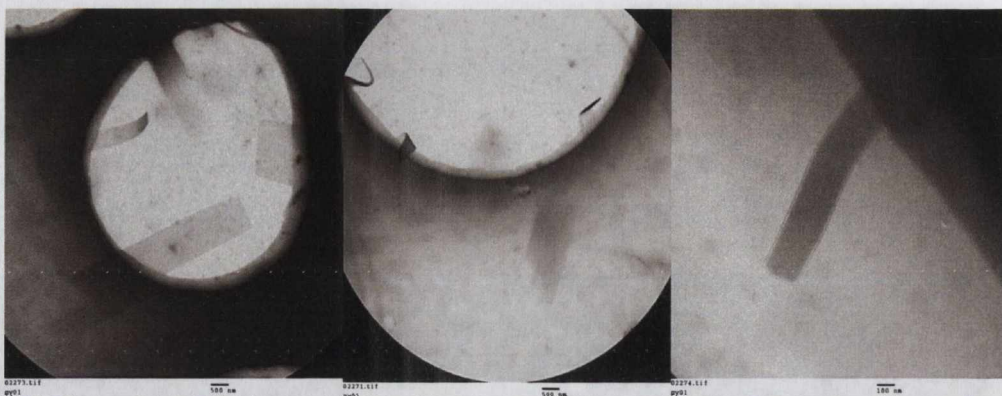


Figure 6.12 TEM micrographs of perylene yellow spectrophotometric grade chloroform solution drop cast onto SiN grids.

Whilst spin cast solutions of perylene yellow show nanocones as in figure 6.11, the drop cast images form very unstable nanobelt aggregates with widths between 100 and 500 nm as shown in figure 6.12. These nanobelts are unstable and are easily bent or melt by a beam of electrons as is evident in the same figure.

Perylene Violet

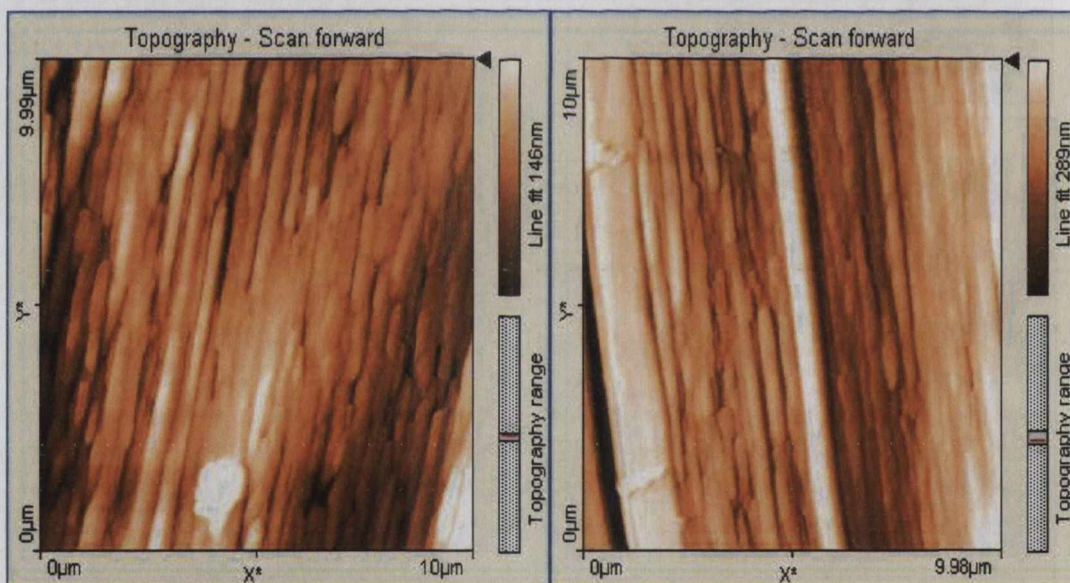


Figure 6.13 AFM micrographs of perylene violet spectrophotometric grade chloroform solution drop cast onto Si(111) wafers.

Perylene violet when drop cast onto silicon wafers produce rodlike nanocrystals of different lengths as shown in figure 6.13. However, when spin cast, different size wedge shaped nanocrystals result depending on the spin speed and concentration as shown in figure 6.14. These micrographs were obtained from 5g/l concentrations of perylene violet due to its high solubility in chloroform.

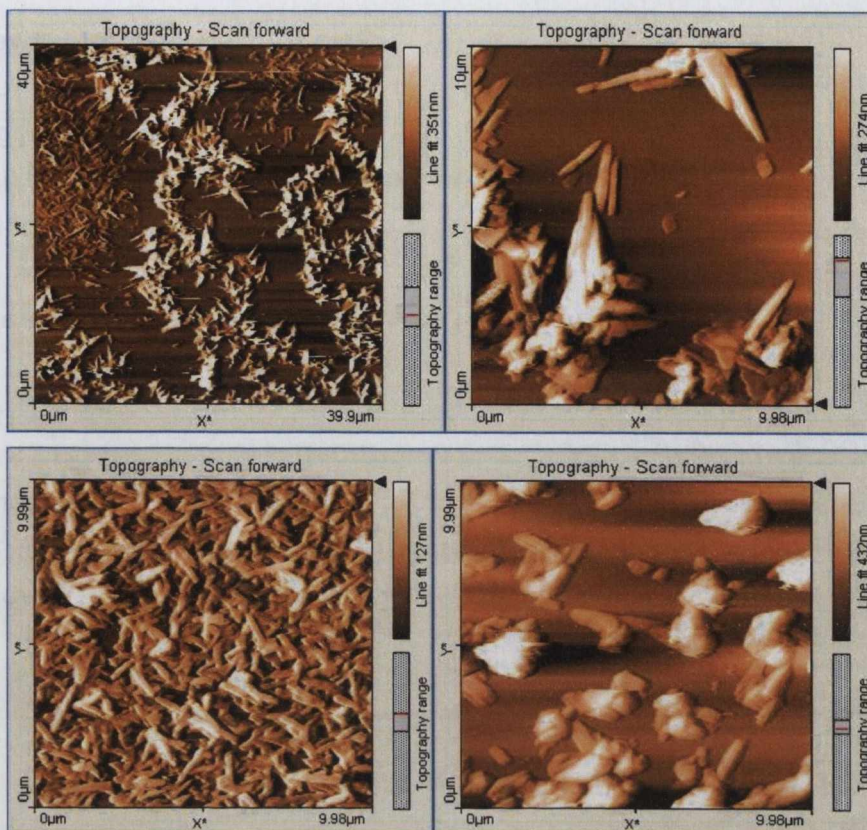


Figure 6.14 AFM micrographs of perylene violet spectrophotometric grade chloroform solution spin cast onto Si(111) wafers.

Thermosublimation on ITO and Glass substrate

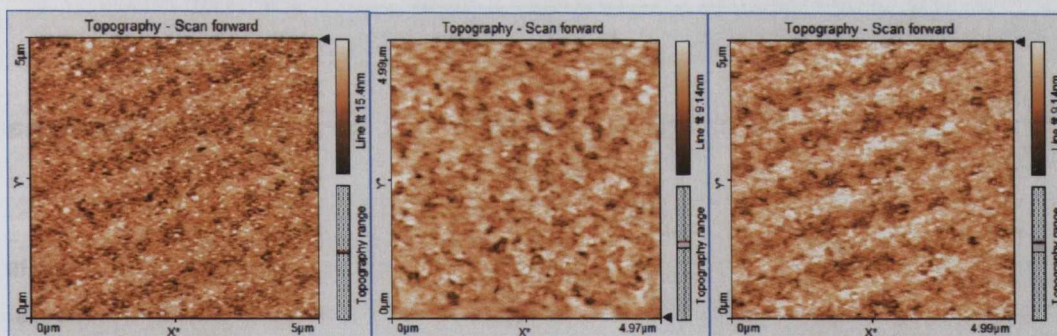


Figure 6.15 AFM micrographs of thin films of (L to R) perylene red, perylene orange and perylene yellow onto ITO substrates.

As shown in figure 6.15, the thin films of the perylene derivatives thermally evaporated onto ITO were very similar and very smooth with roughness of less than 2 nm and in most cases at 1.3 nm. There was no change of film morphology with film thickness over the experimental range from 30 nm to 150 nm. Whilst perylene yellow appears to have films indicative of Stranski-Krastanow (SK) growth mechanism where very small crystals (crystallites) form on top of a smooth

underlayer, this could be available over all the thin films of other derivatives but to an unobservable state limited by the instrument. The increase in intensity of absorption with film thickness evident in Chapter 5 Section 5.3.3 suggests SK growth in all films and may be caused by formation of aggregates in the films(17). Film morphologies on glass substrates were also very smooth with a slightly lower roughness than that of those grown on ITO. This makes these substrates good for device fabrication, particularly ITO which comes along with the ITO side as one of the electrical contacts.

6.3.2 Optical limiting

Open aperture Z-scan was used to investigate the non linear optical properties of the perylene derivatives inorder to test the possibility of their possible application in non-linear optics related applications as listed in the introductions both to this chapter and chapter 4.

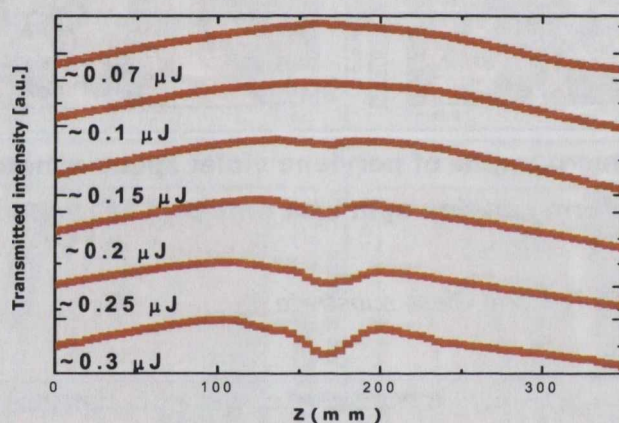


Figure 6.16 A Z-scan signature of a 1g cm^{-3} chloroform solution of perylene orange.

For the perylene orange solutions, strong yellow amplified spontaneous emission (ASE) and cavity lasing were observed when excited by 532 nm lasers. The perylene orange molecule can therefore find use in laser applications. However, optical limiting can occur at very high pulse energy which is not ideal (see Figure 6.16).

Perylene yellow, perylene violet and perylene blue all showed some intensity dependent nonlinear extinction effects. The presence of clear discontinuity in the optical limiting trace for perylene blue as shown in figure 6.17 suggests that the optical limiting is probably due to the non-linear scattering where the initial

scattering centres are nanoparticles formed by the aggregation of the molecules which was confirmed as reported in Chapter 4 section 4.4.5.

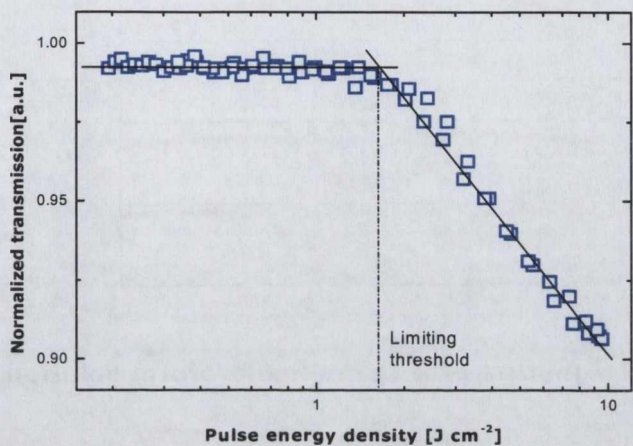


Figure 6.17 Evidence of limiting threshold from optical limiting trace of perylene blue.

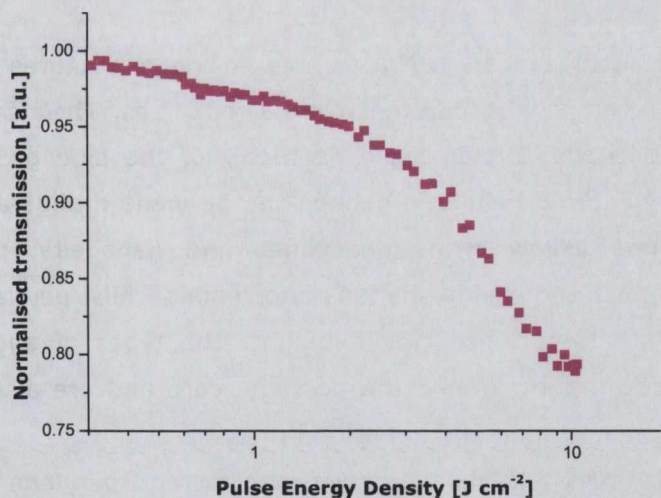


Figure 6.18 Evidence of limiting threshold from optical limiting trace of perylene yellow.

The solutions of perylene red have strong absorption for the 532 nm laser light. The absorption coefficient was determined as 6.83 cm^{-1} for 1g/L. At lower incident energy, typical saturable absorption (SA) was observed. As the energy increases, an apparent dip was seen near the focal spot in z direction (higher intensity region), which indicates the reverse saturable absorption (RSA) behaviour

as shown in figure 6.19. The non-linear absorption of RSA materials is exploited to decrease the transmittance of a material of a high input energy whilst the

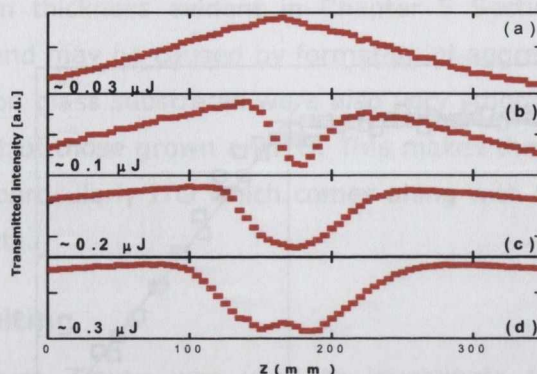


Figure 6.19 A Z-scan signature of a 1g cm^{-3} chloroform solution of perylene red.

material is kept transparent at low input energy as an ideal optical limiter requires(18). Hence the perylene red molecule can find an application as a passive optical limiter in such cases as devices for protection of sensitive optical elements and eyes from laser damage.

6.4 Conclusions

Perylene derivatives can self-assemble in nanostructures with different motifs which can result also in different charge mobilities. Their self-organisation abilities are controlled by changing the geometry of the side groups about the perylene core. Perylene red results in nanopillars, perylene orange aggregates into nanospikes, perylene yellow forms nanocones and nanobelts, perylene violet aggregates into tubular and wedge shaped nanocrystals whilst perylene blue barely forms nanoaggregates less than 7nm in height. The types of aggregates result mainly from the side groups around the perylene core and are also a function of other factors like concentration and deposition method.

Perylene red, perylene violet, perylene yellow and perylene orange do not easily form thin films from solution and hence device fabrication is recommended by thermal sublimation. They also form very smooth films on glass and ITO substrates.

Optical limiting results indicate that all the perylene derivatives studied herein are promising materials for photonic devices based on TPA processes. The optical limiting is controlled by the agglomeration of nanoparticles in solution.

6.5 References

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Chapter 7

7.1 Conclusions

In this dissertation, it has been demonstrated that the side group attached to the perylene core of perylene derivatives controls most if not all the properties of the molecules. Control of properties like absorption, emission, colour, thermal stability and aggregation control by different chromophores attached to the perylene core has been illustrated and investigated. From solutions at 10^{-3} M concentration, the molecules can give ordered structures in a variety of motifs ranging from nanobelts, through nanospikes and nanocones to cylindrical nanopillars. The self organisation of these molecules is dominated by J-aggregate formation.

Dilute solutions of the perylene derivatives showed evidence of monomeric absorption whilst concentrated solutions and thin films were evident of excimer emission or the existence of higher aggregates.

Molecular modelling was found to be a useful tool in predicting most properties of new and nonexistent molecules prior to their synthesis. The geometrically conformable structure were synthesised and characterised as well as compared to the predictions made by the modelling.

This thesis also emphasised the need to design and synthesis new materials that can be processed in solution so making device fabrication less expensive and hence more accessible to most people. A typical blue emitting solution processible perylene derivative was produced with a view to controlled aggregation which was confirmed experimentally by a variety of methods. The bulky alkyl chains on the perylene core reduce aggregation and improve solubility as well as charge carrier abilities. The optical limiting properties of this new molecule were compared to some commercial products and so contributing to the library of the use of perylene derivatives in two photon absorption controlled processes.

The perylene derivatives were established to be thermally stable up to 400 °C so making them very promising candidates in high temperature operations due to their other superiority over their counterparts in terms of photoluminescence and chemical stability. The molecules also form very smooth thin films when thermally deposited onto conventional substrates.

The exciton binding energy of the derivative of perylene was determined to be 1 eV, which is the same as of most organic semiconductors and is typical of Frenkel type excitons.

7.2 Future work

With such a range of attractive properties, the perylene derivatives can have a wide variety of applications. It would be worth the investment to test actual devices made from these materials particularly in more obvious applications such as solar cells, organic light emitting diodes and optical limiters. Perylene derivatives are n-type semiconductors and in contrast to a wide variety of p-type materials, the shortage of electron transporting materials is obvious hence there is the possibility of their use as active layers in photovoltaic devices and field effect transistors. For photovoltaic, bulk heterojunctions could be tested as they are expected to give higher efficiencies than bilayer structures due to increased interfacial areas where the exciton dissociation can occur.

Two photon absorption based applications like optical limiting and two photon pumped up conversion lasing need to be tested for these materials since the derivatives display high absorption cross section. The optical limiting study can be extended to mixtures with other materials like carbon nanotubes.

The perylene derivatives can be used to fill up mesoporous pores in which carbon nanotubes have been partially grown. The resulting nanotube array will be used to fabricate an organic light emitting diode where the tubes form an electron transport layer and the organic material forms the hole transport layer.

By driving current through an STM tip into the nanostructures of the perylene derivatives, resulting photoluminescence can be studied. Where conductivity is high, the nanostructure can act as part of an opto-electronic circuit.

Synthesis of more perylene derivatives and their materials science study will lead to a better understanding of these materials which appear to know no bounds as regards optoelectronic applications simply because they are very chemically tunable.

7.3 List of publications

1. **C. Kufazvinei**, M. Ruether, J. Wang, W. Blau, "A blue light emitting perylene derivative with improved solubility and aggregation control; synthesis, characterisation and optical limiting properties." *Organic Electronics* 10 (2009) 674–680.
2. D. Barreca, W. J. Blau, F. C. Dillon, J. D. Holmes, **C. Kufazvinei**, M. A. Morris, T. R. Spalding, and E. Tondello, "Mesoporous silicas impregnated with cobalt and nickel oxide nanoparticles and the growth of carbon nanotubes there from." *Journal of Nanoscience and Nanotechnology* Vol.8, 1–10, 2008.
3. D. Barreca, W.J. Blau, G.M. Croke, F.A. Deeney, F.C. Dillon, J.D. Holmes, **C. Kufazvinei**, M.A. Morris, T.R. Spalding, E. Tondello, "Iron oxide nanoparticle impregnated mesoporous silicas as platforms for the growth of carbon nanotubes." *Microporous and Mesoporous Materials* 103 (2007) 142–149.

Appendix

A1.1 Introduction

This appendix is a summary of the work done by the author parallel to the PhD research. The work involved a collaborative research with the University College of Cork and Intel Ireland. University College Cork prepared the platforms for carbon nanotube growth whilst the author from Trinity College Dublin characterised the platforms, grew carbon nanotubes in them and characterised the carbon nanotubes. To date two deliverables in the form of publications have resulted from this work. This work can be linked to the PhD research as described in chapter 7 or as indicated at the end of this appendix.

A1.2 Abstract

Tailored pore size mesoporous silica, synthesized by varying methods of incorporating different concentrations of transition metal-based catalysts, has been used as powder and thin film platforms for the growth of carbon nanotubes (CNT) by the catalytic chemical vapor deposition method. Compositional surface analysis by Energy Dispersive X-ray Analysis (EDX) combined with Scanning Electron Microscopy, thermo gravimetric analysis, Raman and Fourier Transform Infrared spectroscopy (FTIR), were employed to characterize the samples prior to CNT growth. The CNT produced were characterized using Raman Spectroscopy, high resolution SEM and Transmission Electron Microscopy (TEM).

For the powder samples, the supercritical fluid based samples were found to be unstable at temperatures above 450°C owing to the degradation of physisorbed materials during sample preparation. Apart from losses attributed to water, the transition metal based phythalocyanines, ferrocenes, iron chloride and iron incorporated by a post synthetic method samples were very stable over the high Catalytic Chemical Vapour Deposition (CCVD) temperature ranges and therefore suitable platforms for CNT growth. Good quality and low defect CNTs were synthesized especially from the phythalocyanine powder samples making them even more preferable over the other samples. Of the phythalocyanines, iron and cobalt doped samples proved to be superior over the nickel counterparts in the production of good quality and high quantities of CNTs over the tested range of 650°C to 800°C. Percentage loading of catalyst does not control the diameter of CNTs, but influences the quantity formed. The matching and direct proportionality of pore size to CNT diameter suggest that in-pore nanoparticles exert most control over CNT diameter. Samples with the highest loading showed more amorphous carbon than those with lower loading.

Ferrocene and phthalocyanine based thin film samples, calcined slowly at high temperatures, preserved the mesostructure during CCVD and hence made better platforms for CNT production by that method. Raman evidence has indicated possible in-pore growth of CNT in both thin film and powder transition metal catalyzed mesoporous silica samples.

A1.3 Motivation and justification

The science of carbon was given a new dimension by the discovery of "fullerenes" (1). The discovery of the elongated fullerene or carbon nanotubes added a new dimension to technology. Since their discovery in 1991 by Iijima(2), carbon nanotubes have attracted research from all fields of science. Their fascinating structural, physical and chemical properties are the backbone to curiosity-driven research with an aim for commercially viable applications. By incorporating carbon nanotubes into appropriate matrices, the resulting composites are expected to have enhanced mechanical, thermal and electrical properties. Recent reports list transparent conducting, low weight structures, antistatic and electromagnetic shielding as realistic applications of carbon nanotube composites(3). Carbon reinforced polymers are well known materials (4), combining the properties of elongation, flexibility and tensile strength of polymers with the stiffness and rigidity of ceramic carbon fibres. Carbon fibres are conveniently prepared but may be of limited strength because of the presence of defects which tend to make them brittle. Due to limited fibre-polymer bonding and effects such as 'pull-out' and crack initiation, the fibre reinforced materials do not have optimum strengths. Carbon reinforcement of ceramics is less well known. Ceramic matrix materials are tough; addition of high thermal conductivity carbon nanotubes (CNTs) will reduce operating temperatures as well as enhance thermal shock resistance(5). Mesoporous silica has been shown to be an effective host for well regularized and patterned carbon nanotubes(6), more so without sintering of catalytic metals(7).

In this study, CNTs will not be used as simple composite filler where material is added randomly to a ceramic precursor, but rather we aim to grow CNTs within the pore system of mesoporous silica. This will give a very homogeneous distribution of reinforcing agent as well as a very uniform material with isotropic properties. By growing the CNTs within the pore system, reinforcement pull out and nanotube size dependent strength problems are avoided. The principal aim is to provide ceramic materials with increased thermal conductivity and mechanical strength for envisaged use as thermally conductive substrates for microprocessor die mountings and as efficient electron transport layer in small molecule organic light emitting diodes. The latter application is attributed to the high electron mobility in carbon nanotubes. The

small molecules for this study will be perylene red, perylene orange, perylene violet, perylene yellow and 3,4,9,10-tetra-(12 alkoxy carbonyl)-perylene all of which have been characterised (see main thesis). Other possible uses include as coatings in the electronics industry, packaging and electronic-textile applications(8). Catalytic chemical vapour deposition (CCVD) is used for the growth of nanotubes due to superior advantages over other conventional methods.

A1.4. Carbon Nanotubes

A1.4.1 Introduction to Carbon Nanotubes

The discovery of geometric cage-like open and closed honeycomb atomic structured carbon allotropes known as fullerenes ushered a whole new dimension to the chemistry of carbon. Kroto et al. reported their discovery of the first such structure, the C₆₀ molecule, in 1985. The subsequent discovery of elongated fullerenes or carbon nanotubes (CNTs) reported by Iijima et al (2) in 1991 added a new dimension to technology. CNTs are rolled up sheets of sp² bonded graphite without any surface broken bonds. The resulting hexagonal carbon walled tubules are about a nanometre in diameter and several microns long thus giving them a high aspect ratio (length to radius ratio). Single walled nanotubes (SWNT) can be regarded as the fundamental cylindrical structure and hence the building blocks of multi-walled nanotubes (MWNT) and ordered arrays of SWNT called ropes or bundles. MWNT result from concentric SWNT of approximately 0.34 nm separation. The CNTs exhibit exceptional material properties mechanically, thermally and electrically. Their possible high performance over conventional materials as well as their microscopic nature has attracted a lot of attention and interest from scientists, journalists, governments as well as the public. A whole new branch of technology called nanotechnology has been born out of studying the possible applications of CNTs.

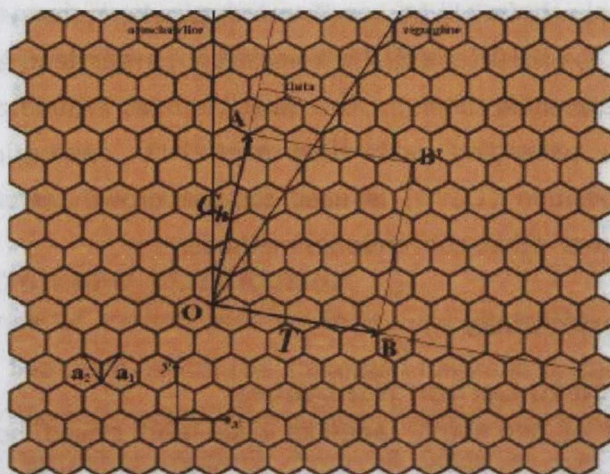


Figure A1.1: Graphene sheet and how it can be “rolled up” to different nanotubes.

A SWNT can be described as an infinite single layer of graphite that has been “rolled up” into a seamless tiny hollow cylinder. The nanotube can be uniquely specified by a pair of integer numbers n, m or by its radius $R = C_h/2\pi$ and chiral angle θ , which is the angle between the chiral vector $\mathbf{C}_h$ and the nearest zigzag of the C-C bonds i.e. the $\mathbf{a}_1$ direction. The chiral or roll-up vector $\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2$ connects two lattice points O and A on the graphene sheet (Figure A1.1.). All different tubes have angles θ between zero and 30° . Achiral tubes have mirror symmetry and can be classified as armchair when $n = m$ and $\theta = 30^\circ$ or zigzag with $m = 0$ and $\theta = 0^\circ$. All other tubes are called chiral. The chiral vector can also define CNT diameter since the interatomic spacing of the carbon atoms is known. The nanotube diameter d_t can be written in terms of the integers (n, m) as:

$$d_t = C_h/\pi = \sqrt{3}a_{cc}(m^2 + mn + n^2)^{1/2}/\pi,$$

where a_{cc} is the nearest neighbor C-C distance ($1.421 \text{ \AA}$ in graphite), and C_h is the length of the chiral vector $\mathbf{C}_h$. The chiral angle θ is given by:

$$\theta = \tan^{-1} [\sqrt{3}m / (m + 2n)].$$

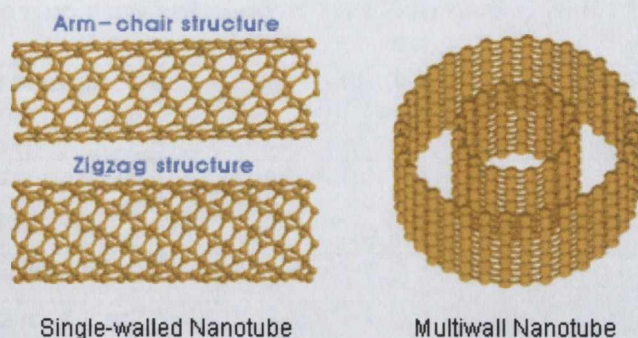


Figure A1.2: Structures of CNTs.

A MWNT can present each structure because it can have several shells, i.e., each of which can be armchair, zigzag or chiral (Figure A1.2).

A1.4.2. Properties of Carbon Nanotubes

The properties of carbon nanotubes depend heavily on the atomic arrangement or how the graphene sheet is "rolled up", their aspect ratio and the morphology or nanostructure. The chirality or helicity has significant implications for the material properties.

Chirality has a strong impact especially on the electronic properties of the CNTs. Whilst graphite is considered a semi-metal, CNTs can either be metallic or semiconducting depending on their chirality(9). The delocalised pi-electron donated by each atom is free to move about the entire structure giving high electrical conductivity to CNTs. Individual tubes have been observed to conduct electrons ballistically with coherence lengths of several microns(10). At 10^9 A/cm² (11), CNTs carry the highest current density of any known material. CNTs are thus nearly perfect 1- dimensional conductors. The CNT band gap varies with chirality of the tube. An armchair tube (n, n) ($\theta = 30^\circ$) will have metallic behaviour. Zigzag ($n, 0$) ($\theta = 0^\circ$) and chiral tubes will have metallic behaviour if $(n-m) / 3 = i$ where i is an integer otherwise semi-conducting behaviour is observed. In this case, the energy gap will depend on the diameter of the tube.

Before the discovery of CNTs, diamond was the best known thermal conductor. Experimental evidence exist that CNTs have a thermal conductivity at least twice that of diamond(12). High frequency C-C bond vibrations provide the intrinsic thermal conductivity.

Table A1.1 Comparison of SWNT properties with current materials

Property	Single-walled nanotubes	Comparisons
Size	0.6 – 1.8 nm in diameter	Electron beam lithography can create lines 50nm wide
Density	1.33 to 1.4 g/cm ³	Aluminium = 2.7 g/cm ³
Tensile strength	45 GPa	Steel alloys break at 2 GPa
Resilience	Can be bent at large angles and re-straightened without damage	Metals and carbon fibres fracture at grain boundaries
Current carrying capacity	Estimated at 1 GA/cm ²	Copper wires burn out at about 1MA/cm ²
Heat transmission	6 kW/m/K	Nearly pure diamond transmits 3.32 kW/m/K
Temperature stability	2,800°C in vacuum, 750°C in air	Metal wires in microchips melt between 600 – 1000 °C

The Young's Modulus and tensile strength of high strength steel are about 200 GPa and 1-2 GPa respectively. The corresponding values for CNTs are 1.4 TPa (13) and 100 GPa, making them the stiffest, strongest and toughest material known to date. These exceptional mechanical properties are attributed to the C-C sp² bonding, the flexibility of the graphene sheet and the possibility for carbon atoms to rehybridize themselves with an sp²/sp³ hybridizing degree dependent on the stress.

CNTs have the chemistry of carbon and hence can be reacted and manipulated with the richness and flexibility of other carbon molecules. At molecular level, they are essentially defect free. Strong Van Der Waals attraction can lead to spontaneous roping of CNTs giving them self-assembling properties. With such intriguing properties, it is not amazing that CNTs have a wide variety of possible applications which can only be realised after intensive research.

A1.4.3 Applications of Carbon Nanotubes

Only a nanometre in diameter, able to be both chemically and physically manipulated, possessing unique properties and high performance advantage over existing products (3), CNTs have found the market as a new product. Their varied superiority over conventional materials gives them an even wider range of applications. The diversity of applications range from electron field emitters, flat

panel displays, electro-catalysis of an oxygen reduction reaction in fuel cells, electrodes in batteries, high capacity hydrogen storage media, electronic devices and in composite materials. In this study, CNTs are used to reinforce ceramic materials. Research in nanotechnology, the creation of functional materials, devices and systems through control of matter at nanometre scale, has grown over the last thirteen years since the discovery of the CNTs and is centred on any promising application in any scientific field and the possibility of producing CNTs of desired properties in bulk quantities.

A1.4.4 Production of Carbon Nanotubes

Carbon nanotubes are generally produced by three main techniques, arc discharge, laser ablation and chemical vapour deposition. In arc discharge, a vapour is created by an arc discharge between two carbon electrodes with or without catalyst. Nanotubes self-assemble from the resulting carbon vapour. In the laser ablation technique, a high-power laser beam impinges on a volume of carbon-containing feedstock gas (methane or carbon monoxide). The target is vaporized in the high temperature argon buffer gas and forms nanotubes. In chemical vapour deposition (CVD), an energy source, such as plasma or a resistively heated coil, is employed to transfer energy to a gaseous carbon molecule from a hydrocarbon source. Table 2-2 summarizes the three most popular CNT production methods.

Table A1.2: Summary of CNT production techniques (14)

Arc discharge method	Chemical vapor deposition	Laser ablation (vaporization)
Ebbesen and Ajayan, NEC, Japan 1992	Endo, Shinshu University, Nagano, Japan	Smalley, Rice, 1996
Connect two graphite rods to a power supply, place them millimeters apart, and throw switch. At 100 amps, carbon vaporizes in a hot plasma.	Place substrate in oven, heat to 600 C, and slowly add a carbon-bearing gas such as methane. As gas decomposes it frees up carbon atoms, which recombine in the form of NTs	Blast graphite with intense laser pulses; use the laser pulses rather than electricity to generate carbon gas from which the NTs form; try various conditions until hit on one that produces prodigious amounts of SWNTs
Typical yield = 30%	20 to 100 %	Up to 70%
Can produce SWNT and MWNTs with few structural defects	Easiest to scale to industrial production; long length	Primarily SWNTs, with a large diameter range that can be controlled by varying the reaction temperature
Tubes tend to be short with random sizes and directions	NTs are usually MWNTs and often riddled with defects	By far the most costly, because requires expensive lasers

Other production methods are the vapour phase, electrolysis and flame synthesis. The vapour method involves synthesis of carbon nanotubes by directly supplying reaction gas and catalytic metal in the chamber without a substrate. The electrolysis of molten lithium chloride using a graphite cell in which the anode is a graphite crucible at approximately 600°C in an argon atmosphere produces MWNT. In flame synthesis, combustion heat is a heating source of carbon nanotubes produced from combustion of CH₄ in the small amount of oxygen atmosphere. MWNT and SWNT are then synthesized by flowing hydrocarbon source like C₂H₂ over catalytic precursors in the diffusion flame atmosphere.

The CNT production method of choice in this study is the thermal catalytic chemical vapour deposition (CCVD). It offers superior advantages in the production of CNTs over other conventional methods(14). Even though accompanied with loss of crystallinity, CCVD is the simplest and most economic method for CNT production at low temperature and ambient pressure. Laser ablation and arc discharge methods have a high yield but rely on evaporation of carbon atoms from solid targets at temperatures higher than 3000°C and the CNTs produced are tangled and thus difficult to both purify and use in applications. In addition, CCVD is versatile by that it can harness a variety of

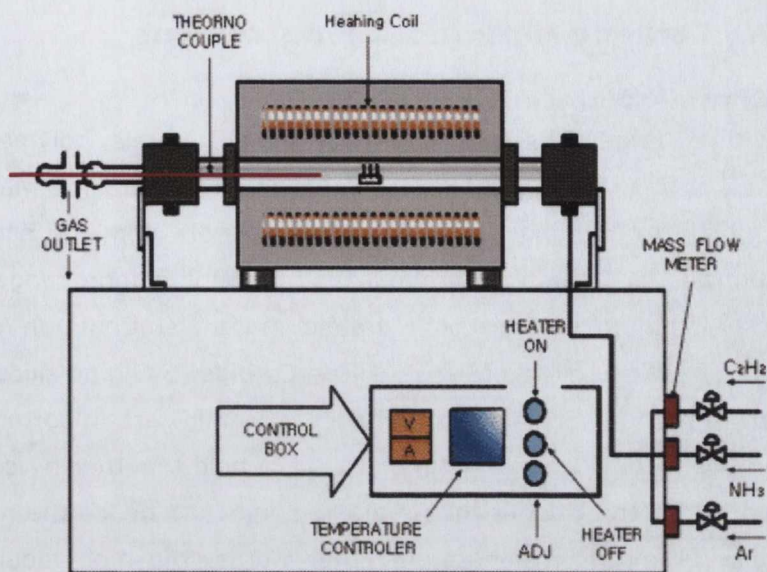


Figure A1.3: Schematic diagram of CNT growth by thermal CCVD.

hydrocarbons in any state, allows use of various substrates like powder, thin or thick films, and CNT growth is allowed in many forms such as aligned or entangled, straight or coiled, or even a desired architecture of CNTs on a patterned substrate. In CCVD, there is better control over growth parameters like temperature, pressure, carrier gas flow rate (3), and easy scale-up and directed placement, nanotube alignment and electronic component construction(15). The purity of the CNTs produced by CCVD can be controlled by careful process control.

A1.5. CNT Ceramic Materials Reinforcement

A1.5.1. Ceramic Materials

The three large classes of solid materials are metals, polymers and ceramics. Ceramics are defined as inorganic, non-metallic and crystalline materials. They are produced mostly by burning clays and other minerals from the earth or chemically processed powders. Though amorphous and without a long range of crystallinity, glass is classified as a subset of ceramic materials. Common ceramics include alumina (Al_2O_3), silicon nitride (Si_3N_4), silicon Carbide (SiC) and silicon dioxide (SiO_2).

Both the atomic and microstructure of ceramics are important in determining their properties. Atoms in ceramic materials are held together by covalent and ionic bonds which are both stronger than metallic bonds and hence the reason for metals' ductility and ceramics' brittleness. In other words, the high mobility of structural defects in metals leads to high ductility and inhibits propagation of cracks. The absence of this feature in ceramics accounts for their brittle nature(16). The microstructure of ceramics can be glassy, entirely crystalline or a combination of crystalline and glassy where the glassy phase usually surrounds small crystals bonding them together. As structural materials, ceramics outshine metals in advantages. With brittleness as the only disadvantage, structurally advantageous ceramic properties include low density, high rigidity, hardness, chemical inertness and low sensitivity to corrosion. Their wide range of properties gives ceramics a multitude of applications from structural through electrical and electronics, coatings and chemical processing. Electronic ceramics include capacitors, insulators, substrates, integrated circuit packages, piezoelectrics, magnets and superconductors. This study focuses on the application of SiO_2 in integrated circuits.

A1.5.2 Reinforcement of ceramics with CNTs

The combination of two or more materials to produce a new material with enhanced properties is called reinforcement and the new material is called a composite. CNTs have outstanding properties as previously outlined. By placing CNTs into appropriate matrices, the resulting composite will have enhanced properties. Composites so formed will benefit from the properties of CNTs. The motivation for CNT based composites for ceramic materials lies in that the incorporation of CNTs enhances toughness or resistance to crack growth. At high temperatures, the CNTs in the composite will provide thermal transport required to reduce material operating temperatures and improve thermal shock resistance. If the CNTs are aligned, they will thermally conduct along their length and will be completely insulating along the direction perpendicular to their length. In addition to the thermal conduction, the

composites will also be electrically conductive because of the presence of the CNTs (5). Thus a CNT reinforced ceramic composite is expected to be tougher than the conventional ceramic, to conduct both electricity and heat as well as act as a thermal barrier depending on tube orientation. It is the purpose of this study to produce such a material and apply it as a thermally conductive substrate in microprocessor die mountings as well as a transport layer in organic light emitting diodes. Other applications of this material would include coatings in the electronics industry.

The development of such a material is necessitated by the advancement of processors as the density of transistors has increased. An increase in transistor density is accompanied by an even higher increase in power density. Computer programming can deal with lowering power consumption but heat dissipation remains an issue. This advancement in density of transistors was predicted by Moore in 1965 (17) who expected the cost per processing cycle to drop but reasoned that power density problems would increase total costs dramatically. Heat dissipation is still determined by the thermal conductivity of the ceramic substrate (on which the chip is mounted) which allows heat to be transferred to the cooling mount. Thus the principle aim of this study is to provide ceramic materials with increased thermal conductivity and mechanical strengths. The ceramic material of choice in this study is mesoporous silica.

A1.5.3. Mesoporous Silica

Mesoporous silica is an excellent platform for the catalyzed growth of aligned arrays of CNTs due to its highly ordered pore structure. Stability of the mesophase at high CVD temperature is a key issue and in this regard, mesoporous silica is preferred over other counterparts like mesoporous alumina which has lower thermal stability, loses its intrinsic mesostructure, with only non-uniform macroporous structure being observed after high temperature exposure making the resultant CNT orientation uncontrollable(15). Also, the pore diameter of mesoporous silica is tunable using various methods and this allows some control of the size of the catalytic nanoparticle which gives rise to CNT growth.

To date, several attempts have been made to synthesize CNTs using iron particles both on the surface and inside the pores of mesoporous silica powders (18, 19) or films(20, 21). Various reports have shown a direct correlation between the size of the nanoparticle and the eventual tube diameter(22). In general, if nanoparticle precursors are incorporated via a post-synthesis technique, a wide range of CNT diameters is observed(23-25). If the nanoparticle precursor is incorporated within the mesoporous silica during its synthesis, the distribution of CNT diameters is much narrower. Li and co-workers were the first to demonstrate CNT

growth on Fe-incorporated mesoporous silica(21). Large-scale synthesis of aligned carbon nanotubes was achieved by a method based on chemical vapour deposition catalyzed by iron-derived nanoparticles embedded in mesoporous silica.

In this study, mesoporous silica samples incorporating different catalysts types and loadings methods are platforms for in-pore CNT growth by CCVD. The methods of preferential in-pore catalysts incorporation into the mesoporous silica matrix are also different. In addition to literature evidence of transition metal phthalocyanines being usable as catalysts for CNT growth, they offer an alternative over metal carbonyls in that they are cheap, non-toxic and non-volatile. This research allows an in-depth study and comparison of other catalyst types when used for CNT production with acetylene as the feedstock.

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A1.6. EXPERIMENTAL

A1.6.1 Platforms for CNT growth

The tailored pore size mesoporous silica samples, incorporating different concentrations of transition metal-based catalysts of Fe, Co and Ni were produced by the Dimensional Solids Group at the University College Cork, which has made considerable progress in the area of mesoporous solid synthesis(26, 27). Apart from the supercritical fluid based samples, the rest were produced in the same manner except for the catalyst source and addition method. Samples produced by the same method also varied in metal catalyst type and percentage loading. Table 5-1 summarizes the groups of mesoporous silica samples provided as platforms for CNT growth in this study.

Table A1.3: Platforms for CNT Growth

SAMPLE GROUP	CATALYST ADDITION
1. Supercritical Fluid (powder)	Post-synthesis formation of metal oxide by degrading transition metal carbonyl in <i>supercritical fluid</i> CO ₂
2. Phythalocyanine (powder and thin films)	In-situ addition of transition metal based <i>phythalocyanine</i>
3. Iron incorporated via a post synthetic route (powder)	OSi-CH ₃ functionalized mesoporous silica stirred in an iron acetate solution to form a thin layer of iron based nanoparticles in the silica pores after calcination.
4. Iron chloride (powder)	OSi-CH ₃ functionalized mesoporous silica stirred in an iron chloride solution to form a thin layer of iron based nanoparticles in the silica pores after calcination
5. Ferrocene (thin films)	In-situ addition of ferrocenes

A1.6.2. CNT Growth

Carbon nanotubes were grown by the catalytic chemical vapour deposition method using a home built CCVD system. The pressure of the system was reduced to 10⁻² mbar and its furnace temperature raised to 800°C. Argon carrier gas was flushed at 0.500 sccm allowing the system to reach equilibrium for 15 minutes. A steady 0.050 sccm flow of the acetylene carbon feedstock was then maintained for an hour over the transition metal-filled sample in a ceramic boat loaded into the CCVD system’s furnace. The sample was removed from the furnace for characterization

only after cooling to room temperature. These growth conditions were maintained on each sample before variations were made. The variations involved changing the CCVD temperature and feedstock flush time initially to 650°C for 10 minutes and then to 675°C for 15 minutes, whilst system pressure, carrier gas, feedstock and flow rates were maintained as in the original conditions.

A1.6.3 Characterisation

Prior to CCVD growth of CNTs, the target ceramic samples were imaged using a scanning electron microscope (SEM) operated in the variable pressure mode at 10 Pa. Compositional and surface analysis were performed using a PGT Spirit Energy Dispersive X-ray (EDX) Analysis system. The heat responses of the catalyst loaded samples in air were obtained using a Perkin Elmer Pyris 1 TGA thermo gravimetric analyzer by initially maintaining the sample temperature at 30°C for one minute and subsequently heating up to 950°C at 10°C per minute with 5580 points between runs. It was found necessary to do an FTIR spectrum analysis on the metal based phythalocyanine powder samples, after thermo gravimetric analysis in an inert environment to complete the characterisation before CNT growth. A NICOLET Nexus FT-IR instrument was used for FTIR. The powder samples were mixed with KBr in a 1:99 ratio with the larger share to KBr, ground to a fine mix and pressed into pellets for the FTIR study.

High resolution SEM imaging of the CNTs was carried out using a Hitachi S-4300 Field Emission Scanning Electron Microscope operating in high vacuum mode at 20 kV. It was necessary to coat the CNTs with a 10 - 15nm gold film due to the high SEM potential being used, so bringing charge build up to a minimum. A Jobin Yvon Raman System with a HeNe 20 mW laser polarized 500:1 at a wavelength of 632.817 nm was employed to characterize the CNTs. Each spectrum was averaged over ten accumulations with intensity variations between 10% and 100% adjusting the exposure times for optimization of noise reduction. TEM images were obtained by using a 0.5 nm resolution JEOL 2000 TEM instrument operated at 200 kV. The TEM grids were prepared by dispersing a very small amount of CNT containing sample in 20ml of chloroform and sonicated for 10 minutes. About 1 to 2 ml of the sonicated solution was then dropped onto a carbon coated copper grid for TEM studies.

A1.7. Results and Discussion

Thermal Stability

Thermo gravimetric analysis allowed comparisons of the thermal stability of catalyst platforms produced by different methods. This study is necessary as it is an important pointer towards whether a specific catalyst platform can be used over the CCVD temperature range.

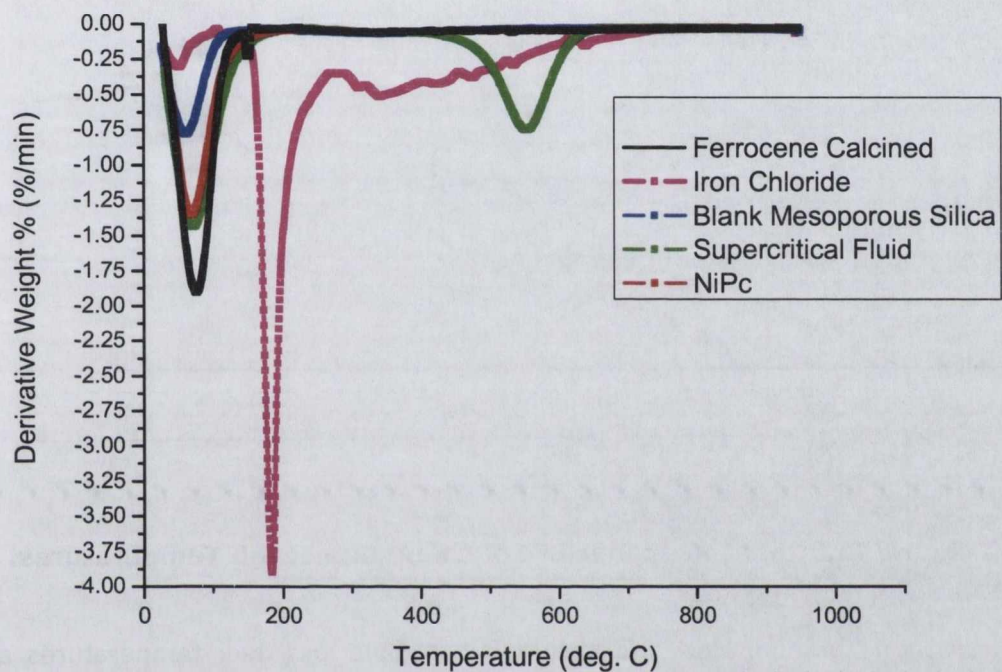


Figure A1.4: Heat Responses of Mesoporous Silica Catalysed Platforms.

All catalysts indicated a common event at around 100°C attributed to loss of absorbed water. Apart from the supercritical fluid based and iron chloride based platforms, all other samples are very stable over the CCVD temperature range. This stability makes them preferred to CNT growth.

The supercritical fluid based samples have weight losses ranging from 10% to 35% occurring between 475°C and 675°C giving them different inflection point temperatures. These losses are attributed to probable decomposition of physisorbed materials. The common occurrence of this decomposition above 450°C is explained by the calcination of these materials at that temperature. The range of decomposition is due to the difference in both the percentage loading and the metal carbonyl types degraded to form catalysts, as well as the surfactant type used in the mesoporous silica preparation. A parallel argument can be given for the iron chloride based samples. More studies towards stabilising these samples are in progress.

Figure A1.4. includes the heat responses of a nickel filled mesoporous silica phythalocyanine sample when heated in air to 950°C. The major event in this heat response occurs at 100°C and is largely attributed to desorption of water adsorbed on the particle surfaces. All metal phythalocyanine based samples show a similar trend only varying in the actual water loss, the largest of which occurs in the iron based phythalocyanine mesoporous silica sample at 45 %.

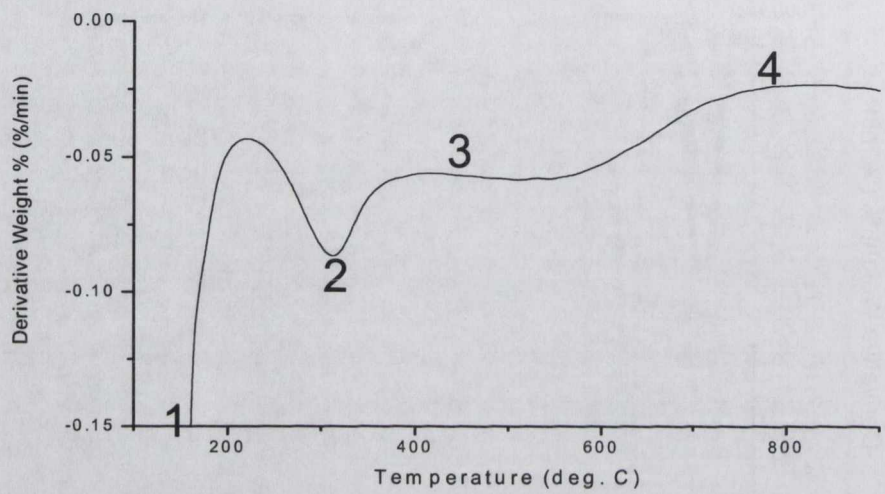


Figure A1.5: Heat Response of CoPc Sample at High Temperatures.

The remaining gradual slow and very low negligible loss over temperatures above 200°C (almost non-existent as observed from Figure A1.4, but clearer when expanded as in Figure A1.5), is attributed to organic substances. Figure A1.5 shows the magnified section for a copper based phythalocyanine sample. This loss can be broken down into three more distinct events as shown in Figure A1.5 where event 1 is still the water loss, event 2 represents the initial degradation contributing 2% to the loss in mass, event 3 represents another degradation of 2.5% loss whilst event 4 is attributed to either burn off or oxidation of 2% losses. The degradations can be explained from the organic constituents of the metal phythalocyanine based mesoporous silica samples.

Fourier Transform Infra Red Spectroscopy (FTIR)

FTIR was used to confirm that the loss at temperatures were insignificant in the production of CNTs. Performed on both the metal based phythalocyanines and on a blank (uncatalysed) mesoporous sample, FTIR after TGA to 950°C in a Nitrogen environment showed the same stretching vibrations and identical fingerprint regions. Since CNT growth was carried out in an Argon and hence inert environment, the very

low gradual losses at high CCVD temperatures would only negligibly affect the end product.

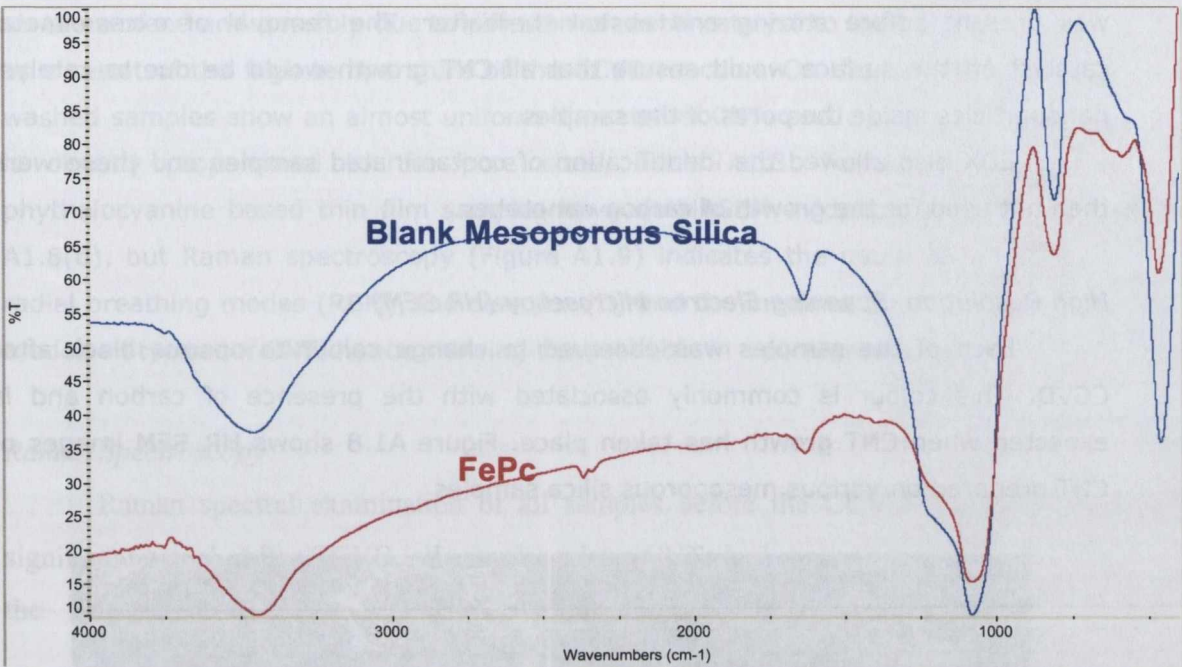


Figure A1.6: Comparison of FTIR Spectra of Blank and FePc Mesoporous Samples

Compositional and Surface Analysis

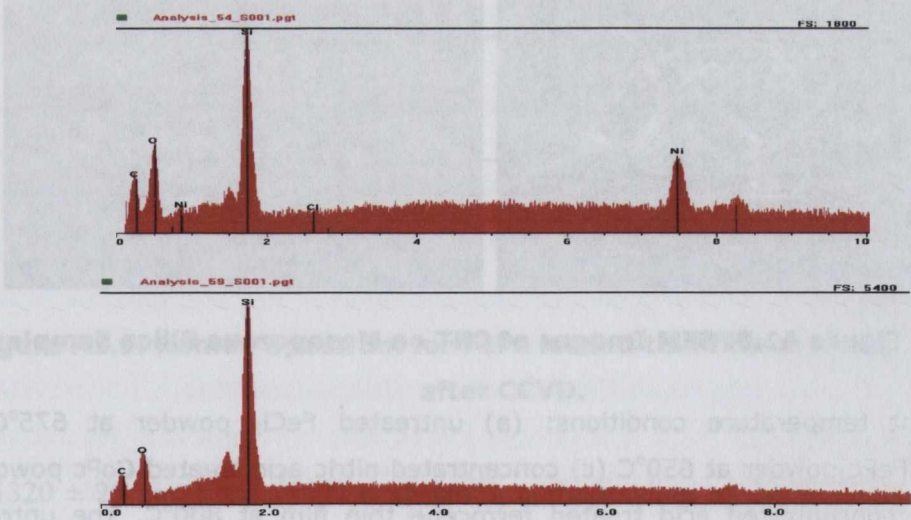


Figure A1.7: EDX/SEM Compositional and Surface Analysis for Ni-filled Mesoporous Silica Before and After Stirring in Concentrated Nitric Acid.

EDX/SEM compositional and surface analysis confirmed the existence of respective metal catalysts in the mesoporous samples as well as the presence of excess metal catalysts on sample surfaces. EDX/SEM studies done on each sample

before and after stirring in concentrated nitric acid confirmed successful removal of excess metal catalysts from the surface. As shown in Figure A1.7, the metal peak was present before stirring and absent thereafter. The removal of excess metal catalyst off the surface would ensure that all CNT growth would be due to catalyst nanoparticles inside the pores of the samples.

EDX also allowed the identification of contaminated samples and these were then not used for the growth of carbon nanotubes.

High Resolution Scanning Electron Microscopy (HR SEM)

Each of the samples was observed to change colour to opaque black after CCVD. This colour is commonly associated with the presence of carbon and is expected when CNT growth has taken place. Figure A1.8 shows HR SEM images of CNT prepared on various mesoporous silica samples

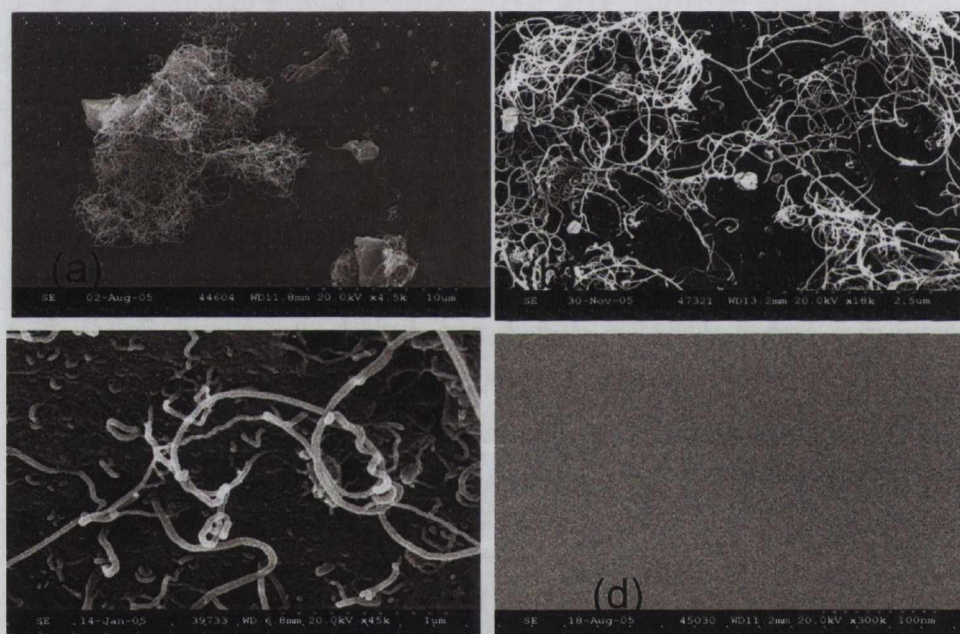


Figure A1.8: SEM Images of CNT on Mesoporous Silica Samples.

at different temperature conditions: (a) untreated FeCl_3 powder at 675°C (b) untreated FePc powder at 650°C (c) concentrated nitric acid treated CoPc powder at 675°C (d) concentrated acid treated ferrocene thin film at 800°C . The untreated samples indicate dense and clustered growth of CNT with wide range of diameters unmatched to the pore sizes. The growth was non-aligned, mostly in dense clusters and “spaghetti” like. The CNTs grown had a wide range of diameters (20 – 90 nm), so suggesting growth was not strictly from the pores as these diameters were not comparable to corresponding mesoporous silica pore diameters. This pattern was

typical of all as-prepared samples. This CNT diameter independence from corresponding sample pore diameter is attributed to the presence of metal catalysts on the surface and possibly due to diffusion of metal catalyst to the template surface as a result of the high temperature of the CCVD reaction. On the contrary, the acid washed samples show an almost uniform diameter of CNTs and overall, the diameter is directly proportional to the pore sizes, Table A1.3. Ferrocene based and phthalocyanine based thin film samples have no HRSEM evidence of CNTs, Figure A1.8(d), but Raman spectroscopy (Figure A1.9) indicates the usual three bands of radial breathing modes (RBM), the disorder (D) and the in-plane bond stretching (G) modes all typical of CNT, hence showing the probable in - pore growth of CNT.

Raman Spectroscopy

Raman spectral examination of all samples before the CCVD run showed no significant signal. After CCVD, all samples where CNTs had grown successfully showed the

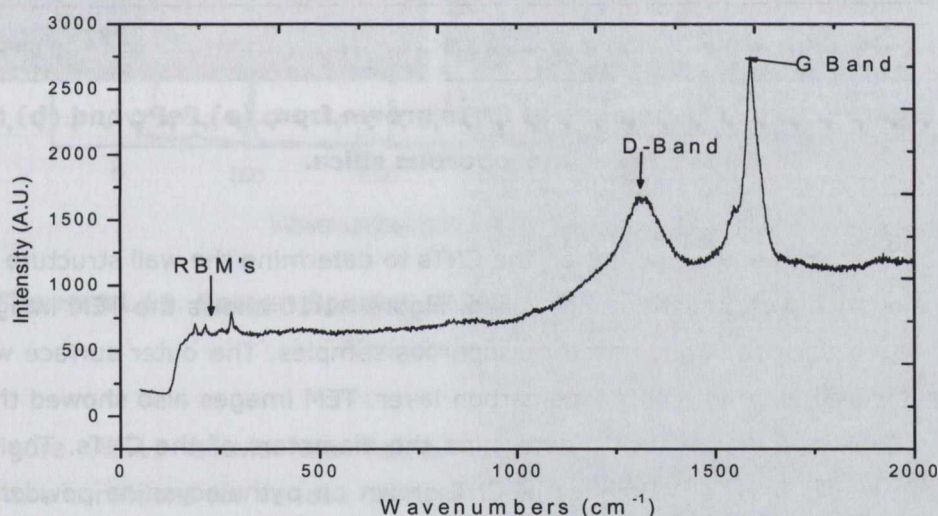


Figure A1.9: Raman Spectrum for FePc loaded thin film mesoporous silica after CCVD.

at $(1320 \pm 25 \text{ cm}^{-1})$ and $(1600 \pm 15 \text{ cm}^{-1})$, corresponding to the D mode for disorder induced and the G mode for graphite or in-plane bond stretching modes(28). As seen from figure 10, the narrow and high G band and a D/G ratio below one show that good quality and highly graphitized CNTs were grown. Not all spectra showed such good quality CNTs, some spectra had two wide distinctive peaks, typical of the presence of crystalline graphitic carbon, microcrystalline graphite as well as amorphous carbon in the

carbon nanotube layer (28). Another band at about 200 cm^{-1} was observed for some of the CNTs. This band represents the radial breathing modes (RBM) which can be used to estimate the diameter of CNTs since their wavenumber is inversely proportional to tube diameter. Some Raman spectra for the samples exhibited G-band splitting, fig. A1.9, characteristic of the quantum confinement effect attributed mostly to SWNT due to their thin diameters. G-band splitting has also been observed in MWNT (29).

Transmission Electron Microscopy (TEM)

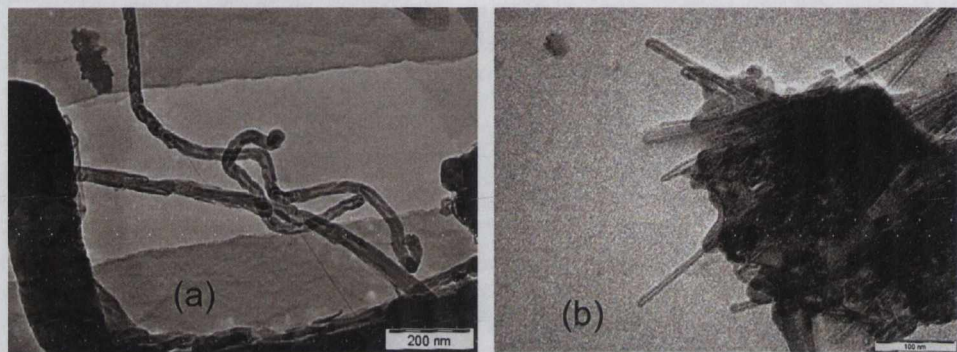


Figure A1.10: TEM images of CNTs grown from (a) FePc and (b) CoPc mesoporous silica.

TEM analysis carried out on the CNTs to determine the wall structure indicated that the CNTs were mostly multi-walled. Figure A1.10 shows the TEM images of (a) FePc based and (b) CoPc based mesoporous samples. The outer surface was found to be covered with an amorphous carbon layer. TEM images also showed the quality of the CNTs and were used to determine the diameters of the CNTs. The diameter measurements from TEM images of CNT grown on pythalocyanine powder samples are compared with the mesoporous silica pore diameters in Table A1.4. The diameters of the CNTs closely compare with that of the corresponding sample template pore, suggesting possible growth from within the pores.

Table A1.4: CNT diameter measurements.

METAL PRECURSOR	METAL WEIGHT (g)	PORE DIAMETER (nm)	CNT DIAMETER (nm)
FePc	0.5	5.0	9 ± 4
FePc	1.0	3.3	6 ± 3
CoPc	0.1	5.0	13 ± 5
CoPc	1.0	5.0	15 ± 7
CoPc	1.0	7.0	8 ± 3
NiPc	0.5	3.3	5 ± 3
NiPc	0.5	5.0	8 ± 3

CNTs with diameters smaller than the pore sizes were not observed. The nanoparticle size must therefore be playing an important role in the growth of CNTs.

CNT Growth Overview

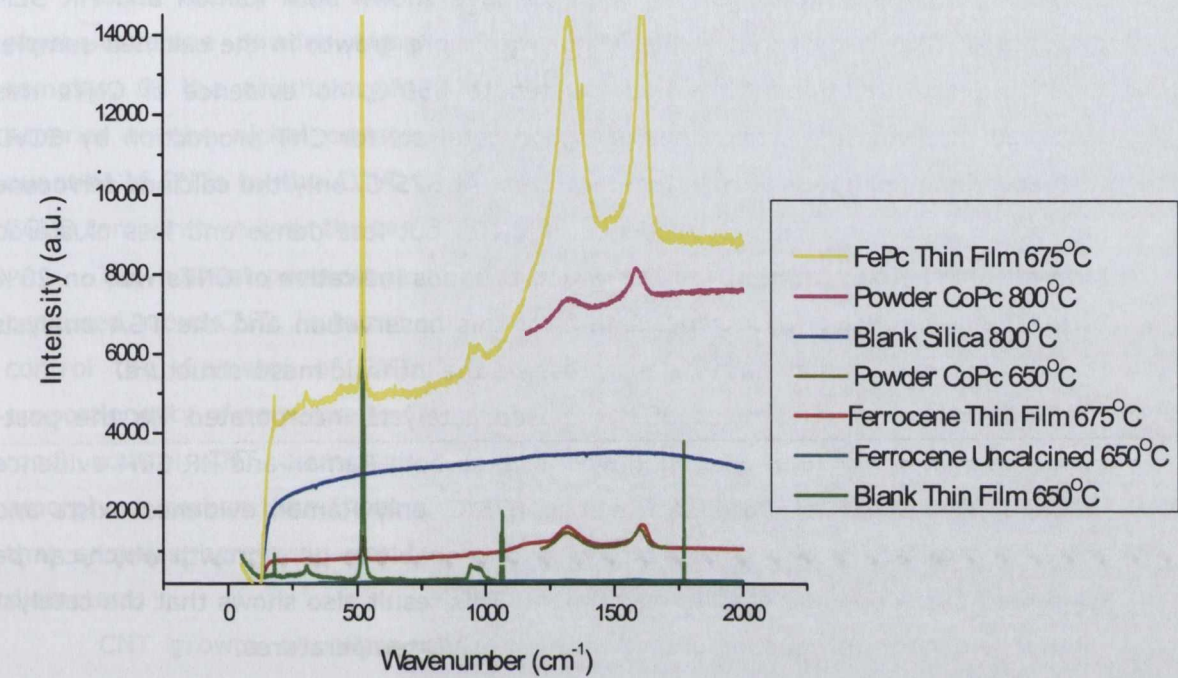


Figure A1.11: Raman Spectra of Different Catalysts at Different Temperatures.

Figure A1.11 shows the Raman spectra of CNTs grown at different temperature conditions for various catalysts. All the acid untreated phthalocyanine based samples show both Raman and HR SEM evidence of carbon nanotubes when CCVD is carried out at 800°C with acetylene feedstock flushed for 1 hour. The growth is dense, clustered and the CNTs have a wide range of diameters for each sample. For nitric acid treated samples, less dense and less clustered CNTs with near uniform diameters are observed for all different loadings of CoPc and the heaviest load of FePc. No evidence of CNTs existed for all different loads of NiPc samples stirred in concentrated nitric acid. When the operating temperature was reduced to 650°C whilst the acetylene flow was maintained for 15 minutes, there was neither Raman nor SEM evidence of CNTs on both acid treated and untreated samples except on the highest loadings of the untreated CoPc and FePc materials. This result is maintained if the operating temperature is increased to 675°C whilst the other conditions are

maintained. This confirms that Fe and Co are superior catalysts to Ni for CNT production using acetylene feedstock

For the same pore dimension and same metal catalyst within the transition metal phythalocyanine based mesoporous silica, the highest percentage metal loaded material produced more dense CNTs than its lower loaded counterparts.

All ferrocene based powder samples have shown both Raman and HR SEM evidence of CNTs after CCVD at 800°C but with more growth in the calcined sample. When the growth temperature was lowered to 650°C, no evidence of CNTs was observed, implying that ferrocenes are good catalysts for CNT production by CCVD with acetylene feedstock at high temperatures. At 675°C, only the calcined ferrocene had both Raman and HR SEM evidence of CNTs, but less dense and less clustered than at 800°C. The occurrence of the G and D bands indicative of CNTs was on 20% of the Raman spectra. It is conclusive from this observation and the TGA analysis that the calcinations may have helped preserve the intrinsic meso-structure.

Both powdered samples of iron based catalysts incorporated via the post-synthetic method and iron chloride have indicated both Raman and HR SEM evidence of CNTs after CCVD at 800°C. However at 675°C, only Raman evidence exists and there is no surface growth. This is indicative of probable in-pore growth which can be confirmed by an ongoing etching experiment. This result also shows that the catalyst method is good for production of CNTs at high CCVD temperatures.

All metal phythalocyanine based thin films have Raman evidence of CNTs after CCVD at 800°C. A similar result is shown by all ferrocene based thin films. Both groups of samples have no surface growth of CNT. The combined results are a strong indicator of probable in-pore growth of CNTs. An ongoing etch study should be able to expose the CNTs for further characterisations.

The range of the D ($1320 \pm 25 \text{ cm}^{-1}$) and G ($1600 \pm 15 \text{ cm}^{-1}$) bands obtained in this research fits well with results from elsewhere where acetylene feedstock was used for CCVD growth of CNTs(30). The G/D (Graphite to Defect) ratio obtained for most CNTs grown from these platforms was unity (1) on average, indicating a poor crystalline quality, consistent with corresponding TEM images. The amorphous carbon deposits on surfaces of the tubes are attributed to the ready pyrolysis of hydrocarbons (in this case acetylene) when heated above 600°C – 700°C (31).

A1.7. Conclusions

A wide range of mesoporous silica platforms for CNT growth differing in catalysis method as well as percentage loading have been tested for in-pore CNT growth by the CCVD using acetylene as the hydrocarbon feedstock. The supercritical fluid based samples were found to be unstable at temperatures above 450°C owing to

the degradation of physisorbed materials during sample preparation. Apart from losses attributed to water, the transition metal based phythalocyanines, ferrocenes, iron chloride and iron incorporated by a post synthetic method samples were very stable over the high CCVD temperature ranges and therefore are suitable platforms for CNT growth.

Good quality and low defects CNTs were synthesized especially from the phythalocyanine powder samples making them even preferable over the other samples. Of the phythalocyanines, iron and cobalt doped samples proved to be superior to the nickel counterparts in the production of good quality and high quantity of CNTs by the CCVD method with acetylene feedstock independent of the CCVD temperature over the tested range of 650°C to 800°C.

The highest percentage loadings of the same materials for same pore sizes produced more CNTs in terms of densities. Percentage loading of catalyst does not control the diameter of CNTs, but influences the quantity formed. The direct proportionality of pore size to CNT diameter suggest that in-pore nanoparticles exert most control CNT diameter. Samples with the highest loading showed more amorphous carbon than those with lower loading. This can be explained by the fact that samples herein do not form SWNT preferentially as they have larger pore diameters.

CNT growth on nitric acid treated sample surfaces was less dense, less clustered and near uniform diameter tubes matched to pore size than untreated samples which produces dense, clustered CNTs of a wide range (20 – 90 nm) of diameters completely unmatched to pore sizes. The difference is attributed to successful removal of excess metal catalyst from sample surfaces. For the acid treated samples, a direct proportionality of pore size to tube diameter was observed, suggesting that the nanoparticles inside the pores control the nanotube diameter.

Samples like ferrocenes and phythalocyanine, calcined slowly at high temperatures, have a high probability of preserving the meso-structure during CCVD and hence make better platforms for CNT production by that method. The stability also depends heavily on the constituent materials used for the whole process of producing a complete catalyzed mesoporous silica platform for CNT growth.

Raman evidence has indicated possible in-pore growth of CNT in both thin film and powder catalyzed mesoporous silica samples. The most suitable platforms for CNT growth by CCVD with acetylene feedstock in an argon environment are the ferrocene and phythalocyanine based thin films.

A1.8. Future Work

The results presented here and the conclusions drawn thereof have revealed valuable information on catalyzed mesoporous silica platforms for reinforcement with CNT using the CCVD method. Further investigations are in progress on in-pore growth and nanotube orientation as well as relationship between nanotube diameter and pore size and /or nanoparticle size. Etching CNT grown samples with HF will reveal the CNT under the surface and inside the pores for further characterization. This characterization will enable the optimization of growth conditions through information like pore filling and the extend to which pores are filled, quality of tubes and catalyst loading. Thereafter substrates preparation will take place and in the case of powders, monolithic structures will be formed. These structures would then be tested for mechanical and thermal robustness as well as electrical properties.

A1.9. Publications

1. **C. Kufazvinei**, R. W. Leahy, S. M. Lipson, W. J. Blau, F. C. Dillon, T. R. Spalding, M.A. Morris, J. D. Holmes, G. Allan and J. Patterson "Growth of carbon nano-structures in ceramic materials"

(a) *Proceedings of SPIE -- Volume 5824 Opto-Ireland 2005: Nanotechnology and Nanophotonics*, Werner J. Blau, David Kennedy, John Colreavy, Editors, June 2005, pp. 149-156

(b) *Technical Proceedings of the 2005 NSTI Nanotechnology Conference and Trade Show, Volume 3, Chapter 3: Nano Devices and Architectures*, pp 221 – 224.

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A1.10 Presentations:

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(a) Oral Presentation at the First Intel Ireland Research Conference, Intel Ireland, Dublin, Ireland, 14th – 15th September 2004

(b) Poster Presentation at the Nanotechnology and Nanophotonics Opto-

Ireland Conference, Royal Dublin Society, Dublin, Ireland, 4th – 5th April 2005.

(c) Oral Presentation at the 2005 NSTI Nanotechnology Conference and Trade Show, Anaheim, CA, USA, 8th – 13th May 2005

(d) Oral Presentation at the Second Intel Ireland Research Conference, Intel Ireland, Dublin, Ireland, 12th – 13th September 2005

2. **C. Kufazvinei**, R. W. Leahy, S. M. Lipson, W. J. Blau, F. C. Dillon, T. R. Spalding, M.A. Morris, J. D. Holmes, G. Allan and J. Patterson "Carbon Nanotube Reinforcement of Ceramic Materials"

(a) Poster Presentation at the International Conference on Science and Technology of Synthetic Materials, Trinity College Dublin, Dublin, Ireland, 2nd – 7th July 2006

(b) Poster Presentation at the Third Intel Ireland Research Conference, Intel Ireland, Dublin, Ireland, 4th – 5th September 2006

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