SYNTHESES AND CHARACTERIZATIONS OF NOVEL ORGANIC SEMICONDUCTORS

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SYNTHESES AND CHARACTERIZATIONS OF

NOVEL ORGANIC SEMICONDUCTORS

BY

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DISSERTATION

Submitted to the University of New Hampshire
in Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy
in
Engineering: Materials Science

December 2014
This thesis/dissertation has been examined and approved in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Engineering: Materials Science by:

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On December 1st, 2014

Original approval signatures are on file with the University of New Hampshire Graduate School.
ACKNOWLEDGEMENT

This dissertation would not be finished without the support and encouragement of numerous people, to whom I need to express my sincere gratitude.

I owe my deepest gratitude to my advisor Prof. Glen P. Miller for his guidance, patience and endorsement, both intellectually and financially to support me all the way through my pursuit of science in chemistry and materials science. I want to thank him the most for providing me the opportunity to work in the various fields of materials science ranging from organic chemistry to nanotechnology. He is a respectful advisor and I thank him for all he had done.

I thank the effort and guidance from other members of my thesis committee: Prof. Arthur Greenberg, Prof. Erik Berda, Prof. Karsten Pohl, Prof. Gonghu Li. They have been approachable and supportive through all my graduate study. They gave me insightful suggestions along the years of my graduate studies, and helped in all aspects of my research. I owe them my heartfelt appreciation.

I also thank all professors who taught me in class. They built me a solid ground on Chemistry and Materials science, and their office doors were always open to me.

I thank Dr. Wenling Jia for her mentoring during my first year in my graduate life. As my background is inorganic materials science, the organic synthesis is a new world to me. Wenling taught me everything in the lab from reaction setup to column purification. I thank her for her patience.
I thank Dr. Chandrani Pramanik for team working with me for the water soluble pentacene project. She shared her knowledge and techniques with me selflessly. The discussions with her always inspire me in my researches. Her enthusiasm is also a big motivation for me.

I thank Dr. Weimin Lin for his great help in my research. He is a great organic synthesis teacher for me as a living organic reaction handbook. My research had been greatly enhanced with his knowledge and experience, and I learnt a lot from his friendly and diligent personality as well.

I am grateful to research scientist Jon Briggs, Dr. Jennifer L. Hodgson, Hao Geng, Dr. Anup Singh from NEU for their helps in crystal structure, computational modeling, and device fabrication.

I also thank all other previous and current group members, Dr. Joyce Xu, Jianyu Zhao, Yanmei Rong, Shunfu Hu, Jinyu Yang, Xiaoyi Zhang, Claire Cho, Julia Chan, Lei Zhou, Dr. Ryan P. Kopreski. They are always friendly and helpful.

I want to thank technician Nancy Cherim for training me with SEM. I also thank Dr. Patricia Wilkinson for helping me all the time with NMR.

The funding support from National Science Foundation and Center for the High-rate Nanomanufacturing is acknowledged and greatly appreciated.

At the end, I owe my deepest and greatest gratitude to my parents for their endless love and continuous support during my study. Without their support, I would not even have a chance to start my graduate life in the states.
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1

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3

4

5

6

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\[
\begin{align*}
\text{R} & = \begin{array}{c}
\text{43} \\
\text{44} \\
\text{45} \\
\text{46}
\end{array} \\
& = \begin{array}{c}
\text{47} \\
\text{48} \\
\text{49} \\
\text{50}
\end{array} \\
& = \begin{array}{c}
\text{51} \\
\text{52}
\end{array}
\end{align*}
\]
Chapter 5

1: \( R = \text{CH}_2\text{CH}_3 \)
2: \( R = \text{n-C}_8\text{H}_{17} \)
3: \( R = \text{phenyl} \)
4: \( R = 1\text{-naphthyl} \)
5: \( R = \text{(CH}_3)_3\text{OH} \)
6: \( R = \text{(CH}_3)_2\text{COOH} \)
7: \( R = \text{COCH}_3 \)

\[
\begin{align*}
1 & : 84 & 85 & 95 & 99 \\
2 & : 86 & 87 & 96 & 100 \\
3 & : 88 & 89 & 97 & 101 \\
4 & : 90 & 91 & 98 & 102 \\
5 & : 92 & 93 & 98 & 103 \\
6 & : 94 & 94 & 27 & 104 \\
7 & : 30 & 31 & 32 & ----
\end{align*}
\]
ABSTRACT

SYNTHESES AND CHARACTERIZATIONS OF NOVEL ORGANIC SEMICONDUCTORS

by

YUSHU LI

University of New Hampshire, December 2014

The desire for portable, flexible and affordable electronic devices provides the driving force for the development of new organic semiconductors. Organic semiconductors can be solution processed, potentially enabling high-rate fabrication of electronic devices on flexible substrates. Devices of interest include organic field effect transistors (OFETs), organic photovoltaics (OPVs) and organic light emitting diodes (OLEDs). Research presented here has focused on the synthesis and characterization of three different classes of organic semiconductors: a water soluble pentacene, a disulfide-linked pentacene oligomer and several [60]fullerene-pentacene adducts. In addition, an aromatization reaction leading to bis(organothio)pentacenes has been systematically studied.

The first water soluble pentacene, potassium 3,3′-(pentacene-6,13-diylbis(sulfanediyl)) dipropanoate (28), has been successfully synthesized and characterized. With an optical HOMO-LUMO gap of approximately 1.91-1.97 eV, indicated by UV-vis spectra in several different solvents, water soluble pentacene was utilized as donor in an active bi-layer photovoltaic cell with C_{60} as acceptor.
Both unsubstituted and \textit{t}-butylphenyl substituted versions of 6,13-diacetyltiophenacene have been successfully synthesized and characterized as precursors to 6,13-dimercaptopenacene. An attempted synthesis of 6,13-dithiopenacene oligomers from 6,13-dimercaptopenacene appears to have been successful. However, due to poor solubility, purification and characterizations are limited.

The Diels-Alder reaction between 5,7,12,14-tetraphenylpentacene (TTP) and [60]fullerene to generate mono- and multi- adducts has been studied both experimentally and computationally. A mono-TPP-C\textsubscript{60} adduct, two regioisomers of a bis-TPP-C\textsubscript{60} adduct, and a symmetric tetrakis-TPP-C\textsubscript{60} adduct have been formed. Moreover, the shape-controlled preparation of nano- and microstructures from the mono-C\textsubscript{60}-TPP adduct have been demonstrated by judicious self-assembly in various solvent systems.

Numerous dihydropentacenes have been prepared using a ZnI\textsubscript{2}-mediated reaction between 6,13-dihydrodioxypentacene and organic thiols. The dehydrogenative aromatization of these dihydropentacenes using \textit{p}-chloranil has been systematically explored. Both syn- and anti- dihydropentacene isomers are observed to form in the ZnI\textsubscript{2} reaction, and each has been taken forward to react with \textit{p}-chloranil. These aromatization reactions have been monitored using \textsuperscript{1}H NMR spectroscopy.
CHAPTER 1

INTRODUCTION

1.1 Organic Semiconductors

1.1.1 Basis Concepts

Organic semiconductors, which are typically organic molecules with conjugated \( \pi \)-system, are now being exploited in electronic device applications in place of conventional inorganic semiconductors such as silicon. The alternating C-C and C=C bonds of the organic molecule form the conjugated \( \pi \)-system. In the conjugated \( \pi \)-system, the atomic \( p_z \)-orbitals along the conjugated molecular plane overlap with one another, creating frontier molecular orbitals (MOs). Further energy level splitting occurs when these MOs of neighboring conjugated molecules interact (illustrated in Figure 1.1).

![Figure 1.1 Schematic of MO energy levels in conjugated system](image)

Figure 1.1 Schematic of MO energy levels in conjugated system
With the increase of conjugation length, the energy difference between the highest-occupied molecular orbital (HOMO) and the lowest-unoccupied molecular orbital (LUMO) decreases. For an organic material to be semiconducting, the HOMO-LUMO gap should be sufficiently small for electrons to be excited into the conduction band at room temperature (300 K), typically in the range of 0.5 - 3 eV. The HOMO-LUMO gap (Figure 1.1) of an individual organic molecule is directly related to the band gap of the corresponding organic semiconductor in solid state, despite their intermolecular interactions in solid-state. ¹ For instance, pentacene, known as the benchmark of small molecule organic semiconductor, has a band gap of around 1.8 - 2 eV depending upon morphology, ² while silicon, the conventional inorganic semiconductor, has a band gap of 1.1 eV. ³

Charge transport is the most important electronic property for organic semiconductors. On the molecular level, conjugation allows the π-electrons in the HOMO to delocalize over the conjugated backbone. However, how charges are transported to the neighboring molecules, eventually through the bulk materials, is more complicated and can be explained through a “variable range hopping” model. ⁴ In the model, electrons can hop from one site to the neighboring neutral molecules through a thermally activated process. The rate of “hopping” \( k_{ET} \) has been can be calculated using the Marcus theory ⁵ of electron transfer, represented by Equation 1.1.

\[
k_{ET} = \frac{\sqrt{\pi}}{h} \frac{t^2}{\sqrt{k_B T \lambda}} \exp \left( -\frac{\lambda}{4k_B T} \right)
\]

Where \( T \) is the temperature, \( \lambda \) is the reorganization energy, \( t \) is the transfer integral, \( h \) is the Planck constant, and \( k_B \) is the Boltzmann constant. At a given temperature, the rate of hopping \( (k_{ET}) \) is governed by two parameters, e.g., transfer integral \( (t) \) and reorganization
energy ($\lambda$). First, with higher transfer integral ($t$), the hopping rate ($k_{ET}$) will be higher. The transfer integral is the amount of overlap between electronic wavefunctions of adjacent organic molecules, depending closely on molecular packing, including factors such as intermolecular distance and orientation. Second, with lower the reorganization energy ($\lambda$), the hopping rate ($k_{ET}$) will be higher. The reorganization energy is the sum of the relaxation energies for the transition from the neutral-state geometry to the charged-state geometry upon accepting a charge and vice versa. For rigid molecules, such as pentacene, the reorganization energies are smaller due to the fact that they are less likely to undergo dramatic nuclear reorganization.  

Compared with inorganic semiconductors, organic semiconductors have a lot of advantage. First of all, organic semiconducting materials are inexhaustible in supply and also inexpensive because they can be synthesized via various routes. Secondly, due to their solubility in common organic solvents, the organic materials can be processed via low-cost solution coating or printing methods to fabricate large area photovoltaic devices. Thirdly, the performance of organic electronic devices can be adjusted by tuning molecular structure and different functionalization. Lastly, the organic devices can be flexible and most of them are semitransparent, different from the common silica solar panels on rooftops. All of these advantages make organic semiconductors commercially attractive, particularly for large area applications such as photovoltaic devices (OPVs) and light-emitting diodes (OLEDs), at a time when there is clear need for both renewable electricity generation technologies and energy efficient solid state lighting.
1.1.2 Classification of Organic Semiconductors

Organic semiconductors can be classified as small molecules and polymers. Organic semiconductors can also be classified as n-type and p-type based on the type of charge carrier (electron or hole). N-type organic semiconductors are electron-transporting materials, which are electron deficient and ready to accept electrons. In organic photovoltaic (OPV) devices for instance, n-type organic semiconductors are generally utilized as acceptor materials. Meanwhile, P-type organic semiconductors are electron efficient and able to donating electrons and transporting holes.

![Examples of organic semiconductors](image)

The electronic properties of the organic semiconductors can be tuned by changing the molecular structures or even just by introducing a functional group. For example, pentacene is well known as a p-type semiconductor working as donor in organic
photovoltaic devices; however, the cyanopentacenes have good electron transfer abilities (n-type) and act as acceptors in a heterojunction solar cells.\textsuperscript{10} Some representative examples of numerous organic semiconductors are shown in Figure 1.2.

Poly(3-hexylthiophene) (P3HT, 1) is the most widely used polymeric donors in OPV devices.\textsuperscript{11} Poly(2-methoxy-5-((2'-ethyl hexyl)oxy)-1,4-phenylene vinylene) (MEH-PPV, 2),\textsuperscript{12} with a band gap of around 2.1 eV, is also working as donor in OPV devices; however, by introducing a cyano group into the polymer chain (CN-MEH-PPV, 3), polymer changed to electron-transporting (n-type) from hole-transporting (p-type).\textsuperscript{13} As for small molecule organic semiconductors, pentacene and its derivatives, such as TIPS-pentacene (4) and dethylthiopentacene (5), are of interest as p-type materials. TIPS-pentacene (4) is now commercially available and widely used in OPVs as alternative of P3HT. Fullerenes, such as [60]fullerene (6), and their derivatives have been extensively investigated as electron-transporting materials in OFET and OPV devices, due to their relatively low LUMO energy level.\textsuperscript{14} Perylene diimides (PDIs) derivatives (7) are n-type semiconductor as well, which can be used in OPVs as good acceptors.\textsuperscript{15}

In this work, the main focus will be small molecule organic semiconductors, including both pentacene derivatives and fullerene derivatives.

1.2 Organic Electronic Devices

Organic semiconductors are acting as the active materials in organic electronic devices, such as organic photovoltaic (OPV), organic light-emitting diode (OLED), and Organic field-effect transistor (OFET). It is important to understand the operation principles of
these devices and the requirements for organic semiconductors to achieve well-performed devices for us in order to design novel organic semiconductors.

1.2.1 Organic Photovoltaic (OPV) Devices

Photovoltaic devices are basically semiconductor diodes, mainly made up of two electrodes and the semiconducting active layer between them. The general basic mechanism of solar cells is based on the photovoltaic effect and semiconductor physics. The semiconducting materials absorb the incoming photons and convert them into electron-hole pairs called excitons. The photogenerated electron-hole pairs are then separated, with electrons drifting to one of the electrodes and holes drifting to the other electrode, because of the internal electric field created by the diode structure of the solar cell.\(^16\) In contrast to the free electron-hole pair generated in inorganic solar cells, the excited electron-hole pairs in organic solar cells are strongly bonded by Coulombic force, known as singlet excitons, which are neutral and mobile.\(^17\) The reason for formation of excitons instead of free charge carriers in organic materials is that the exciton binding energy is much higher than the thermal energy at room temperature.\(^18\) Considering the coulomb attraction of an electron-hole pair as the approximate exciton binding energy, with a dielectric constant \((\varepsilon_r)\) of \(~3\) for organic compounds which is much lower than the dielectric constant of inorganic semiconductors (i.e. \(\varepsilon_r = 11\) for silicon\(^19\)), the coulomb binding energy \((E = \frac{1}{4\pi \varepsilon_r \varepsilon_0} \frac{q^2}{r}\) where \(\varepsilon_0\) is electric constant) is about 0.5 eV for a separation of 1 nm. At room temperature, the thermal energy \((kT)\) is about 0.025 eV, too small to overcome the binding energy to separate electron and hole. Therefore, the primary excitation in organic semiconductors forms excitons. The large binding energy of
the exciton makes it hard to dissociate electron-hole pairs to free charge carriers. In order to generate a photovoltaic current, an electronegative acceptor is necessary for the driving force to yield efficient exciton dissociation. The material with the higher electron affinity or deeper LUMO is known as the electron acceptor (or simply as the acceptor) and the material with the lower electron affinity or shallower LUMO as the electron donor.\textsuperscript{20} The semiconducting polymers in organic solar cells serve as the donor material in this system, while fullerene C\textsubscript{60} and its derivatives are excellent examples of acceptor material.\textsuperscript{21}

As shown in Figure 1.3, when light shines on the device, the incident photons are mostly absorbed by the donor materials. Consequently, the tightly bonded excitons (electron-hole pairs) are generated in the donor materials (a). The excitons formed then have to diffuse to the donor-acceptor interface to get dissociated to form free charge carriers (electrons and holes) during their very short lifetime of about 1 nanosecond\textsuperscript{17} and within the very small diffusion length of 1 - 10 nm\textsuperscript{8} before they get recombined radiatively (b).
At the donor-acceptor interface, with the driving force from the acceptor, the electron-hole pairs can be separated and the electrons can be transferred to the acceptor while the holes stays in the donor \((c, d)\). After electron transferring, the free charge carriers, electrons and holes, can be transported to the respective electrodes and collected to produce electricity \((f)\). However, during the whole process, energy can be lost according to several loss mechanisms. \(^8\) Therefore, in order to determine the performance of the organic photovoltaic device, some parameters such as the power conversion efficiency of organic photovoltaics \((\eta)\), the open circuit voltage \((V_{OC}, \text{in V})\), the short circuit current \((I_{SC}, \text{in mA})\) and the fill factor \((FF)\) are measured. The overall power conversion efficiency of organic photovoltaics \(\eta\), as the ratio between the collected photo-generated charges and the number of incident photons, is introduced as the product of four efficiencies: absorption \((A)\), exciton diffusion \((ED)\), charge separation \((CS)\) and charge collection \((CC)\), giving the overall efficiency as \(\eta = \eta_A \times \eta_{ED} \times \eta_{CS} \times \eta_{CC}\). \(^{22}\) All these parameters can be obtained by measuring the photocurrent and photovoltage under light. A typical solar cell I-V curve is shown in Figure 1.4.

![Figure 1.4 A typical I-V curve of photovoltaic devices](image)

\(\text{Figure 1.4 A typical I-V curve of photovoltaic devices}\)
The overall efficiency can also be related to the three common parameters \((V_{OC}, J_{SC}, \text{ and } FF)\) in the following equation:

\[
\eta = FF \cdot \frac{V_{OC} J_{SC}}{P_{in \cdot A_c}} \tag{Equation 1.2}
\]

The open circuit voltage \((V_{OC})\) is the voltage across the positive and negative terminals under open-circuit conditions when the current is zero.\(^{23}\) The \(V_{OC}\) of a polymer fullerene solar cell is directly linked to the energy difference between the LUMO level of the acceptor and the HOMO level of the donor.\(^{24}\) The short circuit current \((I_{SC}, \text{ in mA})\) is the current produced when the positive and negative terminals of the cell are short-circuited and the voltage between the terminals is zero, which corresponds to a load resistance of zero.\(^{23}\) The actual short circuit current measured in a device is determined by many factors, such as band gap of the active material, carrier mobility, intermolecular interaction and molecular chain packing. Another parameter in the overall behavior of a solar cell is the fill factor \((FF)\), which is defined to be the ratio of the available power at the maximum power point \((P_m)\) and the product of the open circuit voltage \((V_{OC})\) and the short circuit current \((I_{SC})\). The fill factor \((FF)\) of a device depends on the charge dissociation, the charge carrier transport, and the recombination properties of the materials in a complicated way. In order to determine the performance of a photovoltaic device, all these parameters should be considered. In order to get a well-performing organic photovoltaic device, the active layer materials, the architecture of the device, morphologies of active layer and the interface between the active layer and the electrode should all be considered systematically.

Device architecture is one of the key factors to achieve a good photovoltaic performance of organic solar cell. The most basic device architectures of polymer solar
cells (PSCs) with donor-acceptor systems are bilayer (flat-heterojunction), bulk-heterojunction, inverted heterojunction and tandem (multi heterojunction) solar cells (Figure 1.5).

Among these architectures, the organic solar cells with tandem architecture achieved the highest efficiency so far. Tandem solar cells are multijunction photovoltaic devices in which two or more subcells with different absorption characteristics are stacked to achieve higher overall solar absorption. In term of increasing efficiency, tandem solar cells offer a number of advantages over single cell devices, such as a higher $V_{OC}$, and the potential to cover the entire solar spectrum. The open circuit voltage is the sum of the $V_{OC}$’s of the subcells, $V_{OC(tandem)} = V_{OC1} + V_{OC2} + V_{OC3}$. The tandem cells consist of several subcells with different band gaps that have complementary absorption characteristics; hence, they can potentially cover the entire solar spectrum therefore to
achieve higher overall solar absorption. Typical organic tandem cell architecture is comprised of two distinct donor-acceptor active layers with different band gaps stacked on top of each other. As the key of the tandem cell, a transparent intermediate layer, generally a thin inorganic layer is needed between the two active layers in order to prevent charge build-up within the cells by allowing recombination of the electrons created in the first cell with the holes created in the second cell. Additionally, it can act as a protective layer to support the bottom cell during deposition of the top active layer.

1.2.2 Organic Light Emitting Diode (OLED)

Besides the photovoltaic applications, organic semiconductors are also used in organic light-emitting diodes (OLEDs) due to their electroluminescence properties. Electroluminescence (EL), a phenomenon that exists in a wide range of semiconductors, is defined as an electrically driven radiative emission process. The light emission from a semiconductor comes from the radiative decay of singlet excitons resulting from the recombination of electrons and holes injected from the cathodic and anodic electrodes. Typically, OLEDs are multilayer thin film devices including anode, hole injection layer (HIL), hole transporting layer (HTL), emitting layer (EL), electron transporting layer (ETL), electron injection layer (EIL), and cathode (illustrated in Figure 1.6).

When the OLED is under operation, an external voltage source of normally few voltages is applied to the device in order to introduce the two types of charge carriers into the active layer from the electrodes, i.e., electrons from the cathode and holes from the anode, and drift towards each other. The free charge carriers, holes and electrons then transport through the HTL and ETL layers respectively. When the free electrons and
holes meet in the EL, they recombine together to form the strongly bound electron-hole pairs, also known as excitons. The excitons then may decay radiatively and emit light.

![Typical architecture of OLED device](image)

Figure 1.6 Typical architecture of OLED device

All these layers between the two electrodes could be made of organic semiconductors. As the HTL and ETL, the materials need to have good charge transfer mobilities. As for the Emitting Layer, the key requirement for the organic material is the efficient and stable light-emitting ability in the visible spectral range.

### 1.2.3 Organic Field-Effect Transistors (OFETs)

As the fundamental building block in modern circuitry, transistors can be used as either signal amplifiers or on/off switches. Field effect is a phenomenon in which the conductivity of a semiconductor changes as a result of change of the electric field applied. OFETs are composed of three main components, a semiconductor layer, an insulator layer and three electrodes, the source, drain, and gate. Various organic semiconductors can be used as the semiconducting layer of OFET, with SiO₂ as the common insulator layer. The device typically follows one of the two architectures, top-
contact and bottom-contact, depending upon the sequence of deposition of the semiconductor layer and the source-drain electrodes (illustrated in Figure 1.7).

![Diagram of Top-contact and Bottom-contact OFET configurations](Image)

**Figure 1.7** Typical architectures of OFET: Top-contact (left) and Bottom-contact (right)

The “top-contact” geometry corresponds to a deposition of the semiconductor followed by the source and drain electrodes, while the “bottom-contact” geometry corresponds to the reverse. Charges are induced in the semiconductor channel by applying a voltage across the dielectric layer, $V_{GS}$. When a voltage, $V_{DS}$, is then applied across the source and drain electrodes, these charges are able to transport from source to drain under the field-effect and produce a current, $I_{DS}$, which can be modulated by the magnitude of $V_{GS}$.

![Graph of Output Characteristics and Transfer Characteristics](Image)

**Figure 1.8** Typical Output characteristics (left) and transfer characteristics (right) of a pentacene-based top-contact p-channel OFET
The typical output characteristics of an OFET working in accumulation mode are depicted in Figure 1.8 (left), which are produced by sweeping $V_{DS}$ for various given $V_{GS}$. When $V_{GS}$ is small enough, not enough mobile charges are accumulated and therefore no current flows, indicating that the transistor is in an “off” state. When the gate voltage becomes larger, the output characteristics of the transistor show two distinct regimes: linear and saturation. The transfer characteristics (Figure 1.8 (right)), produced by varying $V_{GS}$ while holding $V_{DS}$ constant within the saturation regime, can be used to calculate the field-effect charge transport mobility ($\mu$) of the semiconductor by fitting the transfer graph with the following equation.\textsuperscript{31}

$$I_{DS,sat} = \frac{W}{L}C_{ox}\mu_{sat}(V_G - V_T)^2$$

Equation 1.3

Apart from $\mu$, the $I_{on}/I_{off}$ ratio and threshold voltage ($V_T$) are also figures-of-merit for the performance of an OTFT. Although experimental parameters such as device architecture, organic-metal contact optimization, dielectric engineering and material processing conditions certainly play roles in determining the performance, the intermolecular ordering of the molecules in the solid state, i.e. the crystallinity and packing behavior, is believed to be the key factor that influences the overall performance in organic electronic devices.

1.3  Motivation and Scope of the Thesis

1.3.1 What Makes Good Organic Semiconductor?

From basic knowledge of the principle operation of organic electronic devices discussed, we can reach the criterions for good organic semiconducting molecules. First of all, the organic material should have good charge (hole or electron) transport mobility. For both
OPVs and OLEDs, charges need to be transported through the organic semiconductor layer. Therefore, good charge transport mobility is essential for OPVs and OLEDs. In the case of OFET, as the device is based on the charge transport process, the charge transport mobility is directly related to the device performance.

Secondly, the HOMO-LUMO gap of organic semiconductor should be suitable. Regarding to the future application of the organic material, the HOMO, LUMO energies and HOMO-LUMO gap could be tuned by chemical structure modification. For donors in OPVs, the HOMO-LUMO gap should be large enough to absorb photons over a wide range of wavelengths in the visible or sometimes even near infrared regions. Meanwhile, for acceptors in OPVs, the LUMO energy should be low enough to accept electrons. But at the same time, the difference between the LUMO level of the acceptor and the HOMO level of the donor is directly linked to the open circuit voltage of the OPV device. In the case of materials applied in emitting layer of OLEDs, the HOMO-LUMO gap should be in the range for visible light emitting.

Thirdly, solid state intermolecular ordering is another important character for organic semiconductors, which could affect both charge carrier mobility and band gap of the material. As discussed before, the charge transport mobility of organic semiconductors is largely depending on the solid state intermolecular ordering behavior of the molecule. High crystallinity and good solid state packing properties, like π-π stacking, which can lead to high charge carrier mobility, should be considered during the molecular design for organic semiconductors.

Lastly, the stability and solubility should be taken into consideration. Unlike inorganic materials, organic semiconductors could react with oxygen in the air and degrade.
Therefore, the organic material should be reasonably stable during processing. Furthermore, the targeted organic molecule should possess reasonable solubilities in organic solvents to ensure their solution processability, such as spin coating, blade coating, and printing.

1.3.2 Scope of the Thesis

The aim of the research reported in this thesis is to synthesis several small molecule organic semiconductors by systematically considering the criteris above.

In Chapter 2, the synthesis, characterization and OPV application of the first water soluble pentacene is discussed.

In Chapter 3, the synthesis of novel pentacene oligomers with S-S linkage is discussed. The oligomer has a smaller HOMO-LUMO gap compared to the pentacene monomer as evidenced by UV-vis absorption data.

In Chapter 4, the synthesis and theoretical study of a series of tetraphenylpentacene(TPP)-C₆₀ Diels-Alder adducts is discussed. Among all adducts obtained, the e,e,e,e-tetrakis-TPP-C₆₀ adduct particularly is attractive due to its highly symmetric structure.

In Chapter 5, a systematic study of aromatization reactions leading to 6,13-bis(organothio) substituted pentacenes is discussed.
CHAPTER 2
SYNTHESIS AND CHARACTERIZATION OF WATER-SOLUBLE
PENTACENE DERIVATIVE

2.1 Introduction

2.1.1 Acenes

Acenes, which are made up of linearly fused benzene rings, form a class of organic small molecules belonging to the polycyclic aromatic hydrocarbons (PAHs), which are classified as "alternant catacondensed" polyarenes.\(^{32,33,34}\) The nomenclature of PAHs, including the acene family, was introduced by Eric Clar.\(^{32}\) The smallest acene is anthracene with three linearly fused benzene rings. The larger members of acenes containing four or more fused benzenoid rings are named systematically using a Greek prefix to denote the number (n) of fused benzene rings and the common suffix "acene," as in tetracene, pentacene, hexacene, heptacene and so on (Figure 2.1).

Figure 2.1 Known examples of unsubstituted acenes
The numbering of the acenes is also shown in the figure with examples of the first three acenes, identifying only the carbons, which are chemically bound to hydrogen atoms or other substituents. The numbering always begins with the last ring on the right in the series and starts with the carbon atom at the "12-o-clock" position.

Due to their highly conjugated planar structure, acenes allow extensively delocalization of $\pi$-electrons in the molecules, which result in the fact that acenes will have smaller HOMO-LUMO gaps than other hydrocarbon molecules with the same number of aromatic rings. Among the acenes family, the HOMO-LUMO gap decreases with increasing length of the acene as evident by their UV-Vis absorption spectra and their colors. For instance, the color changes from colorless (anthracene) to orange (tetracene), deep blue (pentacene), and green (hexacene). The reasonable small HOMO-LUMO gaps of acene molecules make them promising candidates for organic semiconductors in various electronic devices, such as organic photovoltaic devices (OPVs), organic light-emitting diodes (OLEDs), and organic field-effect transistors (OFETs). However, the stability decreases dramatically with increasing length of the acene. The largest experimentally existing acene, heptacene, can only be isolated for a short time with assistance of a polymer matrix.

Degradation of acenes result from two principal processes, photooxidation and photodimerization, with photooxidation considered to be more significant. In the photooxidation process, with the presence of light and oxygen, acenes decompose into acene endoperoxide derivatives, which produce the highly stable acene-quinones. According to the theoretical study, the acenes could be oxidized to acene endoperoxide derivatives by reacting either with singlet oxygen in a concerted fashion or with triplet
oxygen in a stepwise radical mechanism. In both pathways, the energy barrier for oxidation decreases with an increase in the ring number of the acene, consisting with the fact that the stability decreases with the increasing length of acene. The resulting endoperoxide derivatives then convert into the respective acene quinones (Scheme 2.1).

The other photodegradation process, namely photodimerization, always occurs along with the photooxidation process. For smaller acenes, such as anthracene and tetracene, photodimerization is more noticeable resulting in the “butterfly” photodimerized adducts as major photodecomposition products.\(^{38,39}\) For a larger acene, like pentacene, photodimerization products dominate in a deoxygenated environment,\(^{40}\) while photooxidation products are major with the presence of oxygen. Various substitutional groups have been introduced in order to slow down the photodegradation of acenes thereby increasing the stability. The substitution effects will be discussed in the following by taking pentacene as example.

![Scheme 2.1 Photooxidation of acenes](image-url)
2.1.2 **Pentacenes**

Pentacene, the most famous member of the acene family in the organic semiconductor research field, consists of five linearly fused aromatic rings with a planar conjugated molecular structure. It has been considered as a benchmark semiconductor in organic electronic devices due to its high charge carrier (hole) mobility ($\geq 1 \text{ cm}^2/\text{Vs}$ \cite{41,42}), which is compatible with amorphous silicon, and therefore has been widely studied. The optical HOMO-LUMO gap in solution is 2.1 eV, while the band gap of the pentacene thin film is 1.7 eV, allowing the application as donor material in OPVs. However, its solution processability is severely limited due to its poor solubility and its propensity to photodegrade within minutes in solutions exposed to light and air. It is worth to emphasize that pentacene in solid state is chemically and thermally stable, the stability in solution is the issue.

2.1.2.1 **Pentacene Derivatives**

Great efforts have been made to design and synthesize functionalized pentacene derivatives aiming at enhanced solubility and solution stability, face-to-face crystal packing arrangements and tunable HOMO-LUMO gaps. \cite{43,44,45,46,47,48,49,50} Solubilities of substituted pentacene derivatives are dependent on the functional groups introduced and generally better than the parent pentacene.

The solution stability, as a key property of pentacene derivatives for solution processing purpose, is basically determined by the substitutional position and the type of the functional groups. The solution stability of a pentacene derivative is represented by its half-life ($t_{1/2}$) in solution with exposure to ambient light air and at room temperature.
Experimentally, the half-life \( t_{1/2} \) is the amount of time required for absorbance \( A \) at a given wavelength to fall to half its initial value \( A_0 \) in UV-vis spectrum due to the fact that the absorbance is linearly related to concentration. Some examples of pentacene derivatives with their half-lives are shown in Figure 2.2.\(^{50}\)

![Figure 2.2 Examples of substituted pentacene derivatives](image)

The position where the substitute groups attach to the pentacene backbone affects the stability of pentacene derivatives significantly. Theoretically and experimentally, as described previously in the acene photooxidation, the center ring (6, 13 position) of pentacene is the most reactive site for photooxidation. Therefore, substitutions at 6 and 13 positions are necessary for improving solution stability, also confirmed by
The type of substitution group is another determining factor of pentacene derivative solution stability. Organothio-substituted pentacene derivatives have been proven to be the most stable among all pentacene derivatives family examined to date.

The HOMO and LUMO energy levels of the pentacene could also be tuned. For instance, Aryl substituent could narrow down the HOMO-LUMO gap of the pentacene derivative due to the fact that the conjugated π-system of the pentacene backbone could be extended to the aryl substituent. Meanwhile, cyanopentacenes (Figure 2.3) have been exploited as acceptors in P3HT-based bulk hetero-junction solar cells, where their ET abilities yielded power conversion efficiencies as high as 0.43 %, indicating the cyano substituents could change the energy levels of the molecule therefore make the pentacene derivatives an uncommon n-type semiconductor.

![17](image1.png) ![18](image2.png)

**Figure 2.3 Examples of cyanopentacene derivatives**

The crystal packing in the solid state, which is an very important factor affecting charge carrier transport and mobility, could also be determined by substituent. Organothio-substituented pentacene derivatives have good π-stacking in crystal structure
which could benefit the charge carrier hopping among the molecules therefore provide higher charge carrier mobility.

The good solubility and solution stability provided by the substituents potentially allow for the fabrication of low cost, robust thin film devices\textsuperscript{51, 52, 53, 54, 55} using solution based processing methods such as spin coating, blade coating, spray coating, ink-jet printing, etc.

2.1.3 Water-Soluble Organic Molecules

Solution processed thin-film devices typically require a multi-layer construction in which successive layers are deposited from solvents of opposite polarity such that the deposition of each new film does not damage the preceding layer. Consequently, both hydrophobic (organic soluble) and hydrophilic (e.g., water soluble) organic semiconductors are needed. Although pentacene and its functionalized derivatives are promising organic semiconductor compounds, no water soluble pentacene is known. Examples of thin-film electronic devices prepared from water soluble organic semiconductors include solar cells that utilize water soluble donors (e.g., polythiophenes and phthalocyanines),\textsuperscript{56, 57, 58} acceptors\textsuperscript{59} or both\textsuperscript{60, 61, 62, 63, 64, 65} with power conversion efficiencies ranging from 0.17% to 0.39%. Several water soluble anthracene\textsuperscript{66, 67, 68, 69} and tetracene\textsuperscript{70} derivatives (Figure 2.4) are known but they have not been utilized for thin film electronic applications and they are not expected to exhibit superior mobility as compared to a pentacene derivative.
2.2 Results and Discussion

2.2.1 Synthesis of Pentacene Diacid and Water Soluble Pentacene

The synthesis of pentacene diacid 27 proceeded as illustrated in Scheme 2.2. 6,13-6,13-Pentacenequinone 24, was prepared with average yield of 90% via an aldol condensation reaction between o-phthalaldehyde and 1,4-cyclohexanedione in basic aqueous ethanol.

In the next step, 6,13-Pentacenequinone 24 was then reduced to 6,13-dihydro-6,13-dihydroxypentacene 25 as a mixture of two diastereomers in 95% isolated yield using a modified Zeynizadeh procedure. Due to the fact that the two diastereomers react similarly in the following step, the isolated diastereomers mixture was taken directly for the next reaction without further separation.
2.2.1.1 Synthesis of syn-3,3’-((6,13-Dihydropentacene-6,13-diyl)bis(sulfanediyl)) dipropanoic Acid Precursor 26

Thiol coupling to afford syn-3,3’-((6,13-dihydropentacene-6,13-diyl)bis(sulfanediyl))dipropanoic acid 26 was achieved via a modified Kobayashi procedure. 6,13-dihydro-6,13-dihydroxypentacene 25 was treated with 3-thiopropanoic acid and ZnI₂ in dry DCM to produce 3,3’-(6,13-dihydropentacene-6,13-diyl)bis(sulfanediyl) dipropanoic acid 26. Upon stirring for 24 hours, a pinkish white precipitate came out of the solution. After filtering and solvent washing (DCM followed by H₂O), a single diastereomer of 26 was isolated in 97% yield as a white solid. The thermogravimetric analysis (TGA) of 26 confirmed that it is stable up to 175 ºC with major weight loss started after 260 ºC. Due to two acid groups present in the molecule, 26 has low solubility in non-polar organic solvents such as DCM or CHCl₃, but it is highly soluble in polar
organic solvents such as acetone, MeOH and DMSO. An X-ray quality crystal was then
grown from a saturated solution in acetone. The X-ray structure was subsequently solved,
revealing syn stereochemistry for 26.

2.2.1.2 Synthesis of 3,3’-(Pentacene-6,13-diylbis(sulfanediyl))dipropanoic Acid 27

The p-chloranil oxidation of 26 to produce 3,3’-(pentacene-6,13-diylbis (sulfanediyl))dipropanoic acid 27 worked best when 1.5 equivalents of p-chloranil was utilized in a sealed reaction vessel in the absence of potassium carbonate. The reaction was attempted using either toluene as solvent at 130 ºC or benzene as solvent at 100 ºC. In both cases, blue solids precipitated and were filtered followed by thorough washing with benzene, hexane and hot water.

For reactions run in toluene at 130 ºC, the blue solids formed within 3 hours and corresponded to insoluble anhydride oligomers, not pentacene diacid 27. The anhydride was efficiently converted to potassium 3,3’-(pentacene-6,13-diylbis(sulfanediyl))dipropanoate 28 using a solution/suspension of potassium carbonate in ethanol. However, the yield of isolated anhydride was found to vary with scale. Thus, when utilizing 50 mg of 26, the p-chloranil oxidation in toluene at 130 ºC produced anhydride oligomer in 48% yield. Upon moving to 100 mg, 500 mg and 700 mg scales, the corresponding yields dropped to 24%, 20% and 14%, respectively.

For p-chloranil oxidation reactions run in benzene at 100 ºC, the isolated blue product is pentacene diacid 27, not anhydride. The reactions run in benzene at 100 ºC were slower (typically 24 hours reaction time) but they produced higher yields of product and were scalable. For example, when the p-chloranil oxidation was run in benzene at 100 ºC

26
using 1.5 grams of 26, 1.05 grams of pentacene diacid 27 was isolated corresponding to a 70% yield.

Pentacene diacid 27 shows limited to decent solubility in a variety of solvents including methanol, acetone, acetic acid, THF, DMSO and DMF. The solutions are stable for a minimum of a few days, excepting the case of THF where degradation to give a yellow solution is observed within 24 hours. Diacid 27 precipitates somewhat rapidly from methanol, ethanol, acetone and acetic acid, suggesting rapid aggregation in those solutions. Likewise, an X-ray quality crystal of diacid 27 was prepared from a supersaturated solution in acetic acid. A parallel displaced arrangement of pentacene backbones is observed in the extended structure (Figure 2.5), a geometry suitable for charge hopping (charge carrier mobility) throughout the crystal, as required in associated thin film electronic devices. The shortest $\pi-\pi$ distance between neighboring pentacene rings is 3.52 Å. The single crystal prepared from acetic acid includes two acetic acid molecules for every molecule of diacid 27.

Figure 2.5 X-ray crystal structure of pentacene diacid 27 that is deprotonated in basic solution to form water soluble pentacene 28. The single crystal was prepared from a saturated solution in acetic acid. Left: Pentacene diacid 27 plus two acetic acid molecules in the crystal structure. Right: Parallel displaced stacking arrangement of pentacene backbones in the crystal structure of 27.
2.2.1.3 Synthesis of Water Soluble Pentacene 28

Treatment of diacid 27 with potassium carbonate in ethanol followed by filtration, evaporation and simple solvent washing yielded amorphous, blue, water soluble pentacene 28 in 84% crude yield. To remove any residual potassium carbonate, the pentacene salt was redissolved in ethanol and the solution was diluted with hexane. Upon cooling to 10 °C, pure polycrystalline 28 was recovered by filtration in 77% isolated yield from diacid 27.

![Scheme 2.3 Interconversion of pentacene diacid (s) and water soluble pentacene (aq).](image)

Compound 28 is soluble in a variety of polar solvents including water, methanol, ethanol, DMSO and DMF. In aqueous solution, 28 and diacid 27 can be interconverted (Scheme 2.3). For example, a suspension of solid diacid 27 in water is converted to a solution of 28 upon addition of base. Likewise, solid 27 precipitates from an aqueous solution of 28 upon addition of an acid.

2.2.2 Spectroscopic and Physical Characterization of Pentacene Diacid 27 and Water Soluble Pentacene 28

Pentacene diacid 27 and water soluble pentacene 28 have been extensively characterized using \(^1\)H and \(^{13}\)C NMR spectroscopies (in D\(_2\)O and CD\(_3\)OD), electrospray ionization high resolution mass spectrometry, MALDI mass spectrometry, IR spectroscopy, UV-vis
spectroscopy (in methanol, water, and buffer solution), melting point and thermogravimetric analysis (TGA).

Figure 2.6 ¹H and ¹³C NMR spectra of WSP in D₂O

The ¹H NMR spectrum of 28 recorded in D₂O includes a singlet at 8.81 ppm corresponding to the four aromatic (X) protons at the 5, 7, 12 and 14 positions of the pentacene backbone. Multiplets at 7.72 - 7.57 and 7.31 - 7.15 ppm correspond to the remaining aromatic (AA’MM’) protons, consistent with other 6,13-disubstituted pentacenes. A pair of triplets at 2.84 and 2.02 ppm is also observed corresponding to the two separate sets of methylene protons on the 6,13-diorganothio substituents. The ¹³C NMR spectrum consists of 2 alkyl signals (37.2 and 33.5 ppm), 6 aromatic signals (130.9 - 125.5 ppm) and 1 carbonyl signal (175 ppm), as expected (Figure 2.6).
The IR spectra of diacid 27 shows a carboxylic acid stretching vibration at 1698 cm\(^{-1}\), whereas the salt 28 shows two stretching vibrations at 1560 cm\(^{-1}\) and 1390 cm\(^{-1}\) (Figure 2.7), similar to those observed for potassium acetate.

In the solid state, 28 is indefinitely stable when refrigerated and protected from light. Crystalline 28 does not melt when heated slowly in an open capillary tube from room temperature to 500 °C. However, 28 melts sharply without decomposition at 276 °C or higher when heated quickly from room temperature to melting temperature in a pre-heated melting point apparatus. A thermogravimetric analysis (TGA) plot for 28 (ramp rate 5 °C/min) reveals ~9% weight loss between room temperature and 200 °C in both air
and \( N_2 \) (Figure 2.8). This loss is likely associated with the evaporation of occluded solvent. Further \( \sim30\% \) and \( \sim50\% \) weight losses are observed between \( \sim240 \) and \( 500 \, ^\circ\text{C} \) for samples heated in \( N_2 \) and air, respectively, with most of the losses occurring between 300 and 500 \( ^\circ\text{C} \), well beyond the recorded melting point for 28. Crystalline diacid 27 melts sharply at 235 \( ^\circ\text{C} \) in a melting point apparatus without decomposition, even with slow heating. However, TGA plots for 27 in air and \( N_2 \) reveal \( \sim14-18\% \) weight loss events between 235 and 300 \( ^\circ\text{C} \), likely associated with escape of occluded solvent. The crystal structure for 27 includes two acetic acid molecules for every diacid (\( \sim20\% \) acetic acid by weight) (Figure 2.9). We conclude that both pentacene diacid 27 and water soluble pentacene 28 are relatively robust species with a high degree of thermal stability and oxidative resistance.
Figure 2.8 TGA of WSP 28 in N₂ (Top) and Air (Bottom)
Figure 2.9 TGA of acid 27 in N\textsubscript{2} (\textit{Top}) and Air (\textit{Bottom})
UV-vis spectra for water soluble pentacene 28 in methanol, water and aqueous buffer (pH = 10) are shown in Figure 2.10. The $\lambda_{\text{max}}$ values for the longest wavelength absorptions vary slightly with solvent (water: 619 nm; pH 10 buffer: 621 nm; methanol: 611 nm). From the onset of absorptions, an optical HOMO-LUMO gap for 28 of 1.91 - 1.97 eV is indicated. For comparison, the optical band gap for pentacene in o-dichlorobenzene is 2.08 eV.  

![Figure 2.10 UV-vis spectra of 28 in water, buffer solution (pH 10) and methanol as well as in solid state](image)

HOMO and LUMO energies of -5.16 and -3.43 eV, respectively, were calculated at the TD-B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level of theory in an aqueous medium (implementing the PCM solvation method) in order to match other calculations reported (see below). The calculated HOMO-LUMO gap for 28 of 1.73 eV is about 0.2 eV smaller than the measured optical gap. UV-vis spectra for water soluble pentacene 28 in
solid form was also measured with BaSO₄ as substrate, as shown in Figure 2.5. The optical band gap for solid state 28 was calculated to be 1.52 eV according to the onset of absorptions, which is even 0.2 eV smaller than the calculation value as the result of good π-π stacking in solid state. The longest λ_max values for diacid 27 also vary slightly with solvent (methanol: 612 nm; CHCl₃: 623 nm; acetone: 614 nm) but are overall quite similar to those of 28 (Figure 2.11). From the onset of absorptions, an optical HOMO - LUMO gap in solution of 1.93 - 1.96 eV is indicated for 27, while the optical band gap in solid state for 27 was calculated to be 1.55 eV.

![Figure 2.11 UV-vis spectra of 28 in water, buffer solution (pH 10) and methanol as well as in solid state](image)

The half-life of 28 in aqueous buffer solution (pH=10) with exposure to light and air is approximately four days (5786 min), making it one of the most solution-stable pentacene
derivatives known. The buffer solution was used to keep the pH of the aqueous solution, therefore to prevent salt converting to acid with presence of CO₂ in the atmosphere.

### 2.2.3 Electrochemistry of Pentacene Diacid 27 and Water Soluble Pentacene 28

Electrochemistry properties of the diacid 27 and WSP 28 were studied, respectively. The cyclic voltammetry of diacid was studied in CHCl₃ with a glassy carbon working electrode, tetrabutylammonium hexafluorophosphate (TBAPF₆) as a supporting electrolyte (Figure 2.12 (right)). Even through the current response signal is low in the cyclic voltammogram due to the poor solubility; it still clearly shows two fully reversible oxidation waves, which is similar to other 6,13-organothio substituted pentacene derivatives. However, the reduction region didn’t show very clearly reduction waves.

![Cyclic Voltammogram](image)

**Figure 2.12** Cyclic Voltammogram of WSP 28 (vs. Ag/AgCl) in methanol (left) and diacid 27 (vs. Ag/AgCl) in CHCl₃ (right)

Electrochemistry of WSP 28 (1 mM) was studied in MeOH with a glassy carbon working electrode, tetrabutylammonium hexafluorophosphate (TBAPF₆, 100 mM) as a supporting electrolyte and ferrocene as an internal reference at the scan rate of 50 mV/sec (Figure 2.12 (left)). Based on the onset values for the first oxidation and first reduction waves, we
calculated HOMO and LUMO energies \( (E_{\text{HOMO}} = -4.89 \text{ eV} \) and \( E_{\text{LUMO}} = -3.34 \text{ eV}) \). The corresponding electrochemical HOMO-LUMO gap of 1.55 eV is found to be significantly lower than the optical HOMO-LUMO gap \( (E_{\text{gap(MeOH)}} = 1.97 \text{ eV}) \). However, these energetic values from the electrochemistry are doubtable because of the unusual CV trace (Figure 2.12) compared to diacid 27 and other pentacene derivatives. Normally, pentacene derivatives show fully reversible oxidation and reduction waves. However, the CV trace for WSP 28 shows largely irreversible waves, consistent with an electrochemical-chemical “EC” mechanism in which rapid chemistry \((C)\) accompanies both oxidation and reduction electrochemical \((E)\) events.

We also observed that the reversibility improves with increasing scan rate and decreases with slower scan rates. This behavior is similar to the electrochemical switching effect as reported by Brown and co-workers for dithienylcyclopentene systems. We tentatively propose a switching mechanism in which six-membered lactone ring formation accompanies oxidation (Scheme 2.4). More work is required to fully understand the electrochemical behavior, but a mechanism of the type described in Scheme 2.4 is encouraging because it suggests the possibility of molecular switching within a thin-film. That is, thin films composed of WSP 28 should show much greater conductivity (ON
state) than a thin film composed of lactone material (OFF state), due to the significantly greater π conjugation within the flat WSP 28 structure.

Single electron oxidation reaction of WSP 28 was carried out as a support of the proposed mechanism (Scheme 2.5). Cerium (IV) ammonium nitrate ((NH₄)₂Ce(NO₃)₆) (CAN), a well known one-electron oxidizing agent, is applied in the reaction. WSP 28 was treated with CAN with present of potassium carbonate in water at room temperature to afford the oxidation product 29, the molecular structure of which is then confirmed by X-ray crystallography. The single crystal of 29 for X-ray crystallography was obtained by slow evaporation of concentrated chloroform solution. Although the structure of product is not same as proposed, the formation of six-member ring on one side of the pentacene backbone indicates that it is possible to form the proposed “off” state molecule with the six-member ring on both side.

![Scheme 2.5 Single electron oxidation of WSP 28 (left) and the X-ray structure of the product 29 (right)](image)

### 2.2.4 Modeling of Water Soluble Pentacene 28

The structure and energetics of 28 were examined using density functional theory methods. The large conformational space of 28 in the gas phase and in aqueous medium was first explored. Table 2.1 shows the structures of several of the most important conformers and gives an overview of the space. The relative energies of the conformers
are shown at the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level when optimized in the
gas phase, and in an aqueous medium represented using the polarizable continuum model
(PCM)\(^7\) as implemented in the Gaussian 03\(^7\) software package. Many other local
minima exist, all with relative energies within the range shown in Table 2.1.

From Table 2.1, it is evident that the lowest energy conformations in the gas phase place
the positively-charged potassium atoms of the CO\_2K groups above one of the pentacene
rings, indicative of a stabilizing cation-\pi interaction. A comparison of conformers B and
d suggests that each cation-\pi interaction in conformer B lowers its energy by
approximately 4 kcal/mol. Cation-\pi interactions between alkali metal cations and
benzene rings are well known. Two recent theoretical studies using B3LYP and MP2
methods calculated distances of 2.855 Å and 2.90 Å, respectively, between K\(^+\) and the
center of a single benzene molecule, and 2.956 Å and 2.93 Å when the K\(^+\) is sandwiched
between the centers of two parallel benzene molecules.\(^7\)\(^8\)\(^9\) In crystal form, these types of
sandwich structures are influenced by the presence of counter ions and have been
measured in two previous cases as having slightly longer distances of 3.14 Å for a
\([\text{K(C}_6\text{H}_5)_2][\text{CB}_{11}\text{Me}_{12}]^+\) system\(^8\)\(^0\) and 2.986 Å for a \(\text{K[B(C}_6\text{H}_5)_4}\) system.\(^8\)\(^1\) The low
energy conformers of 28 in Table 2.1 show cation-\pi interactions that have slightly longer
distances from K\(^+\) to the center of the associated benzene rings, 3.26 Å and 3.08 Å for
conformers A and B, respectively. In the lowest energy conformer A, the K\(^+\) cations are
offset from the centers of penultimate rings in order to simultaneously coordinate to three
separate oxygen atoms as well as the \pi-system of the pentacene (Figure 2.13).
Table 2.1 Relative energies in the gas phase ($E_{\text{gas}}$) and in aqueous solution ($E_{\text{solvn}}$) of symmetric conformers of water soluble pentacene 28.\(^a\)

<table>
<thead>
<tr>
<th>Conformer</th>
<th>Structure</th>
<th>$E_{\text{gas}}$ (kcal/mol)</th>
<th>$E_{\text{solvn}}$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td><img src="image1.png" alt="Structure" /></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B</td>
<td><img src="image2.png" alt="Structure" /></td>
<td>24.4</td>
<td>11.3</td>
</tr>
<tr>
<td>C</td>
<td><img src="image3.png" alt="Structure" /></td>
<td>31.4</td>
<td>8.2</td>
</tr>
<tr>
<td>D</td>
<td><img src="image4.png" alt="Structure" /></td>
<td>31.9</td>
<td>4.7</td>
</tr>
<tr>
<td>E</td>
<td><img src="image5.png" alt="Structure" /></td>
<td>32.2</td>
<td>5.3</td>
</tr>
<tr>
<td>F</td>
<td><img src="image6.png" alt="Structure" /></td>
<td>32.9</td>
<td>10.5</td>
</tr>
</tbody>
</table>

\(^a\) At the B3LYP/6-311+G(d,p)/B3LYP/6-31G(d) level. Optimizations and single-point energies in an aqueous medium were represented using the polarizable continuum model (PCM) with the recommended radii for these calculations (i.e., the united atom topological model applied to radii optimized for the PBE0/6-31G(d) levels of theory).
This complex binding with both K\(^+\) cations located on the same face of conformer A (i.e., syn arrangement) is energetically preferred by almost 25 kcal/mol compared to conformer B where the K\(^+\) cations are located on opposite faces (i.e., anti arrangement). Figure 2.13 shows the arrangement of charges in the CO\(_2\)K groups and the distances between the atoms for conformer A.

![Diagram showing the arrangement of charges in the CO\(_2\)K groups and distances between atoms for conformer A.](image)

Figure 2.13 The C\(_2\) symmetric structure of the lowest energy conformation of water soluble pentacene 28 (conformer A) showing distances (Å) between atoms in the CO\(_2\)K groups, and between K\(^+\) (X) and the carbons in the penultimate ring of pentacene. NBO charges on atoms in the CO\(_2\)K groups (at the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level) are shown in italics.

In the presence of a solvent field, the relative energies of conformers A-F fall within a smaller range of values due to stabilization imparted by the field onto the molecules. This solvation stabilization is greatest when ethylthio substituents are extended from the molecule, as in conformers D and E, allowing for more interaction between the polar CO\(_2\)K groups and the aqueous medium. While conformers D and E are favorable in an
aqueous medium, the complex binding shown in conformer A with \textit{syn} arrangement of K$^+$ cations remains the lowest energy conformer.

Table 2.1 shows discrete water soluble pentacene 28 conformers optimized in the gas phase and in a solvent medium, but it does not necessarily indicate the arrangement of 28 in its crystal form. Figure 2.14 shows the optimized geometries of two possible two-molecule stacks of 28.

![Figure 2.14 B3LYP/6-31G(d) optimized geometries of two possible two-molecule stacks of water soluble pentacene based on conformer B (a) and conformer E (b) of Table 2.1.](image)

**Fig. 2.14 (a)** illustrates the stacking arrangement of two molecules of conformer B and includes four cation-$\pi$ interactions, two located on the interior of the stack (akin to conformer A of Table 2.1) and two located on exterior faces of the stack (akin to conformer B of Table 2.1). **Fig. 2.14 (b)** illustrates the stacking of two molecules of conformer E and also mimics the crystal packing seen in the X-ray crystal structure of the corresponding pentacene diacid 27 (Figure 2.5) in which the primary interaction is $\pi$-$\pi$
stacking between parallel displaced pentacenes. At the B3LYP/6-311+G(d,p)/B3LYP/6-31G(d) level, the relative energy of the structure shown in Fig. 2.14 (b) is 18.0 kcal/mol higher than that of the structure shown in Fig. 2.14 (a). Apparently, stabilization of ions is energetically more important than π−π stacking in solid state 28. We tentatively predict the crystal structure of 28 to resemble the two molecules stack of Figure 2.14 (a). Thus far, all attempts to prepare X-ray quality single crystals of 28 have failed. As its solid state structure critically impacts its thin-film device properties, we continue to investigate structural details of crystalline and thin-film water soluble pentacene 28.

2.2.5 Ink-jet Printing of Water Soluble Pentacene 28

Several inks suitable for ink-jet printing were formulated. Thus, a mixed solvent aqueous ink solution (10 mg/mL 28 in water, glycerol and ethylene glycol [85:9:6 by weight]), a DMSO based ink (8 mg/mL 28) and an alcoholic ink (6.6 mg/mL 28 in 2:1 ethanol:methanol) were all prepared and successfully printed using an unmodified commercial ink-jet printer (Epson C88+). Prior to printing, the inks were purged with Ar and filtered through a 0.45 um PTFE membrane filter. Refillable ink-jet cartridges were also purged with Ar before filling with each ink solution. The inks were printed onto standard printer paper as well as a flexible plastic substrate (Novele polyimide photopaper, Novacentrix) as illustrated in Figure 2.15. The printed samples were thermally annealed between 120 and 130 °C for 1-5 minutes.
2.2.6 Preliminary Bilayer Photovoltaic Devices

A schematic for a bilayer solar cell with the configuration ITO/PEDOT:PSS (80 nm)/C$_{60}$ (55 nm)/C$_{60}$ (25 nm)/Al (110 nm) is shown in Figure 2.16 (a) along with the corresponding Dektak profilometer scan in Figure 2.16 (b).

Figure 2.16 Schematic of a bilayer organic solar cell fabricated using water soluble pentacene 28 (a); composite Dektak profilometer scan (b)
Figure 2.17 Optical images of thin films of C\textsubscript{60} atop water soluble pentacene 28 and PEDOT:PSS (C\textsubscript{60}:28:PEDOT-PSS) when (a) the water soluble pentacene layer was spin coated at room temperature and (b) the water soluble pentacene layer was spin coated at 60-80 °C. Microcrystalline 28 and a lack of thin-film continuity is observed in (a) while (b) illustrates a largely continuous thin-film with occasional defect.

Initially, we attempted to prepare a thin-film of water soluble pentacene 28 via spin coating onto PEDOT:PSS at room temperature using DI water as solvent. However, the PEDOT:PSS layer was visibly damaged in the presence of the slightly basic aqueous solution (pH~7.5 for a 1 mg/mL solution). Upon spin coating an alcoholic solution of 28 at room temperature, the PEDOT:PSS layer remained intact but micro crystals of water soluble pentacene were observed to form as illustrated in Figure 2.17 (a). Uniform films of 28 were ultimately formed (Figure 2.17 (b)) by spin coating a hot ethanolic solution (60 - 80 °C) onto heated substrate such that the rate of evaporation of ethanol exceeded the rate of crystal formation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>PCE\textsuperscript{a} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.125</td>
<td>0.53</td>
<td>0.322</td>
<td>0.084</td>
</tr>
<tr>
<td>3</td>
<td>0.116</td>
<td>0.58</td>
<td>0.209</td>
<td>0.056</td>
</tr>
<tr>
<td>4</td>
<td>0.102</td>
<td>0.50</td>
<td>0.228</td>
<td>0.048</td>
</tr>
<tr>
<td>5</td>
<td>0.112</td>
<td>0.52</td>
<td>0.243</td>
<td>0.056</td>
</tr>
</tbody>
</table>
Despite a lack of optimization, the water soluble pentacene-C$_{60}$ bilayer devices all showed significant photovoltaic response (Table 2.2). Open-circuit voltages ($V_{OC}$) and short circuit current densities ($J_{SC}$) were measured while the fill factors (FF) and power conversion efficiencies (PCE) were calculated after correcting for the incandescent light source. A consistent $V_{OC}$ of approximately 0.5 V was observed in all cells. The best cell (sample 1 of Table 2.2) had a FF of 0.32 and a $V_{OC}$ of 0.53 V. The measured $J_{SC}$ for this cell (0.125 mA/cm$^2$) was low, leading to a corrected PCE of 0.084%.

We observed a pronounced S-shaped J-V curve$^{82,83,84}$ near the open-circuit condition for bilayer solar cells as illustrated in Figure 2.18, leading to reduced fill-factors. The S-shaped dependence could be a contact-driven process$^{84}$ due to formation of barriers for carrier extraction$^{82}$ created by interfacial dipoles, defects, traps or charge carrier accumulation. Optimization of the photovoltaic cells is planned, including optimization of the active layer thicknesses in order to increase short circuit current densities.

![Figure 2.18 J-V curves for sample 1 of Table 2.2 in the dark and under illumination conditions (calibrated halogen lamp).](image)
2.3 **Conclusions and Future Work**

We successfully synthesized and isolated a water soluble pentacene, potassium 3,3’-(pentacene-6,13-diylbis(sulfanediyl))dipropanoate (28). Water soluble pentacene 28 was synthesized in three steps from pentacene-6,13-diol, the last involving deprotonation of the corresponding pentacene diacid 27. The synthesis of 28 is straightforward and scalable, and its isolation does not require time-consuming chromatographic separations.

Water soluble pentacene 28 has been extensively characterized using NMR, IR and UV-vis spectroscopies as well as laser desorption ionization and high resolution mass spectrometries, melting point determination and thermal gravimetric analysis. It is a robust pentacene derivative with excellent solution phase and solid-state stabilities. UV-vis spectra in several solvents indicate an optical HOMO-LUMO gap of approximately 1.91-1.97 eV. A photodegradation study indicates that aqueous solutions of 28 are stable for days. Several water soluble pentacene inks were formulated and successfully printed onto paper and flexible plastic using an unmodified commercial ink-jet printer. Unoptimized bilayer photovoltaic cells using 28 as donor and C$_{60}$ as acceptor were constructed and shown to be active. The crystal structure of the pentacene diacid precursor to 28, compound 27, has been solved and shows a parallel displaced arrangement of pentacene rings, indicative of stabilizing π–π stacking interactions. DFT modeling indicates an unusual conformation for water soluble pentacene 28 in both the gas phase and in polar media, one in which both potassium carboxylate moieties are located on the same face (syn) of the pentacene π system. Likewise, calculated two-molecule stacks of 28 suggest a crystal packing arrangement in which potassium cations are intercalated between adjacent pentacene rings.
Future work will include continued structural investigations of crystalline and thin-film
28 as well as optimization of photovoltaic cells and the fabrication of other thin-film
electronic devices prepared from 28.

2.4 Experimental

2.4.1 Analytical Instrumentation

2.4.1.1 $^1$H NMR Spectra

$^1$H NMR spectra were obtained on a Varian Mercury Plus 400 FT-NMR operating at
399.768 MHz or a Varian INOVA 500 FT-NMR operating at 499.763 MHz. All chemical
shift ($\delta_H$) values are reported in parts per million (ppm) relative to residual solvent
protons unless otherwise noted.

2.4.1.2 $^{13}$C NMR Spectra

$^{13}$C NMR spectra were obtained on a Varian Mercury Plus 400 FT-NMR operating at
100.522 MHz or a Varian INOVA 500 FT-NMR operating at 125.666 MHz. All chemical
shift ($\delta_C$) values are reported in parts per million (ppm) relative to residual solvent signal
or K$_2$CO$_3$ (160.64 ppm in D$_2$O) $^{85}$ unless otherwise noted.

2.4.1.3 Mass Spectrometry

Matrix assisted laser desorption ionization (MALDI-TOF-MS, S$_8$ as matrix) and laser
desorption ionization (LDI-TOF-MS) mass spectra was acquired on a Shimadzu Kratos
Axima-CFR mass spectrometer in reflectron mode. Electrospray ionization high-
resolution mass spectra were acquired at the Notre Dame Mass Spectrometry &
Proteomics Facility in Notre Dame, Indiana.

2.4.1.4 **Solid State FTIR Spectroscopy**

Infrared spectra of solid samples were acquired using a Thermo Scientific spectrometer (NICOLET iS10) with diamond ATR accessory (Smart iTR).

2.4.1.5 **Thermogravimetric Analysis (TGA)**

Thermogravimetric analysis was completed using a TA Instruments TGA Q5000 instrument. Samples weighing between 5 - 15 mg were heated from 35 °C - 550 °C with the ramp rate set to 5 °C/min.

2.4.1.6 **Cyclic Voltammetry**

Cyclic voltammetry (CV) study was carried out on a BAS-100B electrochemical analyzer with three electrodes in a single compartment cell. The choice of either platinum or glassy carbon serves as the working electrode, Ag/AgCl servers as the reference electrode and a Pt wire as the auxiliary electrode. Saturated tetrabutylammonium hexafluorophosphate solution (TBAPF6, 0.1M) was used as the supporting electrolyte and ferrocene as an internal reference.

2.4.1.7 **UV-Vis Spectroscopy**

UV-visible spectra were obtained on a Nicolet Evolution 300 spectrometer using 1 cm quartz cells. In order to obtain the decay profile of WSP 28 in solution with exposure to light and air, dilute solutions (2.0 \( \times \) 10\(^{-4}\) M) of WSP 28 were prepared in aqueous buffer
(pH = 10). The cells were protected from light until each experiment began, at which point an initial spectrum was recorded. The cells were placed in a tank containing water to maintain a constant temperature (25 °C) and irradiated with an overhead 15 watt, 120 volts incandescent light bulb. The solutions were repeatedly scanned at prescribed intervals until less than 5% of WSP 28 remained. Because WSP 28 is slow to decay, water was added periodically to offset evaporation and maintain a constant concentration.

2.4.2 Chromatography

Sand was obtained from Fisher Scientific Co.

Silica Gel (230-400 mesh) was obtained from Natland International Co.

Thin Layer Chromatography Plates obtained from Fisher Scientific Co.

2.4.3 Solvents

*Note: All solvents were used without further purification unless otherwise noted. Solvent drying was carried out as needed by distillation from sodium metal (THF, toluene) or by passing through a silica column in a dry-solvent delivery system.*

Acetic Acid (CH₃CO₂H) was obtained from VWR Chemical Co.

Acetone (reagent grade) was obtained from Pharmco-AAPER.

Benzene (C₆H₆) was obtained from Sigma-Aldrich.

Buffer solution (pH=10) was obtained from Fisher Scientific.

Chloroform (CHCl₃) was obtained from Pharmco-AAPER.

Dichloromethane (DCM) was obtained from Pharmco-AAPER.
Dimethylsulfoxide (DMSO) was obtained from Alfa Aesar.
Ethanol (absolute) was obtained from Pharmco-AAPER.
Methanol was obtained from Pharmco-AAPER.
Tetrahydrofuran (THF) was obtained from Fisher Scientific Co.
Toluene (PhCH₃) was obtained from Fisher Scientific Co.
All NMR solvents including acetone-\(d_6\), methanol-\(d_4\), D₂O and acetic acid-\(d_4\) were purchased from Cambridge Isotope Laboratories.

2.4.4 Reagents

Note: All reagents were used without further purification unless otherwise noted.

Ammonium Cerium(IV) Nitrate \((\text{NH}_4)₂\text{Ce(NO}_3)_6\), 98+%\) was obtained from Sigma-Aldrich.
1,4-Benzoquinone \((\text{C}_₆\text{H}_₄\text{O}_₂)\) was obtained from Acros Organics Co.
\(p\)-Chloranil \((\text{C}_₆\text{Cl}_₄\text{O}_₂)\) was obtained from Aldrich.
\(o\)-Phthalaldehyde \((\text{C}_₈\text{H}_₆\text{O}_₂)\) was obtained from Aldrich Chemical Co.
Potassium carbonate \((\text{K}_₂\text{CO}_₃)\) was obtained from J. T. Baker.
Sodium hydroxide (NaOH) was obtained from EM Science
Sodium borohydride \((\text{NaBH}_₄)\) was obtained from Aldrich Chemical Co.
3-Thiopropanoic acid \((\text{HS(CH}_₂)_₂\text{COOH})\) was obtained from Alfa-Aesar.
Zinc iodide \((\text{ZnI}_₂)\) was obtained from Aldrich.
2.4.5 Syntheses

Note: All routine solvent evaporations were conducted on a standard rotary evaporator using vacuum pump pressure unless otherwise noted.

Pentacene-6,13-dione (24)
Aqueous NaOH (10%, 5.96 g, 149 mmol) was slowly added to a solution of o-phthalaldehyde (10 g, 74.6 mmol) and 1,4-cyclohexanedione (4.18 g, 37.3 mmol) in ethanol (460 mL) under a N₂ atmosphere. The solution turned from yellow to golden brown to dark brown before a yellow solid corresponding to pentacene-6,13-dione precipitated. After stirring the reaction mixture for four hours, the crude reaction mixture was filtered and washed with ethanol, water, and methanol until the washings were colorless. The solid residue was dried under vacuum to obtain 11.02 g (96% yield) of bright yellow pentacene-6,13-dione. ¹H-NMR (500 MHz, CDCl₃) δ (ppm): 8.96 (s, 4H), 8.14 (m, 4H), 7.72 (m, 4H).

6,13-Dihydroxy-6,13-dihdropentacene (25)
Solid NaBH₄ (12.3 g, 324.4 mmol) was slowly added to a 1,000 mL round bottom flask containing a suspension of pentacene-6,13-dione 24 (5 g, 16.2 mmol) in THF (600 mL) at 0 °C. After the addition of NaBH₄ was complete, the reaction vessel was purged with N₂ and water (20 mL) was added. The reaction mixture was heated to 50 to 60 °C until homogeneous. After two hours of heating, THF was evaporated at reduced pressure, water was added, and the reaction mixture was filtered. The solids were washed with copious amounts of water followed by a small amount of cold CHCl₃. After drying, 4.31
g of a white solid was recovered (85% yield) consisting of only one diastereomer of 6,13-dihydroxy-6,13-dihydropentacene. $^1$H NMR (500 MHz, CDCl$_3$) δ (ppm): 8.12 (s, 4H), 7.95 (m, 4H), 7.48 (m, 4H), 6.63 (s, 2H), 5.81 (s, 2H).

syn-3,3'-(6,13-Dihydro-6,13-dihydro-6,13-dihydroxypentacene)bis(sulfanediyl)dipropionic acid (26)

A flame-dried, N$_2$ purged 250 mL round bottom flask was charged with ZnI$_2$ (4.08 g, 12.78 mmol), 6,13-dihydro-6,13-dihydroxypentacene (25) (2.00 g, 6.40 mmol) and 190 mL dry CH$_2$Cl$_2$. To this mixture was added 3-thiopropanoic acid (1.3 mL, 14.91 mmol) and the resulting pink reaction mixture was stirred for 24 hours. A white solid precipitated over the course of the reaction and was isolated by filtration and thoroughly washed with CH$_2$Cl$_2$ followed by warm water. Upon drying in vacuo for 24 hours, compound 26 was isolated as an off-white solid (3.03 g, 97%). An X-ray quality single crystal of 26 was grown by slow evaporation of a saturated solution in acetone. $^1$H NMR (400 MHz, CD$_3$OD) δ (ppm): 7.95 (s, 4H), 7.93 - 7.86 (m, 4H), 7.53 - 7.46 (m, 4H), 5.59 (s, 2H), 2.97 (t, 4H, J = 7.3 Hz), 2.68 (t, 4H, J = 7.3 Hz); $^1$H NMR (400 MHz, DMSO- $d_6$) δ (ppm): 12.32 (bs, 2H), 8.03 (s, 4H), 7.98 - 7.90 (m, 4H), 7.57 - 7.49 (m, 4H), 5.67 (s, 2H), 2.91 (t, 4H, J = 7.2 Hz), 2.67 (t, 4H, J = 7.2 Hz); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ (ppm): 173.17, 135.37, 132.04, 127.52, 127.18, 126.39, 46.74, 34.34, 28.29; $^{13}$C NMR (125 MHz, CD$_3$OD): δ (ppm): 176.02, 136.38, 134.01, 128.66, 128.61, 127.36, 35.52, 29.38. LDI-MS $m/z$: 490.4 [M+2]; ESI HRMS: [M$^+$ + Na] 511.1032 (calculated 511.1008, error -4.7 ppm); IR (COOH 1705 cm$^{-1}$). Melting point: the white solid started to slowly melt and change color in an open capillary tube at 135 °C and was completely melted at 140 °C as a blue-purple liquid.
3,3’-(Pentacene-6,13-diylbis(sulfanediyl))dipropanoic acid (27)

A flame dried, Ar purged 150 mL pressure vessel was charged with 26 (1.50 g, 3.07 mmol), p-chloranil (1.134 g, 4.61 mmol) and benzene (120 mL). The vessel was sealed with a Teflon screw cap. The mixture was heated with stirring to 100 °C in an oil bath for 24 hours in the dark. After cooling to room temperature, the reaction mixture was filtered and washed successively with benzene, hexanes and hot water (60 °C). After drying in vacuo overnight, pentacene 27 was isolated as a dark blue solid (1.05g, 2.16 mmol, 70%).

An X-ray quality crystal of 27 was grown from a supersaturated solution of acetic acid.

\[ ^1H \text{ NMR (500 MHz, CD}_3\text{COOD)} \delta \text{ (ppm): 9.81 (s, 4H), 8.21 - 8.13 (m, 4H), 7.53 - 7.46 (m, 4H), 3.41 (t, 4H, J = 6.9 Hz), 2.64 (t, 4H, J = 6.9 Hz);} \]

\[ ^1H \text{ NMR (500 MHz, CD}_3\text{OD)} \delta \text{ (ppm): 9.75 (s, 4H), 8.13 - 8.07 (m, 4H), 7.48 - 7.42 (m, 4H), 2.47 (t, 4H, J = 6.8 Hz);} \]

\[ ^1H \text{ NMR (500 MHz, acetone-}d_6\text{)} \delta \text{ (ppm): 9.82 (s, 4H), 8.22 - 8.15 (m, 4H), 7.53 - 7.46 (m, 4H), 3.36 (t, 4H, J = 7.0 Hz), 2.54 (t, 4H, J = 7.0 Hz).} \]

\[ ^{13}C \text{ NMR (125 MHz, CD}_3\text{COOD, 80 °C)} \delta \text{ (ppm): 134.24, 133.78, 129.89, 127.94, 127.31, 35.60, 33.35 (coincidental overlap of one aromatic signal; low intensity C=O signal is not observed).} \]

LDI-MS \text{ m/z: 486.1 [M$^+$]; ESI HRMS: [M$^+$] 487.1053 (calculated 487.1032, error -4.3 ppm); IR (COOH: 1698 cm$^{-1}$); UV-vis: 527, 570 and 612 nm in CH}_3\text{OH; 534, 575 and 623 nm in CHCl}_3; 529, 566 and 614 nm in (CH}_3\text{)}_3\text{CO. Melting point: 235 °C.} \]

Potassium 3,3’-(pentacene-6,13-diylbis(sulfanediyl))dipropanoate (28)

A flame dried, Ar purged 250 mL round bottomed flask was charged with 27 (0.80g, 1.64 mmol), K$_2$CO$_3$ (0.908g, 6.57 mmol), and absolute ethanol (250 mL). The reaction
mixture was stirred in the dark at room temperature for 3 hours under Ar. After removing excess K$_2$CO$_3$ by filtration, the filtrate was concentrated under reduced pressure. The crude blue solid was thoroughly washed with chloroform, acetone and hexane and recovered in 84% yield. Crude water soluble pentacene 28 was then re-dissolved in ethanol (200 mL) and diluted with hexane (200 mL). Upon cooling overnight at 10 °C, pure 28 was isolated by filtration as a shiny blue polycrystalline solid (0.711g, 77 % isolated yield from 27). $^1$H NMR (400 MHz, D$_2$O) δ (ppm): 8.81 (s, 4H), 7.72 - 7.57 (m, 4H), 7.31 - 7.15 (m, 4H), 2.84 (t, 4H, $J = 7.2$ Hz), 2.02 (t, 4H, $J = 7.2$ Hz); $^1$H NMR (500 MHz, CD$_3$OD) δ (ppm): 9.69 (s, 4H), 8.07 - 8.02 (m, 4H), 7.42 - 7.36 (m, 4H), 3.27 - 3.22 (pseudo–t, 4H), 2.42 - 2.37 (pseudo–t, 4H); $^{13}$C NMR (125 MHz, D$_2$O) δ (ppm): 174.97, 125.50, 125.31, 124.51, 122.69, 120.33, 120.05, 31.73, 28.06; $^{13}$C NMR (125 MHz, D$_2$O with K$_2$CO$_3$ as internal reference) δ (ppm): 174.97, 160.64 (K$_2$CO$_3$), 125.56, 125.40, 124.63, 122.72, 120.38, 120.12, 31.73, 28.08; $^{13}$C NMR (125 MHz, CD$_3$OD) δ (ppm): 180.03, 133.92, 133.54, 133.49, 129.72, 127.83, 127.00, 39.64, 35.54. MALDI-MS (S$_8$ matrix) m/z: 562.9 [M$^+$]; ESI HRMS: [M$^+$] 563.018 (calculated 563.0150, error -5.8 ppm); IR (COOK: 1560 and 1390 cm$^{-1}$); UV-vis: (538, 575 and 621 nm in pH 10 buffer; 532, 573 and 619 nm in H$_2$O; 526, 565 and 611 nm in CH$_3$OH). Melting point: 276 °C (4 does not melt between 25 °C and 500 °C when the solid is heated slowly. There is a subtle color change from blue to purple during this slow heating. However, freshly prepared samples in open capillary tubes melt sharply at 276 °C or higher when heated quickly via immersion of room temperature capillary tubes into the melting point apparatus at temperature.)
To a flame dried, Ar purged 25 mL round bottomed flask containing solution of CAN ((NH₄)₂Ce(NO₃)₆) (0.10 g, 0.16 mmol) in H₂O (1 ml), a prepared solution of potassium 3,3’-[(pentacene-6,13-diyl)bis(sulfanediyl)] dipropanoate (28) (0.02 g, 0.035 mmol) and K₂CO₃ (0.01 g, 0.07 mmol) in water (5 ml) was added slowly by syringe. The blue color of WSP 28 disappeared immediately after adding into the CAN solution. After addition, the reaction mixture was stirred for 10 min under argon at room temperature. The reaction mixture was extracted with ethyl acetate (3 x 10 ml) and purified using preparative thin layer chromatography with CHCl₃:hexanes (9:1) as eluent. 13'H-spiro[[1,3]oxathiane-2,6'-pentacene]-6,13'-dione was collected. However, 29 was partially oxidized during the purification procedure to form 6,13-pentacenequinone as impurity. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 8.80 (s, 2H), 8.06 (d, 2H, J = 8.1 Hz), 8.04 (s, 2H), 7.99 (d, 2H, J = 8.1 Hz), 7.71 - 7.65 (m, 2H), 7.65 - 7.59 (m, 2H), 3.23 (t, 2H, J = 6.3 Hz), 2.81 (t, 2H, J = 6.3 Hz).

2.4.6 Bilayer Solar Cell Device Fabrication

Bi-layer solar cells with the configuration ITO/PEDOT:PSS/28/C₆₀/Al were fabricated. Indium tin oxide (ITO) coated glass (ITO - 140 nm, glass - 1.1 mm, sheet resistance - 20 Ω/ , Delta Technologies) was diced into 15 x 15 mm chips that were cleaned by ultrasonication in soap water, followed by a DI water rinse, followed by successive ultrasonifications (10 min each) in acetone and isopropyl alcohol. Following this, the chips were again rinsed with DI water. After oven drying for 1 hour at 150 °C, the chips were cleaned using an ICP oxygen plasma treatment (300/50W, plasma/bias power in Plasma-
Therm 7900 etcher) rendering the ITO surface hydrophilic. A solution of PEDOT:PSS (high-conductivity grade from Sigma-Aldrich) was filtered through a 0.45 µm syringe filter and spin coated onto clean substrates at 4000 rpm. The chips were then baked for 20 min at 120 °C, yielding an 80 nm PEDOT:PSS film. Spin coating and thermal annealing of water soluble pentacene 28 were performed inside a glove box (oxygen < 1ppm, H2O < 1ppm) under nitrogen. A solution of 28 (1 wt%) in ethanol was prepared and filtered through a 0.45 µm syringe filter. An infrared lamp (250W) was used to heat both the substrate and the solution of 28 to 60-80 °C just prior to spin coating. A hot solution of 28 was spin coated onto the hot substrate of PEDOT:PSS at 2000 rpm for 1 minute followed by thermal annealing at 120 °C for 2 minute on a hot plate. Outside of the glove box, a 25 nm film of C60 (99.95% from SES Research) and a 110 nm film of aluminum were then deposited in successive steps, the latter through a shadow mask, via thermal evaporation with a base pressure of 5x10^-7 torr. Top view images of water soluble pentacene 4/C60 on PEDOT:PSS were taken using an optical microscope (Accu-Tech Optical Inc) connected to a 3 MP digital camera. The thickness of the films was measured using a Dektak3ST Profilometer. J-V data was acquired with a 4155A HP Semiconductor Parameter Analyzer. The photocurrent was measured under the illumination of a halogen lamp (Dolan Jenner Fiber-lite), which was calibrated to generate 0.4 times the short circuit current (JSC) of natural sunlight with an intensity of 63 mW/cm².
CHAPTER 3

PROGRESS TOWARD SYNTHESIS OF 6,13-DITHIOPENTACENE OLIGOMERS

3.1 Introduction

Pentacene is known as a benchmark semiconductor in organic electronic devices.\textsuperscript{86} However, bare pentacene has very poor solubility and very low stability in solutions with light and air, which limited its solution processability. Among the functionalized pentacenes,\textsuperscript{43, 44, 45, 46, 47, 48, 49, 50} 6,13- bis(organothio) substituted pentacenes has been proved to have decent solubility and solution stability, face-to-face crystal packing arrangements and lower HOMO-LUMO gaps. The functionalized pentacenes have been used to fabricate organic thin film devices\textsuperscript{51, 52, 53, 54, 55} using solution based processing methods such as spin coating, blade coating, spray coating, etc. However, the effect of molecular orientations and thin-film morphologies on device performance is not quite clear due to the limited long-range order. It has already been discussed previously that bare pentacene forms a herringbone arrangement in the solid state. There are also examples where functionalized pentacenes have preferred face-to-face arrangements in the solid state. It would thus be useful if one could control packing arrangement and therefore the thin-film morphology of pentacene in its solid state. One way to control the arrangement would be to chemically force the pentacenes to align themselves in a
particular direction to form a one-dimensional array during a deposition method. This might help to get them further organized into two-dimensional arrangements in a solid-state thin film. In this current project we have proposed to synthesize 6,13-dimercaptopenacene 33, which could potentially form pentacene oligomers through disulfide linkage (Scheme 3.1). This particular oligomer would have two important attributes for producing a better quality thin film of pentacene. Firstly, the end thiol functional group would help to self-assemble on a metal surface through sulfur-metal chemical bonds and second, the di-sulfide linkage would control the pentacene backbone to be oriented in a particular direction to achieve better inter-molecular interactions among the pentacene moieties. As shown in the proposed synthetic route (Scheme 3.1), in order to get 6,13-dithiopentacene oligomers, 6,13-diacetylthiopentacene 32, as an intermediate will be synthesized first and then form 6,13-dimercaptopenacene 33 via the deprotection reaction.

Scheme 3.1 Proposed synthetic route for disulfide-linked pentacene oligomers

Other than the intermediate of 6,13-thiopentacene oligomers, 6,13-acetylthiopentacene 32 itself has potential application in self-assembled monolayer formation. Organic molecular self-assembly is a bottom-up approach to nanodimensional structured self-assembled monolayers (SAMs) on well-defined metal surfaces for molecular electronics. Thiols, thiol esters, and disulfides can be easily chemisorbed on gold to form SAMs by exposure of well-defined gold substrates to solutions of the sulfur-functionalized molecules.
dithioacetylanthracene has been reported to be self assembled on Cu (111) surface with covalently binding to the surface to form rows of molecules.\textsuperscript{89,90}

Here, we successfully synthesized 6,13-diacetylthiopentacene and a more soluble derivative, 2,3,9,10-tetra(4‘-t-butylphenyl)-6,13-diacetylthiopentacene, which has potential to form SAMs on metal surface and also can be act as an intermediate for synthesis one-dimensional aligned pentacene oligomers with S-S linkage.

3.2 Results and Discussions

3.2.1 Synthesis and Characterization of 6,13-Diacetylthiopentacene 32

3.2.1.1 Synthesis of 6,13-Dihydro-6,13-diacetylthiopentacene 30

Thiol coupling to afford 6,13-dihydro-6,13-diacetylthiopentacene was achieved via a modified Kobayashi procedure (Scheme 3.2). 6,13-dihydro-6,13-dihydroxy pentacene 25 was treated with thioacetic acid and ZnI\textsubscript{2} in the presence of 4Å molecular sieves in dry DCM at room temperature under N\textsubscript{2} atmosphere. The molecular sieves were applied in the reaction mixture to prevent side reactions caused by the moisture. Upon the completion of the reaction, the molecular sieves were removed by filtration. The filtrate was then taken for aqueous workup, followed by extraction with DCM, to yield the crude
product as a mixture of syn- and anti- isomers of 6,13-dihydro-6,13-diacetyl thiopentacene with syn- isomer as the major one. After silica column chromatography purification, the syn-6,13-dihydro-6,13-diacetylthiopentacene \(30\) was isolated with an average yield of 80%. The stereochemistry of syn-6,13-dihydro-6,13-diacetyl thiopentacene \(30\) was confirmed by X-ray crystallography.

3.2.1.2 Synthesis of 6,13-Diacetylthiopentacene \(32\)

Syn-6,13-dihydro-6,13-diacetylthiopentacene \(30\) was then taken forward for the next step to produce the corresponding pentacene derivative, 6,13-diacetylthiopentacene \(32\), as shown in scheme 3.2. The aromatization reaction worked best to produce the 6,13-diacetylthiopentacene \(32\) with the yield of 50% when 1.7 equivalents of DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) was utilized in a sealed reaction vessel with toluene as solvent at 130 ºC for 4 hours. Initially, the reaction was attempted by utilizing \(p\)-chloranil, which is commonly used in this aromatization reaction, for several times with different reaction conditions. However, only a very small amount of the starting material was converted to the pentacene derivative, and most of the starting material kept unreacted even with higher equivalent of oxidant (5 eq.) and much longer reaction time (48 h). This might due to the electron-withdrawing nature of the acetyl group attached to the sulfur atom. Therefore, DDQ, as a stronger oxidant in the class, was selected to take the place of \(p\)-chloranil in the reaction. The purification of 6,13-diacetylthiopentacene \(32\) is difficult via the column chromatography due to its poor solubility in most of the organic solvents at room temperature. However, the poor solubility in most organic solvents provides a simpler purification method. After the reaction completion and
evaporation of the reaction solvent, the crude product was thoroughly washed and filtered with methanol, acetone, and hexane, to give 6,13-diacetylthiopentacene 32 as dark blue solid with the isolated yield of 50 %. The crystalline of 6,13-diacetylthiopentacene 32 could be obtained by recrystallization in CHCl₃.

3.2.1.3 Spectroscopic and Physical Characterization of 6,13-Diacetylthiopentacene 32
6,13-Diacetylthiopentacene 32 has been characterized using ¹H and VT-¹³C NMR spectroscopies, electrospray ionization high-resolution mass spectrometry, MALDI mass spectrometry, IR spectroscopy, UV-vis spectroscopy, thermogravimetric analysis (TGA), and cyclic voltammetry. The ¹H NMR spectrum of 6,13-diacetylthiopentacene 32 recorded in CDCl₃ at room temperature includes a singlet at 9.31 ppm corresponding to the four aromatic (X) protons at the 5, 7, 12 and 14 positions of the pentacene backbone. Multiplets at 8.03 - 7.99 and 7.44 - 7.40 ppm correspond to the remaining aromatic (AA'MM') protons, consistent with other 6,13-disubstituted pentacenes. The singlet at 2.59 is corresponding to the methylene protons on the acetyl group (Figure 3.1).
VT-NMR was utilized to get the $^{13}$C NMR spectroscopy due to that the poor solubility of 6,13-diacetylthiopentacene 32 could be improved by raising the temperature. The $^{13}$C NMR spectroscopies were recorded using VT-NMR in both chloroform-$d$ (VT at 40 °C) (Figure 3.2 (Top)) and $o$-DCB-$d_4$ (VT at 80 °C) (Figure 3.2 (Bottom)). The $^{13}$C NMR spectrum in chloroform-$d$ (VT at 40 °C) consists of 1 alkyl signal (30.8 ppm) and 6 aromatic signals (132.8 - 125.9 ppm) as expected, but the carbonyl signal is missing. The carbonyl signal (191.0 ppm) could be observed in the $^{13}$C NMR spectrum in $o$-DCB-$d_4$ (VT at 80 °C).
The IR spectrum of 6,13-diacetylthiopentacene 32 shows a carbonyl stretching vibration at 1693 cm$^{-1}$ indicating the present of acetyl group in the molecule (Figure 3.3). The mass spectra of 6,13-diacetylthiopentacene 32 were obtained for both MALDI-MS with m/z of 426.5 [M$^+$] and ESI HRMS with m/z of 449.0660 [M$^+$ + Na] (calculated 499.0640, error -4.4 ppm).
In the solid state, 6,13-diacetyltiopentacene 32 is indefinitely stable when refrigerated and protected from light. A thermogravimetric analysis (TGA) plot for crystalline 6,13-diacetyltiopentacene 32 (ramp rate 5 °C/min) reveals ~1% weight loss between room temperature and 280 °C in N₂ (Figure 3.4). This loss is likely associated with the evaporation of occluded solvent. Further ~25% sharp weight loss is observed in the range between 280 and 320 °C, followed by a slow weight loss of ~6% between 320 and 500 °C. Therefore, 6,13-diacetyltiopentacene 32 is relatively robust with a high degree of thermal stability, which makes it possible to monolayer self-assemble this compound via thermal evaporation method.
Figure 3.4 Thermogravimetric analysis (TGA) of crystalline 6,13-diacetylthiopentacene 32 in N₂

UV-vis spectroscopies in both CHCl₃ solution and solid state (Figure 3.5), as well as cyclic voltammetry (Figure 3.6), for 6,13-diacetylthiopentacene 32 are recorded. The solid state UV-vis spectrum was measured with BaSO₄ as substrate. As shown in Figure 3.5, the solid state UV-vis spectrum is red shifted compared to the solution state UV-vis spectrum, lead by the fact that in the solid-state pentacene molecules are stacked close together. Therefore, the optical band gap (1.48 eV) calculated from the onset value of the longest maximum absorption wavelength in solid state UV-vis spectrum is much smaller compared to the optical HOMO-LUMO gap (1.93 eV) calculated from the solution state UV-vis spectrum.
Figure 3.5 UV-vis spectra of 6,13-diacetyltioptacene 32 in chloroform solution and solid state

Figure 3.6 Cyclic voltammogram of 6,13-diacetyltioptacene 32 in saturated CHCl₃ solution
The cyclic voltammogram is obtained in a saturated CHCl₃ solution of 6,13-diacetylthiopentacene 32 due to the poor solubility of the compound. Although the current response signal is low in the cyclic voltammogram is low due to the poor solubility; it still clearly shows one fully reversible oxidation wave and the HOMO-LUMO gap could be calculated as 1.72 eV, which is between the optical HOMO-LUMO gap and the optical band gap. With exposure to light and air, the half-life of 6,13-diacetylthiopentacene is 1112 minutes in CHCl₃ solution and 1430 minutes in ODCB, indicating similar solution stability in light and air comparing to other 6,13-diorganothiopentacenes.

As discussed in the introduction, other than the intermediate for pentacene oligomers with disulfide linkage, 6,13-diacetylthiopentacene 32 could also be a potential candidate for preparing a self-assembled monolayer on metal surface, which is beneficial to improve the thin-film device performance.

### 3.2.2 Towards the synthesis of 6,13-dithiopentacene oligomers

6,13-diacetylthiopentacene was then carried on towards the synthesis of pentacene oligomers with disulfide linkage. As discussed in the introduction, the proposed synthetic approach of 6,13-dithiopentacene oligomers consists two steps: (1) deacetylation with presence of base, using K₂CO₃ in methanol following Han and Balakumar’s procedure to afford free thiol and (2) oxidation of free thiol using iodine to form disulfide oligomers (scheme 3.1).
3.2.2.1 Deacetylation of 6,13-Dihydro-6,13-diacetylthiopentacene 30

Due to the fact that 6,13-diacylthiopentacene 32 as other pentacene derivatives is not very stable in solution, we started with attempting of deprotect the acetyl groups of its precursor, 6,13-dihydro-6,13-diacetylthiopentacene 30, as a control reaction (Scheme 3.3).

![Scheme 3.3 Deacetylation of 6,13-dihydro-6,13-diacetylthiopentacene](image)

6,13-dihydro-6,13-diacetylthiopentacene was stirred for 2 hours in MeOH in the presence of K₂CO₃ and NaBH₄ at RT under nitrogen atmosphere to afford 6,13-dihydro-6,13-dithiopentacene 34 as off-white solid. NaBH₄ is utilized to protect formation of the more stable byproduct 6,13-pentacenethioquinone 35.

3.2.2.2 Deacetylation of 6,13-diacylthiopentacene 32

Therefore, we utilized the same reaction condition expect for the present of NaBH₄ to deprotect the acetyl groups of 6,13-diacylthiopentacene 32 as it works well for the dihydro species. However, at room temperature no reaction happened even with longer reaction time. By raising the reaction temperature to refluxing, we were able to push some reaction to occur (Scheme 3.4). After refluxing in methanol for 2 hours with K₂CO₃, the reaction mixture was cooled down to room temperature, filtered and washed with methanol and then H₂O to remove K₂CO₃. The blackish solid collected was slightly
soluble in chloroform. Therefore, we could only characterize it with UV-vis spectroscopy and mass spectroscopy.

![Scheme 3.4 Deacetylation of 6,13-diacetylthiopentacene](image)

**Scheme 3.4 Deacetylation of 6,13-diacetylthiopentacene**

![Figure 3.7 UV-vis spectra of 6,13-diacetylthiopentacene 32 (blue) and the product after deacetylation (red)](image)

**Figure 3.7 UV-vis spectra of 6,13-diacetylthiopentacene 32 (blue) and the product after deacetylation (red)**

The UV-vis spectra of starting material, 6,13-diacetylthiopentacene 32, and the blackish solid product are both shown in Figure 3.7. Surprisingly, the longest $\lambda_{\text{max}}$ of the product (692 nm) is redshifted for 71 nm compared with that of the starting pentacene (621 nm). The optical HOMO-LUMO gap of the product calculated from the onset value of the
longest maximum absorption wavelength is 1.64 eV, while the optical HOMO-LUMO gap of the starting pentacene is 1.93 eV. The redshifted $\lambda_{\text{max}}$ and the corresponding narrowed HOMO-LUMO gap indicate an extended conjugated $\pi$-system, which might results from the oligomerization of 6,13-deacetyltiopentacene 32.

![MALDI spectrum](image)

**Figure 3.8** MALDI spectrum of disulfide-linked pentacene oligomers

The MALDI spectrum of the insoluble solid product is obtained using sulfur crystal as matrix (Figure 3.8). The spectrum shows clusters at around 690, 1046, and 1384, which are close to the mass of oligomers when the repeat unit number are 2, 3, and 4, respectively. Based on the UV-vis and MALDI results, the pentacene oligomers are possibly formed from 6,13-diacetylpentacene in this reaction instead of the proposed 6,13-dithiopentacene. The reason why oligomerization occurs along with deacetylation could be explained by the poor stability of 6,13-thiopentacene 33. Free thiols, which are directly adjacent to aryl rings, could be easily oxidized in the air to form disulfide. Therefore, it could be proposed that the 6,13-dithiopentacene 33 was generated first from the deacetylation of 6,13-diacetyltiopentacene 32 and then oxidized during the reaction.
and workup step, was oxidized by the oxygen from air and oligomerized to give the insoluble 6,13-dithiopentacene oligomers. Although due to the poor solubility of the oligomers formed, it was unable to fully characterize the oligomers to confirm their chemical structures, we found that pentacene oligomerization with disulfide-linkage is possible and the oligomers has a smaller HOMO-LUMO gap which is beneficial for photovoltaic applications as they could absorb more light in the visible light range.

3.2.3 Synthesis and Characterizations of 2,3,9,10-Tetra(4'-t-butylphenyl)-6,13-diacetylthiopentacene 42

In order to resolve the solubility issue of the 6,13-diacetylthiopentacene and the corresponding pentacene oligomer with sulfur-sulfur linkage, t-butylphenyl groups are introduced to the pentacene backbone at 2,3,9,10-pisitions. These positions are chosen to prevent the possible steric hindrance of pentacene oligomers. 2,3,9,10-tetra(4'-t-butylphenyl)-6,13-diacetylthiopentacene 42 was successfully synthesized in several steps from o-xylene. The synthesis will be discussed in the following section.

3.2.3.1 Synthesis of 2,3,9,10-Tetra(4'-t-butylphenyl)-6,13-dihydro-6,13-dihydroxy pentacene 40

The synthetic route for 2,3,9,10-tetra(4'-t-butylphenyl)-6,13-dihydro-6,13-dihydroxypentacene 40 was shown in scheme 3.5. Bromination of o-xylene by slowly adding Bromine into o-xylene at 0 °C with present of catalytic amount of I2 gave 4,5-dibromo-o-xylene 36, which was isolated as colorless crystalline solid after recrystallization in methanol. In next following step, 36 was reacted with 4-t-
butylphenylboronic acid with a catalytic amount of Pd(PPh₃)₄ in THF and 20% sodium carbonate aqueous solution under N₂. The reaction mixture was heated to reflux for 1 day to afford 1,2-di(4'-t-butylphenyl)-5,6-dimethylbenzene 37, which was then purified by trituration using chloroform and methanol after work up. Compound 37 was then brominated using NBS and AIBN in chloroform with irradiating by tungsten lamp to produce 1,2-di(4'-t-butylphenyl)-5,6-di(bromomethyl)benzene 38. Compound 38 was then reacted with 1,4-benzoquinone in presence of potassium iodide in DMF at 155°C for overnight to give 2,3,9,10-tetra(4'-t-butylphenyl)-6,13-pentacenequinone 39 as yellow precipitation. Finally, the pentacenequinone was then reduced to 2,3,9,10-tetra(4'-t-butylphenyl)-6,13-dihydro-6,13-dihydroxypentacene 40 as a mixture of two diastereomers in 90% isolated yield using a modified Zeynizadeh procedure.

Scheme 3.5 Synthesis of 2,3,9,10-tetra(4'-t-butylphenyl)-6,13-dihydro-6,13-dihydroxypentacene 40
3.2.3.2 Synthesis of 2,3,9,10-Tetra(4'-t-butylphenyl)-6,13-diacetyltiopentacene 42

Thiol coupling to afford 2,3,9,10-tetra(4'-t-butylphenyl)-6,13-dihydro-6,13-diacetyltiopentacene 41 was achieved via a modified Kobayashi procedure (Scheme 3.6) similar as described in section 3.2.1.1. 2,3,9,10-tetra(4'-t-butylphenyl)-6,13-dihydro-6,13-dihydroxypentacene 40 was treated with thioacetic acid and ZnI$_2$ in the presence of 4Å molecular sieves in dry DCM at room temperature under N$_2$ atmosphere. The molecular sieves were applied in the reaction mixture to prevent side reactions caused by the moisture. Upon the completion of the reaction, the molecular sieves were removed by filtration. The filtrate was then taken for aqueous workup, followed by extraction with DCM, to yield crude product. After silica column chromatography purification, 2,3,9,10-tetra(4'-t-butylphenyl)-6,13-dihydro-6,13-dihydroxypentacene 41 was isolated with an average yield of 80%. The stereochemistry of compound 41 was assigned by $^1$H NMR comparing to syn-6,13-dihydro-6,13-diacetylthiopentacene 30, the stereochemistry of which has been confirmed by X-ray crystallography. 2,3,9,10-tetra(4'-t-butylphenyl)-
6,13-dihydro-6,13-dihydroxypentacene 41 was then taken forward for the next step to produce the corresponding pentacene derivative, 2,3,9,10-tetra(4'-t-butylphenyl)-6,13-diacetylthiopentacene 42, as shown in scheme 3.6. The aromatization reaction worked best to produce 2,3,9,10-tetra(4'-t-butylphenyl)-6,13-diacetylthiopentacene 42 with the yield of 16% when 1.0 equivalents of DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) was utilized in a sealed reaction vessel with toluene as solvent at 130 °C for 2 hours. After column chromatographic separation using ethyl acetate and hexane (1:3) as eluent at first and followed by CHCl₃, 2,3,9,10-tetra(4'-t-butylphenyl)-6,13-diacetylthiopentacene 42 was recovered as a dark blue solid. Due to the poor solubility of 42 in ethyl acetate, it stayed in the column while other impurities eluted using EtOAc/hexane. After removing all impurities, the eluent was switch to CHCl₃ in which compound 42 is soluble, and the pentacene 42 was collected. For further purification, solid of 42 was washed with EtOAc and filtered. Upon drying in vacuo, compound 42 was isolated as a dark blue solid.

3.2.3.3 Spectroscopic and Physical Characterization of 2,3,9,10-Tetra(4'-t-butylphenyl)-6,13-diacetylthiopentacene 42

2,3,9,10-Tetra(4'-t-butylphenyl)-6,13-diacetylthiopentacene 42 has been characterized using ¹H and ¹³C NMR spectroscopies, and UV-vis spectroscopy. The ¹H NMR spectrum of 2,3,9,10-Tetra(4'-t-butylphenyl)-6,13-diacetylthiopentacene 42 recorded in CDCl₃ at room temperature includes a singlet at 9.26 ppm corresponding to the four aromatic (X) protons at the 5, 7, 12 and 14 positions of the pentacene backbone and one singlet at 8.03 ppm corresponding to the four aromatic (X) protons at the 1, 4, 8 and 11 positions. The
two sets of doublets at 7.27 and 7.18 ppm correspond to the aromatic protons on the phenyl substituents. The singlet at 2.56 is corresponding to protons on the acetyl group and the singlet at 1.33 ppm corresponding to protons on the t-butyl groups. (Figure 3.9).

Figure 3.9 $^1$H NMR spectrum of 2,3,9,10-tetra(4'-t-butylphenyl)-6,13-diacetyldithiopentacene in CDCl$_3$

Due to the improved solubility, $^{13}$C NMR spectroscopy could be recorded at room temperature instead of the VT-NMR in chloroform-$d$ as shown in Figure 3.10. The $^{13}$C NMR spectrum in chloroform-$d$ (VT at 40 ºC) consists of 1 carbonyl signal at 193.77 ppm corresponding to the carbonyl carbon in acetyl group, 9 aromatic signals in the range of 149.88 - 124.78 ppm for pentacene backbone and phenyl substituents (10 signals expected), 1 alkyl signal at 34.64 ppm for methyl carbon in acetyl group, and 1 alkyl signal at 31.51 ppm for methyl carbon and 1 signal at 30.71 ppm for tertiary carbon in the t-butyl group.
UV-vis spectroscopy of 2,3,9,10-tetra(4'-t-butylphenyl)-6,13-diacetyltetraphenylene 42 in chloroform is shown in Figure 3.11. The spectrum shows characteristic three waves for pentacene derivatives with $\lambda_{\text{max}}$ of 644 nm, which is red-shifted 23 nm compared with that of 6,13-diacetyltetraphenylene. It may be explained by the fact that although the four t-butylphenyl substituents at 2,3,9,10-positions are not in the same plain with the pentacene backbone, they could still extend the $\pi$-conjugation system of the pentacene backbone in some extent. The optical HOMO-LUMO gap calculated from the onset value of the longest maximum absorption wavelength is 1.86 eV.
3.2.4 Towards the Synthesis of 2,3,9,10-(4'-t-butylphenyl)-6,13-Dithiopentacene oligomers

Synthesis of S-linked 2,3,9,10-(4'-t-butylphenyl)pentacene oligomers was attempted using the similar reaction condition that was utilized to synthesize the disulfide-linked pentacene oligomers from 6,13-diacetylthiopentacene and starting with 2,3,9,10-(4'-t-butylphenyl)-6,13-diacetylthiopentacene 42 (Scheme 3.7). After refluxing in methanol for 2 hours with K₂CO₃, the reaction mixture was cooled down to room temperature,
filtered and washed with methanol and then H$_2$O to remove K$_2$CO$_3$. Due to the improved solubility in chloroform, preparative TLC plate with CHCl$_3$/Hexanes (2:1) as eluent was used for purification. However, fully isolation was not achieved due to the limited amount of the compound and the reduced solubility after purification. The compound was characterized by UV-vis spectroscopy and mass spectroscopy.

![Figure 3.12 UV-vis spectra of 2,3,9,10-tetra(4'-t-butylphenyl)-6,13-diacetylthiopentacene (blue) and product after deacetylation (red)](image)

The UV-vis spectra of starting material, 2,3,9,10-tetra(4'-t-butylphenyl)-6,13-diacetylthiopentacene 42, and the product after deacetylation reaction are both shown in **Figure 3.12**. The chloroform solution of the product is greenish blue. Similar as the 6,13-diacetylthiopentacene case, a redshift of the longest $\lambda_{\text{max}}$ was observed. However, there is only one big absorption peak in the range of 700 - 800 nm for the oligomer product, which differs a lot from the three characteristic absorption peaks for pentacenes. The
longest $\lambda_{\text{max}}$ of the product (734 nm) is redshifted for 95 nm compared with that of the starting pentacene (649 nm). The optical HOMO-LUMO gap of the product calculated from the onset value of the longest maximum absorption wavelength is 1.61 eV, while the optical HOMO-LUMO gap of the starting pentacene is 1.85 eV. The redshifted $\lambda_{\text{max}}$ and the corresponding narrowed HOMO-LUMO gap indicate an extended conjugated $\pi$-system, which might result from the oligomerization of 2,3,9,10-tetra(4'-$t$-butylphenyl)-6,13-deacetylthiopentacene 42.

![MALDI spectrum of disulfide-linked 2,3,9,10-tetra($t$-butylphenyl)pentacene oligomers](image)

**Figure 3.13** MALDI spectrum of disulfide-linked 2,3,9,10-tetra($t$-butylphenyl)pentacene oligomers

The MALDI spectrum of the oligomer product is obtained using sulfur crystal as matrix (Figure 3.13). The spectrum shows clusters at around 992 and 1904, which are not exactly match with the mass/charge of the oligomers.

Although we was unable to verify if the compound formed is the proposed pentacene oligomers, the UV-vis result indicates its smaller HOMO-LUMO gap and therefore potential application as organic semiconductors. The solubility issue is still the major
limitation for this type of compound. Further study with other substitution groups is necessary for this pentacene oligomer study.

3.3 Conclusion and Future Work

Both 6,13-diacetyltiopentacene 32 and 2,3,9,10-tetra(4'-t-butylphenyl)-6,13 diacetyltiopentacene 42 have been successfully synthesized and characterized. From the UV-vis spectra, we could draw the conclusion that introducing four t-butylphenyl groups at the 2,3,9,10 positions of pentacene backbone is able to narrow down the HOMO-LUMO gap.

Syntheses of 6,13-thiopentacene oligomers and 2,3,9,10-tetra(4'-t-butylphenyl)-6,13-thiopentacene oligomers have been attempted. However, due to the poor solubility, purification and characterizations are limited. The UV-vis absorption spectra indicate that the HOMO-LUMO gaps of both 6,13-thiopentacene oligomers and 2,3,9,10-tetra(4'-t-butylphenyl)-6,13-thiopentacene oligomers are much smaller compared to the corresponding pentacene derivatives.

In the future, the solubility issue needs to be resolved by introducing some other groups, such as alkyl groups instead of the aryl groups.

3.4 Experimental

3.4.1 Analytical Instrumentation

3.4.1.1 $^1$H NMR Spectra

$^1$H NMR spectra were obtained on a Varian Mercury Plus 400 FT-NMR operating at 399.768 MHz or a Varian INOVA 500 FT-NMR operating at 499.763 MHz. All chemical
shift ($\delta_H$) values are reported in parts per million (ppm) relative to residual solvent protons unless otherwise noted.

3.4.1.2 $^{13}$C NMR Spectra
$^{13}$C NMR spectra were obtained on a Varian Mercury Plus 400 FT-NMR operating at 100.522 MHz or a Varian INOVA 500 FT-NMR operating at 125.666 MHz. All chemical shift ($\delta_C$) values are reported in parts per million (ppm) relative to residual solvent signal.

3.4.1.3 Mass Spectrometry
Matrix assisted laser desorption ionization (MALDI-TOF-MS, S$_8$ as matrix) and laser desorption ionization (LDI-TOF-MS) mass spectra was acquired on a Shimadzu Kratos.

3.4.1.4 Thermogravimetric Analysis (TGA)
Thermogravimetric analysis was completed using a TA Instruments TGA Q5000 instrument. Samples weighing between 5 - 15 mg were heated from 35 °C - 550 °C with the ramp rate set to 5 °C/min.

3.4.1.5 Cyclic Voltammetry
Cyclic voltammetry (CV) study was carried out on a BAS-100B electrochemical analyzer with three electrodes in a single compartment cell. The choice of either platinum or glassy carbon serves as the working electrode, Ag/AgCl servers as the reference electrode and a Pt wire as the auxiliary electrode. Saturated tetrabutylammonium hexafluorophosph-
phate solution (TBAPF6, 0.1M) was used as the supporting electrolyte and ferrocene as an internal reference.

3.4.1.6 UV-Vis Spectroscopy

UV-visible spectra were obtained on a Nicolet Evolution 300 spectrometer using 1 cm quartz cells. In order to obtain the decay profile of 6,13-diacetylthiopentacene in solution with exposure to light and air, dilute solutions ($2.0 \times 10^{-4}$ M) of 6,13-diacetylthiopentacene were prepared in chloroform or o-DCB. The cells were placed in a tank containing water to maintain a constant temperature (25 °C) and irradiated with an overhead 15 watt, 120 volts incandescent light bulb. The solutions were repeatedly scanned at prescribed intervals.

3.4.2 Chromatography

Sand was obtained from Fisher Scientific Co.

Silica Gel (230-400 mesh) was obtained from Natland International Co.

Thin Layer Chromatography Plates obtained from Fisher Scientific Co.

3.4.3 Solvents

Note: All solvents were used without further purification unless otherwise noted. Solvent drying was carried out as needed by distillation from sodium metal (THF, toluene) or by passing through a silica column in a dry-solvent delivery system.
Dry methylene chloride (CH₂Cl₂), tetrahydrofuran (THF), acetonitrile (CH₃CN), toluene, diethylether (Et₂O), N,N-dimethylformamide (DMF) and methanol (MeOH) were obtained by passing through a column using an Inovative Technology Inc. solvent delivery system.

Acetone (reagent grade) was obtained from Pharmco-AAPER.

Chloroform (CHCl₃) was obtained from Pharmco-AAPER.

Dichloromethane (DCM) was obtained from Pharmco-AAPER.

Methanol was obtained from Pharmco-AAPER.

Tetrahydrofuran (THF) was obtained from Fisher Scientific Co.

Toluene (PhCH₃) was obtained from Fisher Scientific Co.

All NMR solvents including acetone-d₆, methanol-d₄, D₂O and acetic acid-d₄ were purchased from Cambridge Isotope Laboratories.

### 3.4.4 Reagents

*Note: All reagents were used without further purification unless otherwise noted.*

Thioacetic acid (HSCOCH₃) was obtained from Alfa-Aesar.

2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was obtained from Avocado Research Chemicals.

Tetrakis(triphenylphosphine)palladium(0) was obtained from TCI.

4-tert-Butylphenylboronic acid was obtained from Matrix Scientific.

Bromine (Br₂) was obtained from Acros Organic Co.

Iodine (I₂) was obtained from Acros Organic Co.
\( o \)-Xylene (C\(_8\)H\(_{10}\)) was obtained from Sigma.

Potassium iodide (KI) was obtained from Acros Organic Co.

Sodium carbonate (Na\(_2\)CO\(_3\)) was obtained from Fisher Scientific Co.

N-Bromosuccinimide (NBS) was obtained from Aldrich Chemical Co.

Azobisisobutyronitrile (AIBN) was obtained from Aldrich Chemical Co.

1,4-Benzquinone (C\(_6\)H\(_4\)O\(_2\)) was obtained from Acros Organics Co.

Sodium hydroxide (NaOH) was obtained from EM Science

Sodium borohydride (NaBH\(_4\)) was obtained from Aldrich Chemical Co.

Zinc iodide (ZnI\(_2\)) was obtained from Aldrich.

3-Thiopropanoic acid (HS(CH\(_2\))\(_2\)COOH) was obtained from Alfa-Aesar.

\( p \)-Chloranil (C\(_6\)Cl\(_4\)O\(_2\)) was obtained from Aldrich.

Potassium carbonate (K\(_2\)CO\(_3\)) was obtained from J. T. Baker.

3.4.5 **Syntheses**

*Note: All routine solvent evaporations were conducted on a standard rotary evaporator using vacuum pump pressure unless otherwise noted.*

**syn-6,13-Dihydro-6,13-diacylthiopentacene (30) and anti-6,13-Dihydro-6,13-diacylthiopentacene (31)**

A flame-dried, N\(_2\) purged 100 mL round bottom flask was charged with ZnI\(_2\) (409 mg, 1.28 mmol), 6,13-dihydro-6,13-dihydroxypentacene (200 mg, 0.64 mmol), 4Å molecular sieves and 40 mL dry CH\(_2\)Cl\(_2\). To this mixture was added thioacetic acid (0.1 mL, 1.41 mmol) and the resulting pinkish reaction mixture was stirred for 1 hour in the
dark. The reaction was TLC monitored. After reaction, the reaction mixture was filtered with CH₂Cl₂ and the filtrate was thoroughly washed with water, saturated solution of sodium bicarbonate and brine. Upon evaporating the solvent and followed by drying in vacuo, crude 6,13-Dihydro-6,13-diacetylthiopentacene (13 and 14) was recovered. After column chromatographic separation using dichloromethane and hexanes (1:1) syn isomer 13 was isolated as an off-white solid (Syn: 250 mg, 91%). By collecting several batches, the anti isomer 14 was isolated by three times preparatory TLC chromatography using chloroform and hexanes (1:3). In both column and preparatory TLC chromatography, the syn isomer moves faster than the anti isomer.

**syn-6,13-Dihydro-6,13-diacetylthiopentacene (30):** ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.06 (s, 4H), 7.86 - 7.80 (m, 4H), 7.51 - 7.45 (m, 4H), 6.56 (s, 2H), 2.40 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 194.36, 135.26, 133.09, 127.91, 127.61, 126.66, 46.24, 30.55. ESI HRMS: [M⁺ + Na] 451.0821 (calculated 451.0797, error -4.8 ppm).

**anti-6,13-Dihydro-6,13-diacetylthiopentacene (31):** ¹H NMR (500 MHz, CDCl₃) δ (ppm): 8.11 (s, 4H), 7.87 - 7.81 (m, 4H), 7.50 - 7.44 (m, 4H), 6.38 (s, 2H), 2.53 (s, 6H). ¹³C NMR (125 MHz, CDCl₃) δ (ppm): 193.99, 134.59, 132.72, 127.86, 126.57, 126.03, 47.27, 30.93.

**6,13-Diacetylthiopentacene (32)**

To a flame dried, Ar purged 15 mL pressure vessel compound 13 (200 mg, 0.46 mmol), DDQ (190 mg, 0.78 mmol) and dry toluene (8 mL) was added. The reaction mixture was thoroughly degased and refilled with Ar. The vessel was then sealed with a Teflon screw cap. The mixture was stirred and heated to 130 °C in an oil bath for 4 hours in the dark.
After cooling down to room temperature, the reaction mixture was evaporated to get crude pentacene. After thoroughly washed and filtered with methanol, acetone, and hexane, pentacene 21 was recovered as a dark blue solid (99 mg, 50%). The pentacene 21 was further purified by recrystallization in chloroform (Don’t have any isolated yield after recrystallization). $^1$H NMR (500 MHz, CDCl$_3$) δ (ppm): 9.31 (s, 4H), 8.03 - 7.99 (m, 4H), 7.44 - 7.40 (m, 4H), 2.59 (s, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$, VT = 40 °C) δ (ppm): 132.71, 132.49, 128.77, 127.16, 126.63, 125.97, 30.76. MALDI-MS m/z: 426.5 [M$^+$]; ESI HRMS: [M$^+$ + Na] 449.0660 (calculated 499.0640, error -4.4 ppm).

4,5-Dibromo-o-xylene (36)

To a flame-dry N$_2$ purged 250 mL round bottom flask I$_2$ (0.2 g, 0.79 mmol) and o-xylene (46 mL, 375 mmol) was added. This was followed by dropwise addition of Br$_2$ (40 ml) using dropping funnel over 1 h, maintaining the temperature at 0 °C throughout. After addition the resulting solid was left at room temperature for over night, before being dissolved in Et$_2$O (100 ml), washed with 2N NaOH (2 × 100 ml), H$_2$O (2 × 100 ml), Brine, dried over Na$_2$SO$_4$, filtered and concentrated in vacuo. The pink oil was then recrystallized from MeOH to give white crystal solid 1 (39 g, 40%). $^1$H NMR (500 MHz, CDCl$_3$) δ (ppm): 7.37 (s, 2H), 2.18 (s, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ (ppm): 137.76, 134.34, 121.24, 19.22.

1,2-Di(4'-t-butylphenyl)-5,6-dimethylbenzene (37)

4,5-dibromo-o-xylene (36) (5 g, 18.9 mmol) and 4-t-butylphenylboronic acid (8.2 g, 46.1 mmol) were mixed in 1,4-dioxane (100 mL) under Nitrogen, followed by successive
addition of a catalytic amount of Pd(PPh₃)₄ (140 mg). The resulting mixture was bubbled with N₂ for 20 min and then the aqueous sodium carbonate solution (20%, 80 mL) was added slowly by pipette. The resulting mixture was then heated to reflux for 1 d. After cooling down to room temperature, the product was extracted with DCM, washed with H₂O, brine, and dried over Na₂SO₄. Brownish oil obtained after evaporation was then flashed through a plug column with CHCl₃ as mobile phase and concentrated to give clear light yellow oil, which was further solidified by adding MeOH. The mixture was then filtered and washed with MeOH. After dried under vacuum overnight, the white solid residue was collected to give 37 (4.9 g, 70% yield). ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.21 (s, 2H), 7.20 (d, J = 8.6 Hz, 4H), 7.05 (d, J = 8.6 Hz, 4H), 2.33 (s, 6H), 1.28 (s, 18H). ¹³C NMR (125 MHz, CDCl₃) δ (ppm): 149.08, 138.70, 138.12, 135.61, 132.08, 129.59, 124.71, 34.52, 31.51, 19.52.

1,2-Di(4'-t-butyphenyl)-5,6-di(bromomethyl)benzene (38)

A mixture of 37 (3.0 g, 8.10 mmol), N-bromosuccinimide (5.73 g, 32.4 mmol) and AIBN (0.15 g) in CHCl₃ (150 mL) was irradiated by a 250 W tungsten lamp for 3 h under reflux. After cooling, succinimide precipitated as a colorless powder and was filtered and washed with CHCl₃. Following evaporation of solvent from the filtrate, the crude product was suspended in MeOH (100 mL) and stirred for 5 min to dissolve unreacted NBS and by-products. The resulting suspension was then filtered and washed with MeOH to yield the title compound (3.87 g, 91% crude) as white solid. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.43 (s, 2H), 7.24 (d, J = 8.4 Hz, 4H), 7.06 (d, J = 8.4 Hz, 4H), 4.74 (s, 4H), 1.30
(s, 18H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ (ppm): 150.06, 141.73, 137.35, 135.29, 133.59, 129.43, 124.99, 34.61, 31.46, 30.15.

2,3,9,10-Tetrakis(t-butylphenyl)-6,13-pentacenequinone (39)

To a clear solution of 38 (5 g, 9.47 mmol) in DMF (150 mL) was added 1,4-benzoquinone (0.465 g, 4.3 mmol) and potassium iodide (11.43 g, 68.9 mmol). The resulting reddish brown suspension was heated and stirred at 155°C for 17 h. After cooling to RT, the yellow solids were vacuum filtered and washed with water and acetone followed by drying to yield the desired product (1.2 g, 30 % crude). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ (ppm): 8.97 (s, 4H), 8.15 (s, 4H), 7.30 (d, 8H, $J = 8.3$ Hz), 7.17 (d, 8H, $J = 8.3$ Hz), 1.33 (s, 36H).

2,3,9,10-Tetrakis(t-butylphenyl)-6,13-dihydroxy-6,13-dihydropentacene (40)

Solid NaBH$_4$ (0.163 g, 4.3 mmol) was slowly added to a 100 mL round bottom flask containing a suspension of 39 (0.2 g, 0.24 mmol) in THF (20 mL). After the addition of NaBH$_4$ was complete, the reaction vessel was purged with N$_2$ and water (0.5 mL) was added. The reaction mixture was heated to reflux and stirred for overnight in the dark. After cooling to room temperature and evaporation of THF at reduced pressure, water was added to the reaction mixture and filtered. The resulting solid residue was then washed copious amounts of water followed by a small amount of hexane. After drying, 198 mg of a white solid was recovered consisting of two isomers (76:24) of 5 (98.5 % yield). Major isomer $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ (ppm): 8.07 (s, 4H), 7.91 (s, 4H), 7.28 - 7.24 (m, 8H), 7.14 (d, $J = 8.5$ Hz, 8H), 5.91 (d, $J = 7.1$ Hz, 2H), 3.35 (d, $J = 7.2$ Hz, 2H).
Hz, 2H), 2.30 (d, J = 5.8 Hz, 1H), 1.31 (s, 36H). Minor isomer $^1$H NMR (500 MHz, CDCl$_3$) δ (ppm): 8.13 (s, 4H), 7.92 (s, 4H), 7.28 - 7.24 (m, 8H), 7.14 (d, J = 8.6 Hz, 8H), 6.23 (d, J = 5.9 Hz, 2H), 2.30 (d, J = 5.8 Hz, 2H), 1.31 (s, 36H).

**2,3,9,10-Tetrakis((t-butyl)phenyl)-6,13-dihydro-6,13-diacetylthiopentacene (41)**

A flame-dried, N$_2$ purged 100 mL round bottom flask was charged with ZnI$_2$ (0.75 g, 2.35 mmol), 40 (1 g, 1.19 mmol), 4Å molecular sieves and 75 mL dry CH$_2$Cl$_2$. To this mixture was added thioacetic acid (1 mL, 14.1 mmol), and the resulting pinkish reaction mixture was stirred for 1 hour at room temperature in the dark. The reaction was TLC monitored. After reaction, the reaction mixture was filtered and washed with CH$_2$Cl$_2$ and the filtrate was thoroughly washed with water, saturated solution of sodium bicarbonate and brine. Upon evaporating the solvent and followed by drying in vacuo, the resulting solid was then dissolved in minimum amount of CHCl$_3$ and triturated with MeOH for purification. The mixture was then filtered and washed with MeOH. Upon drying in vacuo, compound 6 was isolated as an off-white solid (0.89 g, 78 %). $^1$H NMR (500 MHz, CDCl$_3$) δ (ppm): 8.09 (s, 4H), 7.87 (s, 4H), 7.25 (d, J = 8.4 Hz, 8H), 7.12 (d, J = 8.3 Hz, 8H), 6.59 (s, 2H), 2.39 (s, 6H), 1.31 (s, 36H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ (ppm): 194.45, 149.64, 140.12, 138.39, 135.51, 132.36, 129.67, 129.25, 127.40, 124.80, 46.42, 34.59, 31.50, 30.58.

**2,3,9,10-Tetrakis((t-butyl)phenyl)-6,13-diacetylthiopentacene (42)**

To a flame dried, Ar purged 15 mL pressure vessel compound 41 (20 mg, 0.46 mmol), DDQ (5.7 mg, 0.78 mmol) and dry toluene (2 mL) was added. The reaction mixture was
thoroughly degased and refilled with Ar. The vessel was then sealed with a Teflon screw cap. The mixture was stirred and heated at 130 °C in an oil bath for 4 hours in the dark. After cooling down to room temperature, the reaction mixture was evaporated to get crude pentacene. After column chromatographic separation using ethyl acetate and hexane (1:3) as eluent at first and followed by CHCl₃, pentacene 42 was recovered as a dark blue solid. Due to the poor solubility of pentacene 42 in ethyl acetate, it was stuck in the column while other impurities eluted using EtOAc/hexane. When switch the eluent to CHCl₃, the pentacene 42 was collected for further purification. The solid of 42 was washed with EtOAc and filtered. Upon drying in vacuo, compound 42 was isolated as a dark blue solid (3 mg, 17 %). ¹H NMR (500 MHz, CDCl₃) δ (ppm): 9.26 (s, 4H), 8.03 (s, 4H), 7.27 (d, J = 8.4 Hz, 8H), 7.18 (d, J = 8.3 Hz, 8H), 2.56 (s, 6H), 1.33 (s, 36H). ¹³C NMR (125 MHz, CDCl₃) δ (ppm): 193.77, 149.88, 140.36, 138.19, 132.41, 131.89, 129.57, 126.53, 125.34, 124.78, 34.64, 31.51, 30.71.
CHAPTER 4

SYNTHESIS AND COMPUTATIONAL STUDY OF TETRA-PHENYL-PENTACENE [60]FULLERENE DIELS-ALDER ADDUCTS

4.1 Introduction

4.1.1 Fullerenes

With the discovery\textsuperscript{91} and the development of a preparative scale-up method,\textsuperscript{92,93} fullerene molecules (e.g., C\textsubscript{60} and C\textsubscript{70}), considered as the third and the only soluble carbon allotrope in addition to diamond and graphite, became a subject of intense research. Fullerenes are spherically shaped molecules with curved fully conjugated $\pi$-system, and a skeleton consisting of pentagons and hexagons. The construction of fullerenes obeys the isolated pentagon rule (IPR), which means that every pentagon is surrounded by hexagons only.

![Molecular structure of [60]fullerene](image)

Figure 4.1 Molecular structure of [60]fullerene

As the smallest and the most prominent member of the fullerenes family, C\textsubscript{60}, also named as Buckminsterfullerene, is made entirely of 60 equivalent carbon atoms with a spherical
shape consisting of 12 pentagons and 20 hexagons. It has been proved\textsuperscript{94} that there are two different types of bonds existing in the fullerene molecule, the shorter 6-6 bonds (ca. 1.38 Å long), shared by two adjacent hexagons, and the longer 6-5 bonds (ca. 1.45 Å long), fusing a pentagon and a hexagon (Figure 4.1). Compared with the 6-5 bonds, the 6-6 bonds have higher electron density and more double bond characteristics, which are more reactive.

Because of the unique chemical structure, C\textsubscript{60} has many extraordinary properties. C\textsubscript{60} is a well-known strong electron acceptor with capability of accepting up to 6 electrons, indicated by the 6 reduction waves in the electrochemistry\textsuperscript{95}, and an excellent electron

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{reaction_diagram.png}
\caption{Chemical reactions of [60]fullerene}
\end{figure}
conductor due to the low reorganization energy. Upon doping of alkali metals like potassium, C\textsubscript{60} shows superconductivity at low temperature. It also has interesting non-linear optical properties providing application potential in non-linear optics such as xerography and holographic imaging. Furthermore, it is highly thermal stable allowing thermal evaporation for thin film growth.

However, the poor solubility of C\textsubscript{60} in common solvents limits its solution processibility. This solubility issue could be resolved by functionalizing the C\textsubscript{60} via chemical reactions while keep its unique properties. The reactions of C\textsubscript{60} have been studied extensively as an important branch of organic chemistry (Figure 4.2). The chemical reactivity of C\textsubscript{60} is typical of an electron-deficient olefin, which could easily react with radicals, various nucleophiles, and carbenes. Cycloaddition reactions are amongst the most important reactions for preparing functionalized fullerenes. The driving force of the cycloaddition reactions is considered to be the relief of strain in the C\textsubscript{60} cage. Fullerenes are well known to participate in a variety of cycloaddition reactions, including [1+2], [2+2], [3+2], [4+2](Diels-Alder reaction), [6+2] and [8+2], at one of the 30 equivalent 6-6 bonds. It is possible to have multi addition to the [60]fullerene due to the fact that there are 30 equivalent reactive 6-6 bonds in the structure. The [4+2] cycloaddition (Diels-Alder reaction) is by far the most useful and studied fullerene cycloaddition reaction. In the Diels-Alder reactions, the dienes including traditional open chain 1,3-dienes, cyclic dienes, and heterodiene are known to react with the dienophile, [60]fullerene across the 6,6 junctions on the [60]fullerene cage. The Diels-Alder reaction of C\textsubscript{60} and 1,3-butadiene is shown as an example (Scheme 4.1).
4.1.2 **Diels-Alder Cycloaddition Between Acenes and [60]Fullerene**

Acenes, as linear polycyclic aromatic molecules, are conjugated cyclic dienes which are proved to be readily reactive with the dienophile [60]fullerene via the Diels-Alder cycloaddition reactions. The first [60]fullerene-acene reaction studied was that between [60]fullerene and anthracene which was reported by Schlueter et al. in 1993.\textsuperscript{108} In their study, [60]fullerene-anthracene monoadduct was formed and isolated in the yield of 13% upon boiling a toluene solution of anthracene and [60]fullerene for 3 days. The reaction between [60]fullerene and anthracene was then figured out to be reversible (Scheme 4.2) with reactants favored at higher temperatures, which also means that the [60]fullerene-anthracene monoadduct is not a thermally stable molecule and will decompose back to [60]fullerene and anthracene upon heating at higher temperature.\textsuperscript{109} The Diels-Alder reaction between [60]fullerene and anthracene was also performed by Komatsu and co-workers\textsuperscript{110} in solid state under HSVM (high speed vibration milling) conditions producing the [60]fullerene-anthracene monoadduct in 55% yield.
Larger acenes and their derivatives also react similarly with $C_{60}$ via Diels-Alder reactions.\textsuperscript{106} It is well known that larger acenes react faster than smaller acenes in Diels-Alder reactions and the reaction will occur at the central ring.\textsuperscript{111} Tetracene cycloadds faster with [60]fullerene than anthracene,\textsuperscript{112} and pentacene reacts noticeably faster with [60]fullerene than does tetracene. However, the trend is opposite in the retro-Diels-Alder reaction of the corresponding [60]fullerene-acene adduct. The [60]fullerene-pentacene monoadduct is less inclined to decompose via a retro-Diels-Alder reaction, while the [60]fullerene-anthracene monoadduct decomposed fast and easily when undergoing a retro-Diels-Alder reaction. Unlike anthracene and tetracene, larger acenes have more than one reaction sites with cyclic diene characteristic in the Diels-Alder cycloaddition reaction with [60]fullerene. Pentacene and its derivatives, for instance, have two possible positions for cycloaddition, i.e. 6,13-position and 5,14-position.
When bare pentacene is applied in the Diels-Alder cycloaddition reaction with [60]fullerene in solution phase, the addition of C$_{60}$ only occurs at the center ring (6,13-position) of pentacene backbone and generate the C$_{2v}$ symmetric [60]fullerene-pentacene monoadduct (Scheme 4.3).$^{113}$ It is also suggested by computational study that in Diels-Alder reaction, the cycloaddition at 6,13-position across the pentacene backbone is both kinetically and thermodynamically preferred to the cycloaddition at 5,14-position.$^{114}$ However, when the reaction was performed in the solid state under HSVM condition, the formation of anti-bis-C$_{60}$-pentacene adduct was observed by Komatsu and coworkers, indicating the cycloaddition at the 5,14-position of the pentacene backbone instead of the preferred 6,13 position.$^{110}$ In their study, a mixture of mono-C$_{60}$-pentacene adduct (19%), C$_{60}$-bis-pentacene adducts (mixture of regioisomers, 15%), and anti-bis-C$_{60}$-pentacene adduct (11%) were all generated with unreacted C$_{60}$ left over (28%) (Scheme 4.4).

When pentacene derivatives with substituents at the 6,13 positions were applied in the Diels-Alder reaction with [60]fullerene in solution phase, the cycloaddition occurs at
5,14-position of the pentacene backbone (Scheme 4.5). Moreover, with different types of substituents, under same reaction conditions different [60]fullerene-pentacene adducts were generated. In the cases where the pentacene are substituted with electron donating phenyl groups, the syn-bis[60]fullerene-pentacene adduct are formed as major product in the Diels-Alder reaction with trace amounts of mono-[60]fullerene-pentacene adduct and anti-bis[60]fullerene-pentacene adducts.

However, in the cases where the 6,13-substituents are electron withdrawing alkynyl groups, the mono-[60]fullerene-pentacene adducts are generated as major products due to the fact that the diene characteristic of the pentacene backbone is reduced by the strong electron withdrawing substituents, which is only efficient enough to cycloadd one [60]fullerene molecule under these conditions. The steric hindrance from the substituents is another factor resulting in the formation of the mono-[60]fullerene-pentacene adducts suggested by the fact that with bulky o-alkyl groups on the phenyl substituents, only the C₈ symmetric mono[60]fullerene adducts are formed. The computational studies carried out by Miller and coworkers¹¹⁷ suggest that in the Diels-Alder reaction between 6,13-substituted pentacene derivatives and [60]fullerene, 5,14-cycloaddition is both kinetically and thermodynamically preferred than 6,13-cycloaddition. They also explained that the
stereoselectivity of the syn-isomer of bis[60]fullerene-pentacene adduct over the anti-isomer is due to π-π stacking interactions between two adjacent fullerene moieties.

Due to the spheric and poly unsaturated nature of [60]fullerene with 30 equivalent 6,6-bonds, multiple acene moieties are possible to cycloadd to one [60]fullerene core via the Diels-Alder reaction to form multi-acenes functionalized [60]fullerene adducts, including bis-, tris-, tetrakis-, pentakis- and hexakis- adducts. However, the problem of regio- and stereoselectivity at the fullerene cores, which limits the preparative scope of multiple Diels-Alder cycloaddition reactions,\textsuperscript{118} is significant for multi-functionalization due to the fact that multi- adducts of C\textsubscript{60} are generally obtained through subsequent additions. After the first addition to either one of the 6,6-bonds of the fullerene core, the remaining 29 6,6-bonds that are still available have lost their equivalence. Therefore, a second addition to one of the remaining 29 6,6-bonds results in eight different regioisomers of bis-adducts due to the high I\textsubscript{h} symmetry of C\textsubscript{60}. The eight regioisomers are officially named according to IUPAC momenclature\textsuperscript{119} (Figure 4.3). Although the inherent regioselectivity of this second addition to the fullerene framework is only moderate, it has
been found that a preference for attack at the e and trans-3 bonds for sterically demanding addends and at e, trans-3 and cis-1 bonds for sterically less demanding addends. 118

4.1.3 Self-assembly of [60]Fullerene Derivatives

The construction of shape-defined nano- and microstructures with [60]fullerene and its derivatives through self-assembly has gained attentions as a key process of the bottom-up approaches in nanotechnology within the organic electronic devices field. 120, 121 Controlling the particle shape and tuning the particle size to a desired range are key factors for preparation of nano- and microstructures with predetermined morphologies in the nanotechnology. 122 Various attempts have been made to prepare stable crystalline C60 nanosize materials with various kinds of morphology such as nanorods, 123 nanotubes, 124 nanosheets 125 and nanowhiskers, 126 etc. 127 Similarly, assembly of alkyl-tail-attached C60 derivatives in various solvents gives nanofibers, nanosheets, spheres, or flower-like nanoobjects. 128, 129, 130, 131

In this chapter, the Diels-Alder reaction between 5,7,12,14-tetraphenylpentacene(TTP) and [60]fullerene to generate mono- and multi- adducts has been studied along with computational studies comparing the energetics of the 8 regioisomers of bisadduct. Moreover, the shape-controlled preparation of nano- and microstructures with mono-C60-TPP adduct through self-assembly in various solvent systems is also presented.
4.2 Results and Discussion

4.2.1 Synthesis of 5,7,12,14-Tetraphenylpentacene (TPP)

4.2.1.1 Synthesis of 5,7,12,14-Pentacenetetrone 71

![Scheme 4.6 Synthetic route of 5,7,12,14-pentacenetetrone]

5,7,12,14-Tetraphenylpentacene was prepared starting from the corresponding pentacenetetrone 71. The four carbonyl functions on the 5-, 7-, 12- and 14-position, offer the possibility of adding the substituents in an analogous manner as for 6,13-disubstituted pentacenes. The 5,7,12,14-pentacenetetrone 71 was synthesized starting from 2-methyl-1,4-naphthoquinone as described in the literature (Scheme 4.6). Although the yield of this reaction is reported to be low (16%), this method was preferred due to the inexpensive starting materials and the straightforward reproducible synthetic route. The reaction mixture was just stirred in the dark for 16 h. Afterwards the pure product 71 was obtained simply by filtration with the yield of 16%.

4.2.1.2 Synthesis of 5,7,12,14-Tetraphenylpentacene (TPP) 73

![Scheme 4.7 Synthetic route of 5,7,12,14-tetraphenylpentacene]
The 5,7,12,14-tetraphenylpentacene 73 was prepared in the same way as other tetra-aryl substituted pentacenes described in the literature (Scheme 4.7). The phenyllithium was slowly added to the THF solution of 5,7,12,14-pentacenetetrone 71 under N\textsubscript{2} at -78 °C and the reaction mixture was slowly warmed up to 0 °C and stirred for 16 h to generate 5,7,12,14-tetraphenyl-pentacene-5′,7′,12′,14′-tetrol 72 as a mixture of diastereomers. The resulting diastereomers mixture of 5,7,12,14-tetraphenyl-pentacene-5′,7′,12′,14′-tetrol 72 was then reduced by sodium iodide and sodium hypophosphite in boiled acetic acid to afford the corresponding 5,7,12,14-tetraphenylpentacene 73 with the yield of 90%. The 5,7,12,14-tetraphenylpentacene 73 has been fully characterized and described by our previous group members.\textsuperscript{133}

### 4.2.2 Synthesis and Isolation of TPP-C\textsubscript{60} Adducts

![Scheme 4.8 Diels-Alder reaction between 5,7,12,14-tetraphenylpentacene and [60]fullerene to synthesize mono-TPP-C\textsubscript{60} adduct](image)

The Diels-Alder cycloaddition between 5,7,12,14-tetraphenylpentacene (TPP, 73) and [60]fullerene to form mono-TPP-C\textsubscript{60} adduct 74 has been studied previously in our group (Scheme 4.8).\textsuperscript{133} When tetraphenylpentacene 73 reacted with [60]fullerene in a 1:2 ratio in refluxing CS\textsubscript{2} solution through Diels-Alder cycloaddition, the C\textsubscript{2V} symmetric mono-TPP-C\textsubscript{60} adduct 74 was formed. The study shows that the phenyl substituents on TPP 73
do not prevent [60]fullerene cycloaddition across the seemingly hindered 6,13-positions of the pentacene backbone. Moreover, phenyl substituents on TPP 73 render the monoadduct 74 soluble in a host of common organic solvents including carbon disulfide, chloroform, benzene and toluene.

As a further progress on this TPP-C\textsubscript{60} adduct study, three more different multi-TPP-C\textsubscript{60} adducts could be generated in the reaction besides the mono-TPP-C\textsubscript{60} adduct by modifying the reaction conditions. Adducts formed were isolated and identified as two of the eight regioisomers of bis-TPP-C\textsubscript{60} adduct and a highly symmetric tetrakis-TPP-C\textsubscript{60} adduct (Scheme 4.9). The reaction conditions and the corresponding isolated yield of products are listed in Table 4.1.

Scheme 4.9 Diels-Alder reaction between 5,7,12,14-tetraphenylpentacene and [60]fullerene to form bis-adducts and tetrakis-adduct
The reaction mixture was separated by column chromatography. Due to the similar polarity of the regioisomers of the bis-adducts, it is difficult to get pure bisadducts and therefore their individual yields. With CS$_2$ as solvent, the bis- and tetrakis- adducts started to form in the reaction when the ratio of TPP : C$_{60}$ increased to 2 : 1. While with the ratio further increasing to 5 : 1 and extended reaction time the mono-adduct was not observed in the reaction mixture and more bis- and tetrakis adducts were formed. With even higher ratio of TPP : C$_{60}$ (10 : 1), more tetrakis-adduct has been formed. Due to the formation of terakis-adduct, the reaction was attempted at higher temperature refluxing in toluene and even longer reaction time to form the higher hexakis-TPP-C$_{60}$ adduct. However, the reaction ended up to the tetrakis-TPP-C$_{60}$ adduct instead of the hexakis-adduct expected. The mono-, 2 regioisomers of bis- and tetrakis- TPP-C$_{60}$ adducts were formed in one pot reaction and then isolated using silica column chromatography with hexane as elute solvent. Although mono-TPP-C$_{60}$ adduct has been reported, the 2 regioisomers of bis-TPP-C$_{60}$ adduct and tetrakis-TPP-C$_{60}$ adduct were obtained for the first time. The mono-TPP-C$_{60}$ adduct and 2 regioisomers of bis-TPP-C$_{60}$ adduct has similar solubility in common organic solvents including carbon disulfide, chloroform, benzene, and toluene, which has been improved compared to petacene-C$_{60}$ adduct, and

<table>
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<tr>
<th>Entry</th>
<th>Reaction Conditions</th>
<th>Temp./ºC</th>
<th>Time/h</th>
<th>mono-74 (%)</th>
<th>bis-1</th>
<th>bis-2</th>
<th>tetradecakis-83 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1:2</td>
<td>CS$_2$</td>
<td>45</td>
<td>24</td>
<td>✓ (24 %)</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>2:1</td>
<td>CS$_2$</td>
<td>45</td>
<td>24</td>
<td>✓ (19 %)</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>3</td>
<td>5:1</td>
<td>CS$_2$</td>
<td>45</td>
<td>48</td>
<td>--</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>4</td>
<td>10:1</td>
<td>CS$_2$</td>
<td>45</td>
<td>48</td>
<td>--</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>5</td>
<td>10:1</td>
<td>Toluene</td>
<td>110</td>
<td>72</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>
the same brown color as other fullerene derivatives. However, tetrakis-TPP-C_{60} adduct has poor solubility in chloroform but is fairly soluble in CS_{2}, benzene, and toluene. Furthermore, the tetrakis-TPP-C_{60} adduct has orange color in both solid and solution phase, which is quite different from the mono- and bis- adducts.

4.2.3 Spectroscopic Characterization of TPP-C_{60} Adducts

4.2.3.1 Spectroscopic Characterization of Mono-TPP-C_{60} Adduct 74

C_{2v} symmetric mono-TPP-C_{60} adduct 74 was able to be characterized using $^1$H NMR spectroscopy in chloroform-$d$ (Figure 4.4). The $^1$H NMR spectra of mono-TPP-C_{60} adduct has the characteristic singlet for the methylene protons on 6,13-carbons of the pentacene backbone at 5.92 ppm (2 protons). The multiplets in the aromatic region are
corresponding to other protons on the pentacene backbone and that on the phenyl substituents.

4.2.3.2 Spectroscopic Characterization of Regioisomers of Bis-TPP-C<sub>60</sub> Adduct

The two major regioisomers of bis-TPP-C<sub>60</sub> adduct formed from the reaction have been characterized using <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies in chloroform-<i>d</i> (Figure 4.5 and 4.6, respectively). As shown in <sup>1</sup>H NMR spectra (Figure 4.5 (a) and 4.6 (a)), for both of the two regioisomers of bis-TPP-C<sub>60</sub> adducts, two characteristic singlets for the bridgehead methylene protons were in the range of 5.00-6.00 ppm, which are well separated from the signals of the aromatic protons. The presence of two symmetry equivalent tetraphenylpentacene addends was indicated in the <sup>1</sup>H NMR spectra for both regioisomers consisting either with C<sub>s</sub>- or C<sub>2</sub>-symmetry. The positions of the singlets varied as a consequence of competing deshielding and shielding effects of the fullerene and acene moieties. The <sup>13</sup>C NMR spectra of the two regioisomers of bis-TPP-C<sub>60</sub> adducts showed two signals for the bridgehead 6,13- carbon atoms of the pentacene moieties near 52 ppm and two signals for the saturated fullerene carbon atoms, which are directly attached to the pentacene addends, near 70 ppm. However, due to the lack of X-ray crystallography demonstration, the structure assignments for the two regioisomers of bis- adduct are relatively difficult only using the spectrometric results.

As discussed in the introduction session, there are 8 possible regioisomers for bis-adducts, including cis-1, 2, 3, e-, trans-1, 2, 3 and 4 regioisomers. It has been proved in the study of bis-anthracene-fullerene adducts that due to the steric inhibition of the first anthracene moiety, the formation of cis-1, 2, 3 bis- adducts by Diels-Alder cycloaddition,
in which both of the addends are bound at the same fullerene-hemisphere, is prohibited. Comparing to the anthracene moiety, the tetraphenylpentacene moiety with four phenyl substituents in our study should have much more steric inhibition for formation of cis-1, 2, 3 regioisomers of bis- adduct, which was also proved in the following preliminary theoretical study. Therefore, the cis-1, 2, 3 structures have been excluded in the assignment. Meanwhile, the $C_s$- or $C_2$-symmetry stuctures indicated by NMR spectra of the two regioisomers are not in agreement with the $D_{2h}$ symmetry of e- regioisomer. For e-isomer, the corresponding $^1H$ NMR spectrum should show nonequivalent pentacene moieties with three characteristic singlets for methylene protons (relative intensity 1:2:1), while the corresponding $^{13}C$ NMR spectrum should show three signals for bridgehead C-atoms and two signals (relative intensity 1:2) of the saturated fullerene carbon atoms. Therefore, the e- isomer is not suitable assignment for these two regioisomers as well. Furthermore, the $^1H$ NMR spectrum of trans-1 isomer with $C_s$ symmetry should show only one singlet for the methylene protons. Therefore, neither of the two regioisomers is trans-1 bis-adduct.

Although we were not able to make clearly structure assignment for these two regioisomers formed, we could still draw the conclusion that they are two out of the three possible regioisomers of bis- adducts, which are trans-2, trans-3, and trans-4.
Figure 4.5 $^1$H NMR spectra (a) and $^{13}$C NMR spectra (b) of the first bis-TPP-C$_{60}$ adduct Bis-1
Figure 4.6 $^1$H NMR (a) spectra and $^{13}$C NMR spectra (b) of the second bis-TPP-C$_{60}$ adduct Bis-2
4.2.3.3 Spectroscopic Characterization of e,e,e,e-Tetrakis-TPP-C\textsubscript{60} Adduct 83

The orange-colored new TPP-C\textsubscript{60} have been characterized using \textsuperscript{1}H and \textsuperscript{13}C NMR spectroscopies and assign as e,e,e,e-tetrakis-TPP-C\textsubscript{60} adduct based on the spectrometric results. Figure 4.7 shows the \textsuperscript{1}H NMR and \textsuperscript{13}C NMR spectra of 83 in benzene-\textit{d}_6. The \textsuperscript{1}H NMR spectrum shows only one singlet for methylene protons, which is in the characteristic chemical shift range for acene-fullerene adduct, with the chemical shift of 5.78 ppm, which shifted to up field compared with the singlet of the mono-TPP-C\textsubscript{60} adduct at 5.92 ppm (in CDCl\textsubscript{3}). Based on the \textsuperscript{1}H NMR results, this adduct is neither mono- adduct nor trans-1 bis- adduct due to the fact that the singlet for trans-1 bis-adduct shifts to down field comparing to that of mono- adduct.\textsuperscript{134} The \textsuperscript{13}C NMR spectrum of e,e,e,e-tetrakis-TPP-C\textsubscript{60} adduct was only recorded in benzene-\textit{d}_6 due to its relatively poor solubility in chloroform (Figure 4.7 (b)). The \textsuperscript{13}C NMR spectrum of e,e,e,e-tetrakis-TPP-C\textsubscript{60} adduct is in full agreement with its D\textsubscript{2h}-symmetrical structure, which has one signal for the bridgehead C atom (52.20 ppm), one signal for the sp\textsuperscript{3} C atoms on the fullerene adjacent to pentacene moieties (70.38 ppm), and 20 sp\textsuperscript{2} C atoms in the aromatic region for fullerene and petacene addends.
Figure 4.7 $^1$H NMR spectra (a) and $^{13}$C NMR spectra (b) of tetrakis-TPP-C$_{60}$ adduct
4.2.4 **Theoretical Study of TPP-C\textsubscript{60} Adducts**

The preliminary computational study of the mono-TPP-C\textsubscript{60} adduct, eight possible regiosomers of bis-TPP-C\textsubscript{60} adduct has been carried out in order to evaluate and compare the frontier orbital energies and the corresponding HOMO-LUMO gaps for these adducts via density functional theory (DFT). The B3LYP density functional and the 6-31G(d,p) basis set have been used to evaluate the single-point energies of these TTP-C\textsubscript{60} adducts. Geometries for each molecule were obtained from the PM6 semi-empirical method (Figure 4.8).

![Geometries of mono-TPP-C\textsubscript{60} adduct and 8 regioisomers of bis-TPP-C\textsubscript{60} adduct optimized at semi-empirical PM6 level of theory](image)

Figure 4.8 Geometries of mono-TPP-C\textsubscript{60} adduct and 8 regioisomers of bis-TPP-C\textsubscript{60} adduct optimized at semi-empirical PM6 level of theory
The total energies of the mono-TPP-C$_{60}$ adduct and 8 regioisomers of bis-TPP-C$_{60}$ adduct are listed in Table 4.2 together with the relative energy of the 8 regioisomers of bis-adduct. The relative energies of the 8 regioisomers were also plotted in Figure 4.9. The results clearly show that the total energies of tran-1, 2, 3, 4 and e isomers of the bis-TPP-C$_{60}$ adduct are similar with the trans-3 isomer having the lowest energy, while the energies of cis-1, 2 are much higher and cis-3 has the moderate energy. The huge energy differences could be explained by the geometry results showed above. It is obvious that comparing to others, the pentacene addants on the fullerene core in cis-1, 2 are closely located, which results in an extremely crowded structure together with four phenyl substituents on the pentacene moieties. Therefore, the energies of them are much higher due the steric effect. We could draw the conclusion that the trans-1, 2, 3, 4 and e- isomers energetically preferred and more thermodynamically stable among the 8 regioisomers.

Table 4.2: Single-point energies of regioisomers of bis-TPP-C$_{60}$ adduct

<table>
<thead>
<tr>
<th>Regioisomer</th>
<th>E (kcal/mol)</th>
<th>Relative E (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-1-bis-75</td>
<td>-3657308.859</td>
<td>1.42</td>
</tr>
<tr>
<td>trans-2-bis-76</td>
<td>-3657309.326</td>
<td>0.95</td>
</tr>
<tr>
<td>trans-3-bis-77</td>
<td>-3657310.279</td>
<td>0</td>
</tr>
<tr>
<td>trans-4-bis-78</td>
<td>-3657305.118</td>
<td>5.16</td>
</tr>
<tr>
<td>e-bis-79</td>
<td>-3657307.222</td>
<td>3.06</td>
</tr>
<tr>
<td>cis-1-bis-80</td>
<td>-3657217.845</td>
<td>92.43</td>
</tr>
<tr>
<td>cis-2-bis-81</td>
<td>-3657243.223</td>
<td>67.06</td>
</tr>
<tr>
<td>cis-3-bis-82</td>
<td>-3657296.325</td>
<td>13.95</td>
</tr>
</tbody>
</table>

*At B3LYP/6-31G(d,p)//PM6 level.*
As determining characteristics for organic semiconductors, the HOMO, LUMO energies of the mono-adduct and the 8 regioisomers of bis-adduct were also calculated in the single-point energy computation. The results are listed in Table 4.3 and plotted in Figure 4.10. Figure 4.10 also shows the electronic structures of both HOMO and LUMO molecular orbitals for all molecules.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$E_{\text{HOMO}}$ (eV)</th>
<th>$E_{\text{LUMO}}$ (eV)</th>
<th>HOMO-LUMO Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mono-74</td>
<td>-5.63</td>
<td>-2.98</td>
<td>2.65</td>
</tr>
<tr>
<td>trans-1-bis-75</td>
<td>-5.41</td>
<td>-2.86</td>
<td>2.55</td>
</tr>
<tr>
<td>trans-2-bis-76</td>
<td>-5.41</td>
<td>-2.85</td>
<td>2.56</td>
</tr>
<tr>
<td>trans-3-bis-77</td>
<td>-5.36</td>
<td>-2.74</td>
<td>2.62</td>
</tr>
<tr>
<td>trans-4-bis-78</td>
<td>-5.32</td>
<td>-2.72</td>
<td>2.61</td>
</tr>
<tr>
<td>e-bis-79</td>
<td>-5.45</td>
<td>-2.76</td>
<td>2.69</td>
</tr>
<tr>
<td>cis-1-bis-80</td>
<td>-5.37</td>
<td>-2.83</td>
<td>2.54</td>
</tr>
<tr>
<td>cis-2-bis-81</td>
<td>-5.38</td>
<td>-2.80</td>
<td>2.58</td>
</tr>
<tr>
<td>cis-3-bis-82</td>
<td>-5.27</td>
<td>-2.70</td>
<td>2.57</td>
</tr>
</tbody>
</table>

*At B3LYP/6-31G(d,p)//PM6 level.

Although the HOMO-LUMO gaps of all molecules are in the range of 2.54-2.69 eV, which indicates the semiconducting characteristics similar as $C_{60}$ and its other derivatives, the HOMO and LUMO energies are both slightly higher in bis-adduct
regioisomers comparing to that of the mono-adduct. The electronic structures of all molecules at HOMO and LUMO molecular orbitals are also shown in Figure 4.10. Although the pentacene moieties are highly \( \pi \)-conjugated, the HOMO and LUMO molecular orbitals of mono-TPP-C\(_{60}\) adduct were only considerably distributed on the C\(_{60}\) surface cage. For bis-TPP-C\(_{60}\) adduct, the electronic structures of HOMO and LUMO molecular orbitals are affected by the interaction between two pentacene moieties. In the cases where the two TPP moieties are located relative far away from each other on the fullerene surface to avoid \( \pi-\pi \) interactions (i.e. trans-1, 2, 3, 4, e-, and cis-3 bis-adducts), the HOMO and LUMO molecular orbitals were considerably distributed on the C\(_{60}\) surface cage similar as in mono-adduct. When the two pentacenes are getting closer as in cis-2 bis-adduct, the HOMO molecular orbital was distributed on both the C\(_{60}\) surface and one of the pentacene moieties, while the LUMO molecular orbital was only distributed on the C\(_{60}\) surface cage. However, when the two pentacenes are located very closely as in cis-1-bis adduct where the \( \pi-\pi \) interaction between pentacene moieties are significant, the HOMO molecular orbital was only distributed on pentacene backbones, while the LUMO molecular orbital was only distributed on the C\(_{60}\) surface cage.
Figure 4.10 HOMO and LUMO energies and molecular orbitals at HOMO and LUMO energy levels of all molecules (at B3LYP/6-31G(d,p)//PM6 level)
4.2.5 Morphology study of Mono-TPP-\textit{C}_{60} adduct

4.2.5.1 Morphology of Spray-coated Mono-TPP-\textit{C}_{60} adduct Thin Film

The mono-TPP-\textit{C}_{60} adduct, similar as \textit{C}_{60}, has the potential application in organic photovoltaic device as a promising electron acceptor. Therefore, the morphology of its thin film is of interest due to the importance of thin film morphology in device performance determination. For preliminary study, the simple and convenient spray coating method was chosen. The mono-TPP-\textit{C}_{60} solution was sprayed onto a glass substrate using an airbrush system with \textit{N}_{2} as a carrier gas. Two organic solvents, toluene or orthodichlorobenzene (\textit{o}-DCB), are used for comparison. After spray coating, the film was left for drying in the air at room temperature. The SEM images of the prepared mono-TPP-\textit{C}_{60} adduct thin film from the two solvents are shown in Figure 4.11.

![SEM images of spray coated mono-TPP-\textit{C}_{60} adduct from toluene (a) and \textit{o}-DCB(b) solutions](image)

**Figure 4.11** SEM images of spray coated mono-TPP-\textit{C}_{60} adduct from toluene (a) and \textit{o}-DCB(b) solutions
Obviously, a continuous thin film of mono-TTP-C$_{60}$ adduct could not be formed from this spray coating method. However, more interestingly, during the spray coating and solvent evaporating process, nano or microstructures are formed all over the substrate. In the case of o-DCB as spray coating solvent (Figure 4.11 (b)), some flower shape islands, which are composed of extra thin curved sheets with thickness of around 100 nm are formed on the substrate. These micro sheets are growing together. Meanwhile, in the case of toluene (Figure 4.11 (a)), the SEM images indicate that individual particles are formed, including nanorods, microrods, microrectangles and some nanorod clusters. The nanorods has widths ranging from 100 to 500 nm, and lengths of about five microns. The size of the micro rectangles are about 15 µm × 5 µm (length × width). Similar nanostructures of pure C$_{60}$ (nanorods and microhexagon) has been reported by using a liquid interface perception method.$^{127}$ However, the shape-defined nanostructure of our compound formed by spray coating and solvent evaporation process are hard to collect for further bottom-up nanotechnology.

4.2.5.2 Morphology of Mono-TPP-C$_{60}$ Adduct Particles
As encouraged by the previous interesting results of the preliminary thin film morphology study carried out by using spray coating, as well as the reported nanostructure studies of pure C$_{60}$, the controllable formation of mono-TPP-C$_{60}$ adduct nanostructures via sonication assisting liquid-liquid perception (LLP) has been studied. It is well known that the liquid-liquid interface of a good solvent and a poor solvent acts as nucleation sites of crystals.$^{135}$ The liquid-liquid perception (LLP) is applied by using a good solvent for mono-TPP-C$_{60}$ adduct, such as toluene, o-DCB, and CS$_2$, together with a
poor solvent for the compound, like alcohols, hexane, acetone, etc. In the LLP method, generally, a solution of mono-TPP-C$_{60}$ adduct in one of the good solvent with certain concentration is prepared. Then, the solution is added slowly into the poor solvent using syringe without or without sonication. The perception occurs immediately after the addition with the help of sonication. In the case where sonication is not applied, the perception occurs slowly with addition of the solution. After addition the mixture is left for 30 min. The suspension is then drop casted onto a small piece of glass and left drying in the air for SEM characterization. The formed nano- and microstructures could be collected by filtration and disperse in the poor solvent again for thin film casting. The shape of the structures formed by this method could be controlled by adjusting several affecting factors, including sonication, adding procedure, temperature, solvents system, and concentration of the solution, which will be discussed in the following.

4.2.5.2.1 Effect of Sonication

The sonication applied during the mixing process might accelerate the perception by increasing the liquid-liquid interface and also reduce the formed particle size. Therefore, the effect of sonication on the mono-TPP-C$_{60}$ adduct nanostructure formation has been studied by comparing the morphology of formed particles with and without sonication (Figure 4.12).

Depending on the solvent system applied, the mono-TPP-C$_{60}$ adduct particles differ a lot from each other. Figure 4.12 (a) and (b) are the SEM images of mono-TPP-C$_{60}$ adduct particles formed from the toluene/isopropanol (IPA) solvent system with and without sonication, separately. It is obvious that in this case with the assistance of sonication, it
can form very uniform and regular structure, microcubes with length of \( \sim 1 \ \mu m \) (Figure 4.12 (a)). The overgrown particles with various morphologies are obtained without sonication (Figure 4.12 (b)). Therefore, for the solvent system of toluene/IPA, sonication is beneficial for controlling of the microstructure size and shape. In the case where \( \text{CS}_2 \) is applied as good solvent in the solvent system, even with the same poor solvent IPA, the resulting nano- and microstructures are quite different from the toluene/IPA case (Figure 4.12 (c) and (d)). Nanorods with widths of \( \sim 100 \text{ nm} \) and length of \( \sim 1 \ \mu m \) are formed with sonication (Figure 4.12 (c)), while without sonication, the rods grow up to micro scale, with length of about \( 20 \ \mu m \) and width of about \( 1 \ \mu m \) in average (Figure 4.12 (d)). Sonication during the mixing procedure helps to reduce the size of structure formed dramatically as expected. Unlike these two solvent systems, it didn’t show formation of regular shaped in the \( o\)-DCB/IPA system (Figure 4.12 (e) and (f)).

Therefore, in general sonication is helpful for the nano- and microstructures formation using LLP method. Furthermore, by comparing the structures generated from the three solvent systems with IPA as poor solvent under sonication, we could draw the conclusion that the good solvent is determining the shape of nano- and microstructures. When the good solvent change from toluene to \( \text{CS}_2 \), the architectures formed change accordingly form microcubes (Figure 4.12 (a)) to nanorods (Figure 4.12 (c)), providing a simple and easy way to control the shape of mono-TPP-C\(_{60}\) adduct nano- and microstructures.
Figure 4.12 SEM images of mono-TPP-C$_{60}$ adduct prepared in various solvents combination with and without assistance of sonication.
4.2.5.2.2 Effect of Temperature

Temperature is an important experimental parameter for crystal growth. The effect of temperature on the mono-TPP-C\textsubscript{60} adduct microparticle formation has been carried out by taking toluene/methanol system as example. Toluene solution of mono-TPP-C\textsubscript{60} adduct was slowly added into methanol under sonication at different temperatures, i.e. 0 °C (ice water bath), 20 °C (room temperature), and 50 °C, respectively (Figure 4.13).

![Figure 4.13 SEM images of mono-TPP-C\textsubscript{60} adduct particles prepared in toluene/methanol at different temperatures (a) 0 °C, (b) 20 °C and (c) 50 °C](image)

At 0 °C uniform microcubes with dimension of approximately 3 µm × 7 µm are formed (Figure 4.13 (a)). When the temperature increases to 20 °C, the size of the microcubes decreases to about 3 µm × 3 µm, and a thickness of about 500 nm could be obtained from the SEM image as some of the particles are perpendicular to the surface (Figure 4.13 (b)). However, some unregulated shaped particles with smaller size are formed instead of the cubic shaped ones at 50 °C (Figure 4.13 (c)). It could be explained by the temperature effect on the crystal nucleation and growth process. As discussed before, the liquid-liquid interface is where the crystal nucleation occurs. After the nucleation, the crystal start to grow and when the size is big enough, it will precipitate out from the solution mixture.
Higher temperature could lead to more nucleation sites, and accelerated crystal growth. Therefore, at higher temperature the particles formed are smaller in size when start from same concentration of compound. Furthermore, if the temperature is too high, the crystal growth will be out of control, and form the particles with unregularly shape. From the results, we could draw the conclusion that moderate room temperature is good for generating regular-shaped microstructures with relatively small size.

4.2.5.2.3 Effect of Concentration

The concentration of mono-TPP-C\textsubscript{60} adduct in the good solvent is another controlling factor for the formation of nano- and microstructures. Figure 4.14 shows the SEM images of microstructures formed from CS\textsubscript{2}/IPA solvent system with different concentration of mono-TPP-C\textsubscript{60} adduct in CS\textsubscript{2}, 5 mg/ml, 2 mg/ml, and 0.5 mg/ml, respectively.

![Figure 4.14 SEM images of mono-TPP-C\textsubscript{60} adduct particles prepared in CS\textsubscript{2}/IPA with different concentrations (a) 5 mg/ml, (b) 2 mg/ml, and (c) 0.5 mg/ml](image)

When start from a concentrated solution (Figure 4.14 (a)), both microrods and larger microbricks are formed with the microbricks as the major structure. The amount and size of microbricks reduce dramatically when the concentration of the compound in CS\textsubscript{2}
reduces to 2 mg/ml (Figure 4.14 (b)). With further reduce of the concentration, there are only microrods formed. After the crystal nuclear formed at the interface of two solvents, higher concentration in the good solvent means more molecules surrounding an individual nuclear site, leading to a faster growing of the crystal in all directions. However in a dilute solution, the growth process is slower and it has more chance for the crystal to grow in a preferred direction making the microrods with high aspect ratio. Therefore, in order to obtain shape-defined microstructure, the concentration in the range from moderate to dilute (≤ 2 mg/ml) is preferred.

4.2.5.2.4 Effect of Solvent System

As learned from the results in section 4.2.4.2.2, the good solvent in the solvent system is a determining factor of the microstructure morphology of mono-TPP-C₆₀ adduct. Furthermore, the other component of the solvent system, the poor solvent, could extensively affect the morphology as well. Figure 4.15 shows the SEM results for adding toluene solution of mono-TPP-C₆₀ adduct into various poor solvents, including methanol (a), ethanol (b), i-propanol (c), hexane (d), acetone (e), as well as ethyl acetate (f), under sonication. In all alcohol cases, uniform microcubes are formed; while random-shaped particles forms in other cases. Therefore, the combination of toluene/alcohol is suitable for microcube structure formation. Among the cases where microcubes are formed, the size of microcubes formed in toluene/IPA system is the smallest (about 1 µm × 1 µm) (Figure 4.15 (c)). While in methanol, the microcubes formed are the largest in size (about 3 µm × 3 µm). For the case of ethanol, the size of microcubes formed is in between of these two. Here comes the conclusion that toluene/alcohol system is efficient for growing
microcubes of mono-TPP-C$_{60}$ adduct, whose size could be controlled by changing alcohol used in the system.

![Figure 4.15 SEM images of mono-TPP-C$_{60}$ adduct particles prepared by addition of its toluene solvent into different poor solvents including methanol (a), ethanol (b), i-propanol (c), hexane (d), acetone (e), as well as ethyl acetate (f), under sonication.](image)

In summary, shape and size of the nano- and micro-structures of mono-TPP-C$_{60}$ adduct formed via LLP method could be controlled by adjusting the experimental conditions, such as sonication assistance, temperature, concentration, and solvent system. Uniform microcubes, nanorods, and microrods are grown in different conditions. The system with toluene as good solvent and alcohol as poor solvent leads to the formation of microcubes. IPA gives smallest microcubes, and methanol gives the largest ones. While in the system of CS$_2$/IPA, the nanorods form with sonication and microrods forms without sonication.
4.3 Conclusions

In one pot Diels-Alder reaction between tetraphenylpentacene (TPP) and [60]fullerene, mono-TPP-C$_{60}$ adduct, two regioisomers of bis-TPP-C$_{60}$ adduct, and tetrakis-TPP-C$_{60}$ adduct were successfully synthesized. Although the chemical structures of the two regioisomers of bis-TPP-C$_{60}$ adduct were difficult to determine the possible structures for these two regioisomers could be narrowed down to trans-2, trans-3, and trans-4 according to NMR results. Tetrakis-TPP-C$_{60}$ adduct was successfully synthesized and isolated as orange colored crystalline solid, the chemical structure of which was identified by $^1$H and $^{13}$C NMR spectrometry.

The single point energies of mono-TPP-C$_{60}$ adduct and eight regioisomers of bis-TPP-C$_{60}$ adduct were calculated using DFT B3LYP/6-31G(d,p) level of theory with geometry obtained from PM6 semi-empirical method. The trans-1, 2, 3, 4 and e- isomers of bis-adduct have lower energies indicating that they are thermodynamically preferred, which is in agreement with the experimental results. The HOMO and LUMO energies were also evaluated. The HOMO-LUMO gaps of all molecules are in the semiconducting range. Compared with mono-adduct, the regioisomers of bis-adduct all have both higher HOMO and LUMO energy levels. The molecular orbitals at HOMO and LUMO are investigated to be distributing only on the fullerene surface for most of the molecules with exception of cis-1, 2 and 3.

The shape controlled self-assembly of mono-TPP-C$_{60}$ adduct has been studied. By controlling the formation conditions including solvents, methods, solvent systems, and temperature, nanosheets, nano- and micro- rods, micro cubic structure, and flower shape microstructures could be obtained with uniform size distribution. These nano- and micro-
structures have potential applications as building blocks in nanostructured organic electronic devices.

4.4 Experimental

4.4.1 Analytical Instrumentation

4.4.1.1 $^1$H NMR Spectra

$^1$H NMR spectra were obtained on a Varian Mercury Plus 400 FT-NMR operating at 399.768 MHz or a Varian INOVA 500 FT-NMR operating at 499.763 MHz. All chemical shift ($\delta_H$) values are reported in parts per million (ppm) relative to residual solvent protons unless otherwise noted.

4.4.1.2 $^{13}$C NMR Spectra

$^{13}$C NMR spectra were obtained on a Varian Mercury Plus 400 FT-NMR operating at 100.522 MHz or a Varian INOVA 500 FT-NMR operating at 125.666 MHz. All chemical shift ($\delta_C$) values are reported in parts per million (ppm) relative to residual solvent signal unless otherwise noted.

4.4.1.3 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM), model Amry 3300 FE, was used for experiments at acceleration voltages of 7 kV. Prior to analysis, all samples were coated with a 100 Å Au/Pd layer using a Hummer V sputter coater. The samples were drop/spin/spray coated on to glass, which was pre-washed using D. I. water, acetone, hexanes, and dichloromethane.
4.4.2 Chromatography

Sand was obtained from Fisher Scientific Co.
Silica Gel (230-400 mesh) was obtained from Natland International Co.
Thin Layer Chromatography Plates obtained from Fisher Scientific Co.

4.4.3 Solvents

Note: All solvents were used without further purification unless otherwise noted. Solvent drying was carried out as needed by distillation from sodium metal (THF, toluene) or by passing through a silica column in a dry-solvent delivery system.

Acetic acid (CH₃CO₂H) was obtained from VWR Chemical Co.
Acetone (reagent grade) was obtained from Pharmco-AAPER.
Benzene (C₆H₆) was obtained from Sigma-Aldrich Chemical Co.
Carbon disulfide (CS₂) was obtained from EM Science.
1,2-Dichlorobenzene (o-DCB) was obtained from Aldrich Chemical Co.
Dichloromethane (DCM) was obtained from Pharmco-AAPER.
Ethanol (absolute) was obtained from Pharmco-AAPER.
Ethyl acetate (CH₃CO₂CO₂CH₃) was obtained from Fisher Scientific Co.
Hexanes was obtained from Fisher Scientific Co.
Isopropyl alcohol (IPA) was obtained from Fisher Scientific Co.
Methanol was obtained from Pharmco-AAPER.
Tetrahydrofuran (THF) was obtained from Fisher Scientific Co.

Toluene (PhCH₃) was obtained from Fisher Scientific Co.

All NMR solvents including chloroform-d and benzene-d₆ were purchased from Cambridge Isotope Laboratories.

### 4.4.4 Reagents

*Note: All reagents were used without further purification unless otherwise noted.*

Diethylamine (C₄H₁₁N) was obtained from Alfa Aesar Chemical Co.

[60]Fullerene (C₆₀) was obtained from MER Chemical Co.

2-Methyl-1,4-naphthoquinone (Menadione or vitamin K₃, C₁₁H₈O₂) was obtained from TCI America.

Phenyllithium (LiC₆H₅) was obtained from Acros Organics Co.

Sodium hypophosphite (NaH₂PO₂) was obtained from Sigma-Aldrich Chemical Co.

Sodium iodide (NaI) was obtained from J.T. Baker Chemical Co.

### 4.4.5 Syntheses

*Note: All routine solvent evaporations were conducted on a standard rotary evaporator using vacuum pump pressure unless otherwise noted.*

#### 5,7,12,14-Pentacenetetrone 71

To a solution of 2-methyl-1,4-naphthoquinone (10.0g, 0.058 mol) in ethanol (200 ml) diethyl amine (2 ml, 0.02 mol) was added. The reaction mixture was stirred in the dark
for 16 h. The reaction mixture was filtered and washed thoroughly with ethanol. After drying \textit{in vacuo} overnight, pure tetrone 71 was isolated as yellow solid (1.57g, 4.64 mmol, 16%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) $\delta$ (ppm): 9.26 (s, 2H), 8.52 - 8.28 (m, 4H), 7.99 - 7.78 (m, 4H).

**5,7,12,14-Tetrahydro-5,7,12,14-tetraphenyl-pentacene-5',7',12',14'-tetrol 72**

PhLi (10.5 ml, 20 mmol) was added to a solution of 5,7,12,14-pentacenetetrone 71 (1.0 g, 3.0 mmol) in dry THF (100 ml) at -78 °C under nitrogen atmosphere. After addition, the reaction mixture was allowed to warm up to room temperature and stirred overnight. The reaction was worked up with 1M HCl and extracted with ethyl acetate, followed by drying over MgSO\textsubscript{4} and evaporation. After drying \textit{in vacuo} overnight, the crude product was collected with a crude yield of 64%. The product is mixture of stereoisomers and it was carried for the next step of reaction to synthesize the corresponding pentacene derivative.

**5,7,12,14-Tetraphenylpentacene 73**

A suspension of the stereoisomers mixture of 5,7,12,14-tetrahydro-5,7,12,14-tetraphenyl-pentacene-5',7',12',14'-tetrol 72 (500 mg, 0.77 mmol), NaI (1.155 g, 7.7 mmol) and NaH\textsubscript{2}PO\textsubscript{2} (0.68 g, 7.7 mmol) in acetic acid (100 ml) was heated at reflux in the dark for 1.5 h under nitrogen atmosphere. After cooling down to room temperature, the purple blue precipitation was isolated by vacuum filtration and washed thoroughly with water (3x75 ml), methanol (2x50 ml), and hexanes (2x50 ml) in the dark with nitrogen flow to
afford pure 5,7,12,14-tetraphenylpentacene 73 (405 mg, 90%). $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.21 (s, 2H), 7.66 (m, 4H), 7.39 (m, 10H), 7.15 (m, 4H).

**Mono-tetraphenylpentacene-C$_{60}$ adduct 74**

[60] Fullerene (24.7 mg, 0.0343 mmol) was pre-dissolved in CS$_2$ (10 mL) in a N$_2$ flushed round bottom flask in the dark. 5,7,12,14-tetraphenylpentacene 73 (10.0 mg, 0.0172 mmol) was added and the resulting solution was heated up to reflux for 24 h under a blanket of N$_2$ and in the dark. The mixture was cooled down to room temperature and concentrated under reduced pressure. The product was purified by column chromatography on silica gel using chloroform: hexane (20:80) as eluent to afford pure mono-tetraphenylpentacene-C$_{60}$ adduct 74 as brown solid (5.4 mg, 24 %). $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.61 - 7.53 (m, 4H), 7.46 - 7.33 (m, 16H), 7.21 (t, 4H, $J = 7.5$ Hz), 7.02 (d, 4H, $J = 7.7$ Hz), 5.92 (s, 2H).

**Regioisomers of bis-tetraphenylpentacene-C$_{60}$ adduct**

[60] Fullerene (10.0 mg, 0.0139 mmol) was pre-dissolved in CS$_2$ (20 mL) in a N$_2$ flushed round bottom flask in the dark. 5,7,12,14-tetraphenylpentacene 73 (40.5 mg, 0.0694 mmol) was added and the resulting solution was heated up to reflux for two days under a blanket of N$_2$ and in the dark. The mixture was cooled down to room temperature and concentrated under reduced pressure. After purification using column chromatography on silica gel using chloroform: hexane (5:95) as eluent, two regioisomers of the bis-tetraphenylpentacene-C$_{60}$ adduct have been separately isolated.

*First regioisomer of bis-TPP-C$_{60}$ adduct Bis-1*
$^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.81 - 7.66 (m, 4H), 7.59 - 7.27 (m, 48H), 7.12 (t, 2H, $J = 7.5$ Hz, 2H), 6.98 (t, $J = 7.5$ Hz, 2H), 6.81 (d, $J = 7.4$ Hz, 2H), 6.74 (d, $J = 7.6$ Hz, 2H), 6.05 (s, 2H), 5.83 (s, 2H).

Second regioisomer of bis-TPP-C$_{60}$ adduct Bis-2

$^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.74 - 7.67 (m, 4H), 7.63 - 7.58 (m, 4H), 7.57 - 7.27 (m, 62H), 7.01 - 6.91 (m, 6H), 6.92 - 6.82 (m, 4H), 6.50 (d, $J = 7.9$ Hz, 2H), 5.94 (s, 2H), 5.53 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm): 156.49, 156.37, 155.77, 149.22, 148.68, 148.58, 148.28, 148.14, 145.90, 145.84, 145.40, 145.29, 145.07, 144.92, 144.79, 144.10, 143.99, 143.62, 142.45, 141.77, 141.34, 141.20, 139.35, 137.83, 137.64, 137.56, 136.92, 136.68, 136.41, 136.29, 136.22, 136.01, 135.56, 132.52, 132.38, 132.34, 132.19, 131.01, 130.95, 130.78, 130.69, 130.58, 128.73, 128.59, 128.47, 128.36, 128.24, 128.07, 127.93, 127.64, 127.50, 127.36, 127.30, 127.24, 127.05, 126.96, 126.86, 126.54, 125.89, 125.78, 76.84, 70.90, 52.82, 51.55.

Tetrakis-tetraphenylpentacene-C$_{60}$ adduct 83

[60] Fullerene (5.0 mg, 0.0069 mmol) was pre-dissolved in CS$_2$ (20 mL) in a N$_2$ flushed round bottom flask in the dark. 5,7,12,14-tetraphenylpentacene 73 (40 mg, 0.0690 mmol) was added and the resulting solution was heated up to reflux for two days under a blanket of N$_2$ and in the dark. The mixture was cooled down to room temperature and concentrated under reduced pressure. After purification using column chromatography on silica gel using chloroform: hexane (5:95) as eluent, the tetrakis-TPP-C$_{60}$ adduct has been isolated (2.7 mg, 13 %). $^1$H NMR (500 MHz, C$_6$D$_6$) δ (ppm): 7.87 - 7.78 (m, 4H), 7.54 - 7.47 (m, 2H), 7.39 (t, $J = 7.5$ Hz, 2H), 7.33 - 7.28 (m, 7H), 7.26 (t, $J = 7.3$ Hz, 4H), 7.23 -
7.17 (m, 6H), 7.14 - 7.11 (m, 1H), 7.07 (t, J = 7.5 Hz, 2H), 5.78 (s, 2H). $^{13}$C NMR (125 MHz, C$_6$D$_6$) δ (ppm): 159.45, 157.07, 152.45, 148.97, 148.24, 144.68, 142.99, 142.60, 140.79, 138.44, 138.34, 136.83, 136.77, 132.84, 131.50, 131.20, 131.04, 129.04, 128.81, 126.27, 70.38, 52.20.

### 4.4.6 Self-assembly of Mono-TPP-C$_{60}$ Adduct Nano- or Microstructures

Solutions of mono-TPP-C$_{60}$ adduct 74 in various solvents including toluene, CS$_2$ and o-DCB) with different concentrations were prepared by dissolving 74 in the respective solvent (10 mL) followed by ultrasonication for 5 min. Although the compound is pretty soluble in these solvents, the resulting solution was filtered to remove undissolved 74.

For nanostructures formed directly on the glass via spray coating method, the solution of mono-TPP-C$_{60}$ adduct 74 (toluene and o-DCB) was loaded into the spray coating gun. With assistance of the applied air pressure, the solution loaded was sprayed on to the pre-cleaned glass slide surface. The coated slide was then left in the fume hood at room temperature to dry for overnight with cover. All samples were coated with a layer of Pt (100 Å) before putting into the SEM chamber.

For nano- or microstructures of mono-TPP-C$_{60}$ adduct formed via liquid-liquid precipitation method (LLP), the solution of mono-TPP-C$_{60}$ adduct (toluene, CS$_2$, or o-
DCB) was added slowly into a pre-cleaned glass vial containing poor solvent (MeOH, EtOH, IPA, hexanes, acetone, or EtOAc) using syringe without or without sonication. The perception occurs immediately after the addition with the help of sonication. In the case where sonication is not applied, the perception occurs slowly with addition of the solution. After addition the mixture was left stable for 30 min. By removing the top clear solvent, the formed particles were collected. The formed particles was then suspended in hexanes for drop casting on the pre-cleaned glass slide for SEM characterization. All samples were coated with a layer of Pt (100 Å) before putting into the SEM chamber.

4.4.7 Computational Modeling

Semi-empirical geometry optimizations and subsequent DFT single-point energies of all molecules were refined at B3LYP/6-31G(d,p)//PM6 level of theory using Gaussian '03 (Linux) on a Dell PowerEdge 2970 Server running 6 Dell PowerEdge R610 nodes (Quad-Core AMD opteron x86, 64-bit, 2.8 GHz, 24 GB memory) via a Dell PowerConnect 5458 Network Switch, each operating OpenSuSE 11.2, unless otherwise noted.
CHAPTER 5

AROMATIZATION REACTION OF 6,13-DIHYDRO-6,13-

DIORGANOTHIOPENTACENES

5.1 Introduction

Pentacene is one of the most widely utilized organic semiconductor compounds. However, the poor solubility and stability displayed by the parent species has resulted in the preparation of more experimentally useful pentacene derivatives bearing either solubilizing or stabilizing substituents that allow for improved solubility, processability, stability and HOMO-LUMO gap tuning. The most commonly prepared pentacene derivatives are those with phenyl or silylethynyl functionality, although other groups such as phenethynyl, cyano, trifluoromethyl, pentafluoromethyl and halogens have also been shown to result in stabilized species. One of the more recently developed classes of pentacene substituents, organothio groups, has shown great promise in the area of thin-film electronic device applications. 6,13-bis(phenylthio)pentacenes and 6,13-bis(n-decylthio)pentacenes were shown to have a relatively small HOMO-LUMO gaps, excellent solubility in a variety of organic solvents and significantly, and higher half-lives than TIPS-pentacene under identical photooxidation conditions.

A large family of 6,13-bisorganothiopentacenes has been developed in our group with synthetic methods modified from the original synthesis developed by Kobayashi and
coworkers. In their synthesis, 6,13-pentacenequinone was reduced to trans-6,13-dihydroxy-6,13-dihydropentacene with NaBH₄ and reacted with various alkylthiols or thiolphenol to produce trans-6,13-bis(alkylthio)-6,13-dihydropentacene or trans-6,13-bis(phenylthio)-6,13-dihydropentacene. A dehydrogenative aromatization with p-chloranil was then used to produce 6,13-bis(alkylthio)pentacene or 6,13-bis(phenylthio)pentacene in reasonable to good yields depending upon the alkyl group. In their work, the trans diastereomers of the 6,13-dihydropentacene intermediates in each of the reaction steps were selectively synthesized. Indeed, the workers report that the syn isomer of 6,13-bis(octylthio)-6,13-dihydropentacene shows no reactivity towards p-chloranil. However, the reactivity difference between the syn- and anti- isomers is barely discussed after this. Furthermore, with deepening of our 6,13-bisorganothiopentacenes researches, we found some interesting conflicts with the literature. Therefore, a systematic combined experimental and computational study of the key steps, the ZnI₂-mediated reaction and the following dehydrogenative aromatization with p-chloranil, has been carried out. Experimentally, the ZnI₂-mediated reaction to directly synthesize 6,13-dihydropentacene intermediates from 6,13-bishydroxypentacene has been studied by coupling seven different organothiols with various functionalities. The stereochemistry (syn- or anti-) of the 6,13-dihydropentacene intermediates synthesized has been verified by single crystal X-ray crystallography. Both the syn- and anti- isomers isolated have been taken forward to react with p-chloranil in order to compare the reactivity difference. The 6,13-bisorganothiopentacenes generated has also been fully characterized. Furthermore, kinetic study of the dehydrogenative aromatization has been carried out by monitoring the reaction mixture composition using ¹H NMR during the
reaction. Computationally, the dehydrogenative aromatization reaction with \( p \)-chloranil was studied.

5.2 Results and Discussion

5.2.1 ZnI\(_2\)-mediated Synthesis of 6,13-Diorganothio-6,13-dihydropentacenes

Compound 6,13-dihydro-6,13-dihydroxypentacene was synthesized following a reported procedure.\(^{140}\) Product obtained is generally a mixture of syn- and anti- isomers of 6,13-dihydro-6,13-dihydroxypentacene with various ratios. It has been proved that the ratio of syn- and anti- isomers of the product is independent with the ratio of isomers of starting material. It could be explained by the fact that the ZnI\(_2\)-mediated thiolation from alcohol is a SN\(_1\) reaction.\(^{141}\) Therefore, the diastereomer mixture of 6,13-dihydro-6,13-dihydroxypentacene was directly applied in the ZnI\(_2\)-mediated reaction with organothiols (Scheme 5.1).

![Scheme 5.1 ZnI\(_2\)-mediated Synthesis of 6,13-diorganothio-6,13-dyhydroxypentacenes](image)

1: R = CH\(_2\)CH\(_3\)  
2: R = n-C\(_8\)H\(_{17}\)  
3: R = phenyl  
4: R = 1-naphthyl  
5: R = (CH\(_2\))\(_4\)OH  
6: R = (CH\(_2\))\(_2\)COOH  
7: R = COCH\(_3\)
The reaction of 6,13-dihydro-6,13-dihydroxypentacene with organothiols in the presence of ZnI$_2$ (2 equiv) in CH$_2$Cl$_2$ at room temperature in the dark produced a mixture of syn- and anti- isomers of 6,13-bis(organothio)-6,13-dihydropentacenes, respectively. The two diastereomers share the same molecular mass and also have similar pattern in $^1$H NMR spectroscopy with a chemical shift difference of ~0.2 ppm for the characteristic methylene proton, which makes it difficult to distinguish them from each other by spectroscopic method. This problem was then solved with the help of the single crystal X-ray crystallography. The single crystals of isolated syn- and/or anti isomers were grown and resolved by Jonathan Briggs in our group. The stereochemistry of both
isomers was confirmed by X-ray crystallography in most cases, except for the case where $R = n-(\text{CH}_2)_r\text{CH}_3$ due to the oily nature of the compound and where $R = (\text{CH}_2)_2\text{COOH}$. In the case of $R = (\text{CH}_2)_2\text{COOH}$, the syn- isomer is the only product and its stereochemistry is confirmed by X-ray crystallography. The results are summarized in Table 5.1.

Determined by the $^1$H NMR results of crude reaction mixture, syn- isomer is either the only product (when $R = \text{ethyl}$ and $(\text{CH}_2)_2\text{COOH}$) or the major product with a relative quality greater than 80% (other cases), while the anti- isomer is produced as a minor product with a relative quality less than 20%. Although syn- isomer is the major product of the reaction, for several cases, like where $R = \text{ethyl}$, octyl, and phenyl, freely epimerization of the syn- isomers to form anti- isomers has been observed in many situations. When $R = \text{ethyl}$, the epimerization reaction of syn- isomer occurs in solution phase at room temperature with or without exposing to light, providing us a handy method to synthesize anti- isomer from syn- isomer of 6,13-bis(ethylthio)-6,13-dihydropentacenes. The preliminary time dependent study of epimerization reaction of 6,13-dihydro-6,13-diethylthiopentocene at room temperature was carried out by keeping the CDCl$_3$ solution of the mixture of syn- and anti- isomers (85:15) in the NMR tube in the dark for up to 72 h (Figure 5.1). The amount of anti- isomer increases at the expense of syn- isomer with time. After 72 h, the mixture of syn- and anti- isomers with a roughly ratio of 2:3 is obtained. For the case of $R = \text{octyl}$, the epimerization occurs even in oily state and during the silica chromatography purification process, leading to the result that the isolated yield of anti- isomer is higher than its content in the crude mixture. The epimerization between the syn- and anti- isomers also happens during the aromatization
reaction, which will be discussed in the next portion. It is worth to mention that, this ZnI$_2$-mediated reaction is moisture sensitive. Therefore, dry DCM is applied for the reaction and for entry 5 and 7, where R = butanol and acetyl, 4Å molecular sieves were used in the reaction to remove moisture from the starting organothiols. Another important point necessary to mention is that the reaction time of this ZnI$_2$-mediated thiolation reaction varies with the nature of R groups. For instance, the reaction finished within 1 h in the case where R = ethyl, whereas the reaction time extended to 24 h where R = propanoic acid due to its poor solubility in DCM.

![Figure 5.1 Relative quantities of syn- and anti- isomers of the 6,13-diorganothio-6,13-dihydropentacenes](image)

Figure 5.1 Relative quantities of syn- and anti- isomers of the 6,13-diorganothio-6,13-dihydropentacenes
5.2.2 Aromatization Reactions of Syn- and Anti- Isomers of 6,13-Dihydrodiorganothiopentacenes

The dehydrogenative aromatization of both isolated syn- and anti- 6,13-dihydro-6,13-diorganothiopentacenes in sealed vessel, as the final step in the synthesis of 6,13-bis(organothio)pentacenes, have been studied systematically (Scheme 5.2). The results are summarized in Table 5.2. The result is quite surprising that both of the syn- and anti-isomers could be aromatized and form the desired pentacene derivatives under this modified conditions for most of the cases, unlike in the previously reported literature\(^\text{49}\) where only one of the isomers could be aromatized. In the following session, details regarding reaction conditions and product will be discussed.

![Scheme 5.2 Synthesis of 6,13-diorganothiopentacenes](image)

The aromatization reaction is carried out in sealed vessel with Argon atmosphere and protected from light. The sealed vessel is chosen for this reaction instead of conventional heating for two reasons: the vessel is filled with Argon and then sealed, which could prevent oxygen at the most extent during the reaction course; More important, the reaction time generally could be reduced dramatically to a couple of hours comparing to several days (60 h)\(^\text{49}\) when using conventional heating method due to the fact that when the vessel is sealed, higher reaction temperature (approximately 20 °C higher than boiling temperature of the solvent) and also higher pressure in the vessel could be achieved and therefore accelerate the aromatization reaction. The reduction of reaction time is
beneficial to the reaction as the desired pentacene derivative product is unstable in solution.

Table 5.2 Synthesis of 6,13-diorganothiopentacene from both isolated syn- and anti- 6,13-dihydro-6,13-diorganothiopentacenes

<table>
<thead>
<tr>
<th>Cmpd</th>
<th>-SR =</th>
<th>Reaction condition</th>
<th>Relative quantities in crude reaction mixtures</th>
<th>Isolated yield of pentacene derivative</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Oxidant</td>
<td>eqv. of Oxidant</td>
<td>Solvent</td>
</tr>
<tr>
<td>84</td>
<td>-SCH(_2)CH(_3) (syn)</td>
<td>p-Chloranil</td>
<td>1.15</td>
<td>C(_6)H(_6)</td>
</tr>
<tr>
<td>85</td>
<td>-SCH(_2)CH(_3) (anti)</td>
<td>p-Chloranil</td>
<td>1.15</td>
<td>C(_6)H(_6)</td>
</tr>
<tr>
<td>86</td>
<td>-S(CH(_2))(_2)CH(_3) (syn)</td>
<td>p-Chloranil</td>
<td>1.35</td>
<td>C(_6)H(_6)</td>
</tr>
<tr>
<td>87</td>
<td>-S(CH(_2))(_2)CH(_3) (anti)</td>
<td>p-Chloranil</td>
<td>1.35</td>
<td>C(_6)H(_6)</td>
</tr>
<tr>
<td>88</td>
<td>-SPh (syn)</td>
<td>p-Chloranil</td>
<td>2</td>
<td>CHCl(_3)</td>
</tr>
<tr>
<td>89</td>
<td>-SPh (anti)</td>
<td>p-Chloranil</td>
<td>2</td>
<td>CHCl(_3)</td>
</tr>
<tr>
<td>90</td>
<td>-S-1-Naphthyl (syn)</td>
<td>p-Chloranil</td>
<td>2</td>
<td>CHCl(_3)</td>
</tr>
<tr>
<td>91</td>
<td>-S-1-Naphthyl (anti)</td>
<td>p-Chloranil</td>
<td>2</td>
<td>CHCl(_3)</td>
</tr>
<tr>
<td>92</td>
<td>-S(CH(_2))(_2)OH (syn)</td>
<td>p-Chloranil</td>
<td>1.375</td>
<td>C(_6)H(_6)</td>
</tr>
<tr>
<td>93</td>
<td>-S(CH(_2))(_2)OH (anti)</td>
<td>p-Chloranil</td>
<td>1.375</td>
<td>C(_6)H(_6)</td>
</tr>
<tr>
<td>26</td>
<td>-S(CH(_2))(_2)COOH (syn)</td>
<td>p-Chloranil</td>
<td>1.5</td>
<td>C(_6)H(_6)</td>
</tr>
<tr>
<td>30</td>
<td>-SCH(_2)CO(_2)H (syn)</td>
<td>DDQ</td>
<td>1.7</td>
<td>Toluene</td>
</tr>
<tr>
<td>31</td>
<td>-SCH(_2)CO(_2)H (anti)</td>
<td>DDQ</td>
<td>1.7</td>
<td>Toluene</td>
</tr>
</tbody>
</table>

a: determined by \(^1\)H NMR integration
b: 10 eq. of K\(_2\)CO\(_3\) was used in the reaction
c: published

The reaction conditions were adjusted for optimized result according to the substituted groups, while with the same substituent the reaction conditions used for syn- and anti-isomers are kept identical for comparison purpose. The dehydrogenative oxidant, which works well in this reaction, is \(p\)-chloranil in most of the cases except for the case where \(R = \text{acetyl}\). In the case of \(R = \text{acetyl}\), a stronger oxidant DDQ (2,3-Dichloro-5,6-dicyano-1,4-benzoquinone) is applied because there were barely any reaction happening when use \(p\)-chloranil under the same conditions. The equivalent of the oxidant is in the range of 1.15 ~ 2. The minimum equivalent of oxidant for sufficient reaction is 1 equivalent, higher equivalent is favored for reaction completion. However, at the mean time, the oxidant could react with the pentacene derivatives generated in the reaction mixture via
the Diels-Alder reaction forming the undesired D-A byproduct, which not only lowers yield of the desired pentacene derivatives, but also brings difficulty to the purification process due to the fact that the 6,13-diorganothiopentacene product and its D-A cycloadduct byproduct of it have very similar polarity in silica gel chromatography. Therefore, a balance between reaction completion and minimized D-A cycloadduct production is considered for deciding the equivalent of oxidants.

The choice of solvent for running reaction is associated with the reaction temperature, which is approximately 20 ºC greater than the boiling point of the selected solvent. Benzene is suitable for most of the case. When high reaction temperature is required (in the case where R = acetyl), toluene is chosen. Meanwhile, chloroform is selected when low reaction temperature is favored (in the case where R = phenyl and naphthyl). It is noticed that K₂CO₃ is not necessary for this aromatization reaction and reaction is even cleaner without K₂CO₃ in most of the cases with the exception when R = (CH₂)₄OH. In the case where R = (CH₂)₄OH, 10 eq. of K₂CO₃ was applied.

The reaction conditions discussed above are optimized for relatively large reaction scales for syn- isomers, i.e. 100 mg or more. For larger scale, the reactions are complete under these conditions. However, due to the fact that the anti- isomers are always the minor product in the previous step leading to a limitation on the amount of isolated anti-isomers. Therefore, the reaction scale of the starting material are kept as 20 mg for both syn- and anti- isomers under the optimized reaction condition for large-scale aromatization.

From ¹H NMR spectra of crude reaction mixtures, the relative quantities of products are obtained and listed in Table 5.2. There are four main compounds which could be
identified in the crude $^1$H NMR, namely the desired pentacene derivatives, syn-dihydro species, anti-dihydro species, and the corresponding D-A cycloadduct, no matter start with syn- isomers or anti- isomers of the dihydro species. As mentioned before, we compare the reactivity of syn- and anti- isomers of the dihydrodiorganopentacenes in this aromatization reaction by keep identical reaction conditions. The special case is \( R = \) propionic acid \((-\text{(CH}_2\text{)}_2\text{COOH})\), for which the syn- isomer of the dihydro species is the only one could be obtained in the previous step, therefore, we were unable to compare the reactivity of the two isomers as in other cases. Due to the great polarity of the acid functionality, the pentacene derivative formed in the reaction is insoluble in the reaction mixture and precipitate out from the solution. After the reaction, the pentacene derivative could be obtained by simply filtration and washing with non-polar solvents. There was only the pentacene derivative shown in the $^1$H NMR. Therefore, \( R = \) propionic acid \((-\text{(CH}_2\text{)}_2\text{COOH})\) is exclusive for the following discussion regarding comparing the reactivity of syn- and anti- isomers.

For all the other cases, under the reaction conditions applied, the two isomers react with the oxidant similarly to form the desired pentacene derivative with the exception where \( R = \text{(CH}_2\text{)}_4\text{OH} \), which is opposite to the knowledge we had before that only one isomer of the dihydro species is reactive. The reason might be that the reaction temperature we used which is 20 °C higher than the refluxing temperature applied in previous study, is high enough to overcome the large energy barrier for the less reactive isomer. When \( R = \text{(CH}_2\text{)}_4\text{OH} \), the syn- isomer reacted well with the oxidant \( (\rho\text{-chloranil}) \) and formed the pentacene derivative with good yield, while the anti isomer barely reacted at the exact same condition.
Another fact discovered from the results is that during the aromatization reaction the epimerization of the dihydro species happened for many of the cases. Starting with pure syn-isomers, anti-isomers are generated during the reaction. Similarly, starting with pure anti-isomers, syn-isomers are generated during the reaction. However, the nature of the R group affects the result a lot. When R = alkyl (ethyl and octyl), the epimerization occurred for both syn- and anti-isomers, and furthermore, in the reaction mixtures for these cases, the relative quantities of the anti-isomers are all higher than the syn-isomers. When R = aryl (phenyl and naphthyl), the epimerization happened for all the cases except for the syn-isomer of phenylthiodihydro species where both syn- and anti-isomers were undetectable in the crude reaction mixture. And the relative quantities of the syn-isomers are higher than the anti-isomers. When R = alcohol group (-(CH₂)₄OH), the anti-isomer was formed during the reaction when start with the syn-isomer, while no syn-isomer was detected and only trace amount of pentacene derivative formed in the crude reaction mixture when start with the anti-isomer. When R = acetyl, epimerization was not happening during the reaction. When start with either one of the two isomers, only pentacene derivative and that isomer was shown in the reaction mixture.

The systematic experimental study for this aromatization reaction with various functional groups apparently proved that generally both the syn- and anti-isomers of the dihydro species are similarly reactive in the reaction to form pentacene derivative. However, the epimerization observed during the aromatization reaction makes it more complicated because there is another possibility that there is only one isomer which could be aromatized (syn- or anti-), and when we start with the isomer which can not aromatized (anti- or syn-), it could transform to the reactive one via epimerization and then react with
the oxidant to form the pentacene derivative. Therefore, in order to understand more about the nature of this reaction, the detailed dynamic study of the aromatization reaction has been carried out.

5.2.3 Characterization of 6,13-Diorganothiopentacenes

All 6,13-diorganothiopentacenes obtained from the aromatization reaction have been isolated and characterized by $^1$H NMR, $^{13}$C NMR, Mass Spectrometry, and as well as UV-vis spectroscopy. UV-vis spectra for all pentacene derivatives synthesized in this work in solution and solid state are shown in Figure 5.2. The results are summarized in Table 5.3, along with the optical HOMO-LUMO gap and band gap calculated from the solution and the solid state UV-vis spectra, respectively. The optical HOMO-LUMO gaps of pentacene derivatives with organothio substituents are in the range of 1.92 eV to 1.95 eV, calculated from the UV-vis data in solution state, which are similar as other reported organothio substituted pentacene derivatives with semiconducting character. The solid state UV-vis spectra were measured with BaSO$_4$ as substrate.

As shown in Figure 5.2, for every pentacene derivative the solid state UV-vis spectra are red shifted compared to the solution state UV-vis spectra. Therefore, the optical band gap calculated from the onset value of the longest maximum absorption wavelength decreased significantly compared to the optical HOMO-LUMO gap. For instance, the band gap is 1.60 eV, which is 0.35 eV smaller than the HOMO-LUMO gap of 1.95 eV when $R = \text{ethyl}$. The largest difference between optical band gap (solid state) and HOMO-LUMO gap (solution) was observed in the case of $R = \text{acetyl}$, where the band
gap is 0.44 eV smaller than the HOMO-LUMO gap. It could be explained by the fact that organothio substituted pentacene derivative molecules are generally well packed in solid state as a result of intermolecular π-π interaction of the pentacene backbones, while in solution state the molecules are isolated from each other by the solvent molecules.

Figure 5.2 UV-vis spectrum of all 6,13-diorganothiopentacene in both solution and solid states
Table 5.3 UV-vis spectroscopic results and the corresponding optical HOMO-LUMO or band gaps of 6,13-dioorganothiopentacenes

<table>
<thead>
<tr>
<th>Compd</th>
<th>-R</th>
<th>solution state UV-vis</th>
<th>solid state UV-vis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td>$\lambda_{\text{onset}}$ (nm)</td>
</tr>
<tr>
<td>95</td>
<td>-CH$_2$CH$_3$</td>
<td>529, 569, 617</td>
<td>635</td>
</tr>
<tr>
<td>96</td>
<td>-(CH$_2$)$_3$CH$_3$</td>
<td>530, 570, 617</td>
<td>638</td>
</tr>
<tr>
<td>13</td>
<td>-phenyl</td>
<td>536, 577, 626</td>
<td>644</td>
</tr>
<tr>
<td>97</td>
<td>-1-naphthyl</td>
<td>538, 579, 628</td>
<td>647</td>
</tr>
<tr>
<td>98</td>
<td>-(CH$_2$)$_4$OH</td>
<td>530, 571, 618</td>
<td>638</td>
</tr>
<tr>
<td>27</td>
<td>-(CH$_2$)$_2$COOH</td>
<td>534, 574, 623</td>
<td>643</td>
</tr>
<tr>
<td>32</td>
<td>-COCH$_3$</td>
<td>533, 573, 621</td>
<td>644</td>
</tr>
</tbody>
</table>

5.3 Preliminary Dynamic Study of the Aromatization Reaction with Epimerization

5.3.1 Epimerization Between Syn- and Anti- Isomers

Due to the fact that the epimerization reaction between syn- and anti- isomers of the dihydro starting materials always occurs during the aromatization reaction, it would be beneficial for us to study the epimerization reaction under conditions that are same as applied in the aromatization reaction with absence of oxidant. The epimerization reaction was studied by taking syn-6,13-dihydro-6,13-diethylthiopentacene 84 and syn-6,13-dihydro-6,13-diphenylthiopentacene 88 as examples.

5.3.1.1 Epimerization of syn-6,13-Dihydro-6,13-diethylthiopentacene

As discussed in previous section, it is observed that syn-6,13-dihydro-6,13-diethylthiopentacene 84 could form anti-6,13-dihydro-6,13-diethylthiopentacene 85 via the epimerization reaction even at room temperature in solution. Herein the epimerization
reaction is studied at high temperature by heating the benzene solution of syn-6,13-dihydro-6,13-diethylthiopentencene 84 in a sealed vessel with Argon atmosphere at 90 ºC in the dark, which is exactly the same as the reaction condition in aromatization reaction (Scheme 5.3).

![Scheme 5.3 Epimerization of syn-6,13-dihydro-6,13-diethylthiopentencene](image)

**Table 5.4 Reaction conditions and relative quantities of products of epimerization reaction of syn-6,13-dihydro-6,13-diethylthiopentencene**

<table>
<thead>
<tr>
<th>Entry No.</th>
<th>Reaction conditions</th>
<th>Relative quantities in crude reaction mixtures a</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Starting materials</td>
<td>Syn- (84) Anti- (85) K$_2$CO$_3$ Rxn. time Syn- (84)</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

a: determined by $^1$H NMR integration
b: 6,13-pentacene quinone 24 (byproduct)

As shown in **Table 5.4**, for Entry 1 the reaction time was kept the same as in the aromatization reaction (3 h), while for Entry 2 the reaction time was extended to 6 h. Meanwhile, in Entry 3 ten equivalent of K$_2$CO$_3$ was applied and the reaction time was kept as 3 h. The relative quantities of products in the crude reaction mixture are listed in the table as well. Without the presence of K$_2$CO$_3$ in the reaction, a mixture of syn- and anti- isomers of the dihydro compound with the ratio of approximately 1:1 is obtained from pure syn-isomer. The 1:1 ratio of the two isomers is kept the same with longer
reaction time, indicating that the epimerization reaction between the two isomers reached the equilibrium with 3 h. With the addition of K$_2$CO$_3$, the ratio of the syn- and anti-isomers in the resulting mixture is about 9:1. It is obvious that the addition of K$_2$CO$_3$ is helpful to prevent the epimerization reaction under the same reaction conditions.

5.3.1.2 Epimerization of syn-6,13-Dihydro-6,13-diphenylthiopenecene

![Scheme 5.4 Epimerization of syn-6,13-dihydro-6,13-diphenylthiopenecene](image)

**Table 5.5 Reaction conditions and relative quantities of products of epimerization reaction of syn-6,13-dihydro-6,13-diphenylthiopenecene**

<table>
<thead>
<tr>
<th>Entry No.</th>
<th>Reaction conditions</th>
<th>Relative quantities in crude reaction mixtures $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>Starting materials</strong></td>
<td><strong>Rxn. time</strong></td>
</tr>
<tr>
<td></td>
<td>Syn- (88)</td>
<td>Anti- (89)</td>
</tr>
<tr>
<td>a: determined by $^1$H NMR integration</td>
<td></td>
<td></td>
</tr>
<tr>
<td>b: 6,13-pentacene quinone 24 (byproduct)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In contrast to the easy conversion from syn-6,13-dihydro-6,13-diethylthio pentencene to its anti-diastereomer at room temperature, the epimerization of syn-6,13-dihydro-6,13-diphenylthiopenecene barely occurred at room temperature. The epimerization reaction is studied by heating the chloroform solution of syn-6,13-dihydro-6,13-diethylthiopenecene in a sealed vessel with Argon atmosphere at 80 °C in the dark for 4 h, which is exactly the same as the reaction condition in aromatization reaction (Scheme
5.4. Calculated from the $^1$H NMR of the crude reaction mixture, only approximately 5% of the syn-isomer converted to the anti isomer after heating at 80 °C for 4 h (Table 5.5).

5.3.2 Preliminary Dynamic Study of Aromatization Reaction

By taking syn-6,13-dihydro-6,13-diethylthiopentencene and syn-6,13-dihydro-6,13-diphenylthiopentacene as representative examples, the dynamic study of this epimerization-aromatization reaction was carried out by monitoring the relative quantities of reactant and products in the reaction mixture during the reaction course. The reactions were taken place in the sealed NMR tubes instead of the sealed vessels. After every time slot, the NMR tube was taken out from the oil bath and then cooled down in a cold-water bath to “freeze” the reaction. After taking NMR of the reaction mixture, the sealed NMR tube was soaked in to the oil bath again.

5.3.2.1 Preliminary Dynamic Study of Aromatization Reaction of syn-6,13-Dihydro-6,13-diethylthiopentencene 84

The aromatization reaction of syn-6,13-dihydro-6,13-diethylthiopentencene (Scheme 5.5) was monitored during the reaction course. The relative quantities of compounds in the reaction mixture at different reaction time were calculated from the $^1$H NMR spectra (Table 5.6). The relationship between relative quantities and reaction time are plotted accordingly as well (Figure 5.3). There are four main components in the reaction mixture, the unreacted syn-isomer, the anti-isomer formed via epimerization, the desired pentacene derivative, and the D-A cycloadduct of the pentacene derivative and $p$-chloranil as a byproduct.
Scheme 5.5 Aromatization of syn-6,13-dihydro-6.13-diethylthiopentacene

Table 5.6 Relative quantities of major compounds in crude reaction mixtures at different reaction time during aromatization of syn-6,13-dihydro-6.13-diethylthiopentacene

<table>
<thead>
<tr>
<th>Reaction time</th>
<th>Relative quantities in crude reaction mixtures *&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pentacene derivative (95)</td>
</tr>
<tr>
<td>0 min</td>
<td>0</td>
</tr>
<tr>
<td>10 min</td>
<td>0.17</td>
</tr>
<tr>
<td>20 min</td>
<td>0.33</td>
</tr>
<tr>
<td>30 min</td>
<td>0.44</td>
</tr>
<tr>
<td>45 min</td>
<td>0.54</td>
</tr>
<tr>
<td>60 min</td>
<td>0.63</td>
</tr>
<tr>
<td>80 min</td>
<td>0.72</td>
</tr>
<tr>
<td>100 min</td>
<td>0.73</td>
</tr>
<tr>
<td>120 min</td>
<td>0.72</td>
</tr>
<tr>
<td>150 min</td>
<td>0.71</td>
</tr>
<tr>
<td>180 min</td>
<td>0.69</td>
</tr>
</tbody>
</table>

a: Determined by <sup>1</sup>H NMR integration, assuming total amount as 1 for these four major compounds with some other minor unidentified byproducts.

During the reaction course of 3 h, the relative quantity of the starting material decreased exponentially from 1 to about 0.04. It is clear that with the consumption of the starting material, which is the syn-isomer of the dihydro species, the pentacene derivative, the D-A adduct byproduct and the anti-isomer are formed as discussed in the following. The anti-isomer was formed with a relative quantity of 0.04 after 10 min reaction. However, the relative quantity of the anti-isomer was kept in the range of 0.04 - 0.05 with increasing reaction time up to 3 hours. The relative quantity of the pentacene derivative increased steadily up to 0.72 within the first 80 min, followed by a slight increase to 0.73 first when the reaction time reached 100 min and a little decrease afterward to 0.69 at the
end of 3 hours. Meanwhile, the relative quantity of the D-A adduct, which was generated by the reaction between the pentacene derivative formed and the excess of \( p \)-chloranil, increased with reaction time. The plots indicates that during the reaction, the majority of syn- isomer reacted with \( p \)-chloranil to form the pentacene derivative, which could further react with \( p \)-chloranil leading to a reduced quantity of pentacene derivative; while a minor portion of the syn- isomer converted to the anti- isomer and another small portion of syn- isomer left over in the reaction mixture.

Figure 5.3 Relative quantities of major compounds in crude reaction mixtures at different reaction time during aromatization of syn-6,13-dihydro-6,13-diethylthiopentacene

The reaction time should not be extended longer than 3 hours to consume all starting material because with longer time the quantity of the pentacene derivative will decrease even more. It should be noticed that the relative quantity of anti- isomer formed remains almost the same during the reaction, indicating that the epimerization reaction is slower
than the aromatization reaction for the syn-isomer, and the aromatization reaction of the anti-isomer is less reactive with \( p \)-chloranil.

5.3.2.2 Preliminary Dynamic Study of the Aromatization Reaction of syn-6,13-Dihydro-6,13-diphenylthiopentacene

![Scheme 5.6 Aromatization of syn-6,13-dihydro-6,13-diphenylthiopentacene](image)

**Table 5.7 Relative quantities of major compounds in crude reaction mixtures at different reaction time during aromatization of syn-6,13-dihydro-6,13-diphenylthiopentacene**

<table>
<thead>
<tr>
<th>Reaction time</th>
<th>Pentacene derivative (13)</th>
<th>Syn (88)</th>
<th>Anti (89)</th>
<th>D-A cycloadduct (101)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 min</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10 min</td>
<td>0.08</td>
<td>0.72</td>
<td>0.2</td>
<td>0</td>
</tr>
<tr>
<td>20 min</td>
<td>0.15</td>
<td>0.64</td>
<td>0.20</td>
<td>0.01</td>
</tr>
<tr>
<td>30 min</td>
<td>0.20</td>
<td>0.61</td>
<td>0.18</td>
<td>0.01</td>
</tr>
<tr>
<td>60 min</td>
<td>0.40</td>
<td>0.45</td>
<td>0.13</td>
<td>0.02</td>
</tr>
<tr>
<td>120 min</td>
<td>0.67</td>
<td>0.17</td>
<td>0.03</td>
<td>0.13</td>
</tr>
<tr>
<td>180 min</td>
<td>0.82</td>
<td>0</td>
<td>0</td>
<td>0.18</td>
</tr>
<tr>
<td>240 min</td>
<td>0.90</td>
<td>0</td>
<td>0</td>
<td>0.10</td>
</tr>
</tbody>
</table>

*Relative quantities in crude reaction mixtures\(^a\)*

*a: Determined by \(^1\)H NMR integration, assuming total amount as 1 for these four major compounds with some other minor unidentified byproducts.

The aromatization reaction of syn-6,13-dihydro-6,13-diphenylthiopentacene was monitored during the reaction course as another representative example (Scheme 5.6). The relative quantities of compounds in the reaction mixture at different reaction time were calculated from the \(^1\)H NMR spectra (Table 5.7). The relationship between relative quantities and reaction time are plotted accordingly as well (Figure 5.4). There are four
main components in the reaction mixture, the unreacted syn-isomer, the anti-isomer formed via epimerization, the desired pentacene derivative, and the D-A cycloadduct of the pentacene derivative and p-chloranil as a byproduct.

Figure 5.4 Relative quantities of major compounds in crude reaction mixtures at different reaction time during aromatization of syn-6,13-dihydro-6,13-diphenylthiopentacene

After 3 h of reaction, the relative quantity of the starting material decreased exponentially from 1 to 0, indicating the completion of the reaction. But the reaction was monitored for 4 hours for consistence. With the consumption of the starting material, which is the syn-isomer of the dihydro species, the pentacene derivative, the D-A adduct byproduct and the anti-isomer are formed. The formation of the anti-isomer with a relative quantity of 0.2 in 10 min is unexpected because no remarkable epimerization was observed in the control study. The relative quantity of anti-isomer increased up to 0.2 in 10 min, and started to decrease slowly after 20 min. After 180 min, no anti-isomer could be detected. Within 180 min, the relative quantity of the pentacene derivative increased steadily up to
0.82 along with that of the D-A adduct. However, unlike the ehtylthio case, after 1 more hour the amount of pentacene further increased to 0.90 at the expense of decrease of D-A adduct quantity. It could be explained as that the D-A adduct of diphenylthiopentacne is unstable due to the steric hindrance caused by the phenyl substituent and could form the pentacene derivative by retro Diels-Alder reaction. The plots indicates that the anti-isomer was formed first from the syn- isomer and then consumed to generate pentacene derivative product. Therefore, in this case, both of the syn- and anti- isomers are reactive with p-chloranil.

5.4 Conclusions

In the ZnI\textsubscript{2}-mediated reaction between 6,13-dihydro-6,13-dihydroxypentacene and organothiols, a mixture of syn- and anti- isomers of 6,13-bis(organothio)-6,13-dihydro pentacenes is produced with syn- isomer as either the only product (when R = ethyl and (CH\textsubscript{2})\textsubscript{2}COOH) or the major product with a relative quality greater than 80% (other cases), while the anti- isomer is produced as a minor product with a relative quality less than 20%. Although syn- isomer is the major product of the reaction, for several cases, like where R = ethyl, octyl, and phenyl, freely epimerization of the syn- isomers to form anti- isomers has been observed in many situations. The stereochemistries of syn and anti isomers for most of the cases have been confirmed by crystallography. In the dehydrogenative aromatization reaction using p-chloranil or DDQ in sealed vessel, for most cases, both syn- and anti- 6,13-dihydro-6,13-diorganothiopentacenes could be aromatized and form the desired pentacene derivatives, unlike in the previously reported literature \textsuperscript{49} where only one of the isomers could be aromatized. During the aromatization
reaction the epimerization of the dihydro species happened for many of the cases. The pentacene derivatives generated have been isolated and characterized thoroughly. The UV-vis absorption spectroscopies indicate their applications as organic semiconductors.

5.5 Experimental

5.5.1 Analytical Instrumentation

5.5.1.1 $^1$H NMR Spectra

$^1$H NMR spectra were obtained on a Varian Mercury Plus 400 FT-NMR operating at 399.768 MHz or a Varian INOVA 500 FT-NMR operating at 499.763 MHz. All chemical shift ($\delta_H$) values are reported in parts per million (ppm) relative to residual solvent protons unless otherwise noted.

5.5.1.2 $^{13}$C NMR Spectra

$^{13}$C NMR spectra were obtained on a Varian Mercury Plus 400 FT-NMR operating at 100.522 MHz or a Varian INOVA 500 FT-NMR operating at 125.666 MHz. All chemical shift ($\delta_C$) values are reported in parts per million (ppm) relative to residual solvent signal unless otherwise noted.

5.5.1.3 Mass Spectrometry

Matrix assisted laser desorption ionization (MALDI-TOF-MS, $S_8$ as matrix) and laser desorption ionization (LDI-TOF-MS) mass spectra was acquired on a Shimadzu Kratos Axima-CFR mass spectrometer in reflectron mode. Electrospray ionization high-
resolution mass spectra were acquired at the Notre Dame Mass Spectrometry & Proteomics Facility in Notre Dame, Indiana.

5.5.1.4 UV-Vis Spectroscopy

UV-visible spectra were obtained on a Nicolet Evolution 300 spectrometer using 1 cm quartz cells. Solid state UV–visible spectra were obtained on a Cary 50 Bio spectrophotometer fitted with a Barrelino diffuse reflectance probe using BaSO₄ as a standard and powder samples pressed on BaSO₄ pellets.¹⁴²

5.5.2 Chromatography

Sand was obtained from Fisher Scientific Co.
Silica Gel (230-400 mesh) was obtained from Natland International Co.
Thin Layer Chromatography Plates obtained from Fisher Scientific Co.

5.5.3 Solvents

Note: All solvents were used without further purification unless otherwise noted. Solvent drying was carried out as needed by distillation from sodium metal (THF, toluene) or by passing through a silica column in a dry-solvent delivery system.

Acetic Acid (CH₃CO₂H) was obtained from VWR Chemical Co.
Acetone (reagent grade) was obtained from Pharmco-AAPER.
Benzene (C₆H₆) was obtained from Sigma-Aldrich.
Buffer solution (pH=10) was obtained from Fisher Scientific.
Chloroform (CHCl₃) was obtained from Pharmco-AAPER.

Dichloromethane (DCM) was obtained from Pharmco-AAPER.

Dimethylsulfoxide (DMSO) was obtained from Alfa Aesar.

Ethanol (absolute) was obtained from Pharmco-AAPER.

Methanol was obtained from Pharmco-AAPER.

Tetrahydrofuran (THF) was obtained from Fisher Scientific Co.

Toluene (PhCH₃) was obtained from Fisher Scientific Co.

All NMR solvents were purchased from Cambridge Isotope Laboratories.

5.5.4 Reagents

Note: All reagents were used without further purification unless otherwise noted.

o-Phthalaldehyde (C₈H₆O₂) was obtained from Aldrich Chemical Co.

1,4-Benzoquinone (C₆H₄O₂) was obtained from Acros Organics Co.

Sodium hydroxide (NaOH) was obtained from EM Science

Sodium borohydride (NaBH₄) was obtained from Aldrich Chemical Co.

Zinc iodide (ZnI₂) was obtained from Aldrich.

Zinc bromide (ZnBr₂) was obtained from Aldrich.

3-Thiopropanoic acid (HS(CH₂)₂COOH) was obtained from Alfa-Aesar.

p-Chloranil (C₆Cl₄O₂) was obtained from Aldrich.

Potassium carbonate (K₂CO₃) was obtained from J. T. Baker.

DDQ was obtained from Aldrich.
5.5.5 Syntheses

Note: All routine solvent evaporations were conducted on a standard rotary evaporator using vacuum pump pressure unless otherwise noted.

syn-6,13-Dihydro-6,13-diethylthiopentacene (84)

A flame-dried, N₂ purged 100 mL round bottom flask was charged with ZnI₂ (0.402 g, 1.25 mmol), 6,13-dihydro-6,13-dihydroxypentacene (0.2 g, 0.64 mmol) and 30 mL dry CH₂Cl₂. To this mixture was added ethanethiol (0.23 mL, 3.11 mmol) and the resulting pinkish reaction mixture was stirred for 0.5 hour in the dark. The reaction was TLC monitored. The reaction mixture was filtered and the filtrate was thoroughly washed with water, saturated solution of sodium bicarbonate and brine. Upon evaporating the solvent and followed by drying in vacuo, crude compound solely containing syn-6,13-dihydro-6,13-diethylthiopentacene was recovered. After hexane wash pure syn-6,13-dihydro-6,13-diethylthiopentacene (84) was isolated as an off-white solid (0.207g, 81%).

Alternative method to synthesize syn-6,13-dihydro-6,13-diethylthiopentacene (84): To a flame-dry N₂ purged 250 mL round bottom flask anhydrous ZnBr₂ (2.16g, 9.6 mmol), 6,13-dihydro-6,13-dihydroxypentacene (1.5g, 4.8 mmol) and 150 mL dry CH₂Cl₂ was added. To the mixture was added ethylthiol (2.8 mL, 38.4 mmol). The reaction mixture turned to a light yellow brown solution and completed within 30 minutes confirmed by TLC test. The reaction mixture was filtered and the filtrate was thoroughly washed with water, saturated solution of sodium bicarbonate and brine. Upon evaporating the solvent and followed by drying in vacuo, crude compound containing syn-6,13-dihydro-6,13-diethylthiopentacene was recovered. The resulting solid was passed through a short silica
column with hexane as an eluent to yield off-white solid of syn-6,13-dihydro-6,13-diethylthiopentacene 84 (1.83 g, 95% yield). $^1$H NMR (500 MHz, CDCl$_3$) δ (ppm): 7.87 (s, 4H), 7.86 - 7.82 (m, 4H), 7.49 - 7.45 (m, 4H) 5.48 (s, 2H), 2.78 (q, 4H, J = 7.3 Hz), 1.41 (t, 6H, J = 7.4 Hz). $^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm): 135.23, 132.64, 127.68, 127.42, 126.26, 47.98, 27.95, 14.33. LDI-MS $m/z$: 402 [M$^+$ + 2], 401 [M$^+$ + 1]; ESI HRMS: [M$^+$ + Na] 423.1220 (calculated 423.1212, error -1.9 ppm).

anti-6,13-Dihydro-6,13-diethylthiopentacene (85)

syn-6,13-Dihydro-6,13-diethylthiopentacene (84) was stirred under air and hood light/room light for 3 days at room temperature to recover a mixture of syn and anti isomers of 6,13-dihydro-6,13-diethylthiopentacene. (Comment: The isomerization in solution state is also possible in the dark. The amount of the second isomer was increased from 0% to 37% within 11 hours in NMR tube. In the solid state, the conversion was much slower under light at room temperature. Therefore isolated 84 was stored cold in the dark). Upon column chromatographic separation using hexane anti-6,13-dihydro-6,13-diethylthiopentacene (85) was isolated. $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.19 (s, 4H), 7.91 - 7.87 (m, 4H), 7.51 - 7.47 (m, 4H), 5.66 (s, 2H), 2.58 (q, 4H, J = 7.4 Hz), 1.34 (t, 6H, J = 7.4 Hz). $^{13}$C NMR (100 MHz, CDCl$_3$): δ (ppm): 135.15, 132.60, 127.81, 126.49, 126.25, 48.99, 26.09, 14.63. ESI HRMS: [M$^+$ + Na] 423.1232 (calculated 423.1212, error -4.9 ppm).

6,13-Diethylthiopentacene (95)
To a flame dried, Ar purged 35 mL pressure vessel compound 84 (0.5 g, 1.25 mmol), p-chloranil (0.36 g, 1.44 mmol) and benzene (15 mL) was added. The reaction mixture was thoroughly degased and filled with Ar. The vessel was sealed with a Teflon screw cap. The mixture was stirred and heated to 90 °C in an oil bath for 3 hours in the dark. After cooling to room temperature, the reaction mixture was filtered and solvent was evaporated to get crude pentacene. Upon column chromatographic separation using dichloromethane and hexane (10% DCM in hexane), 6,13-diethylthiopentacene (95) was isolated as a dark blue solid (0.21g, 42%). $^1$H NMR (500 MHz, CDCl$_3$) δ (ppm): 9.71 (s, 4H), 8.07 - 8.03 (m, 4H), 7.42 - 7.38 (m, 4H), 3.06 (q, 4H, J = 7.4 Hz), 1.18 (t, 6H, J = 7.4 Hz). $^{13}$C NMR (125 MHz, CDCl$_3$) δ (ppm): 132.97, 132.24, 132.10, 128.87, 126.99, 125.97, 31.97, 15.43. MALDI-MS m/z: 398.3 [M$^+$]. ESI HRMS: [M$^+$] 398.1142 (calculated 398.1157, error 4 ppm).

### syn-6,13-Dihydro-6,13-dioctylthiopentacene (86) and anti-6,13-Dihydro-6,13-dioctylthiopentacene (87)

A flame-dried, N$_2$ purged 100 mL round bottom flask was charged with ZnI$_2$ (0.215 g, 0.67 mmol), 6,13-dihydro-6,13-dihydroxypentacene (0.2 g, 0.64 mmol) and 25 mL dry CH$_2$Cl$_2$. To this mixture was added octanethiol (0.25 mL, 1.44 mmol) and the resulting pinkish reaction mixture turned to clear solution and finished in 10 minutes as monitored by TLC. The reaction mixture was filtered and the filtrate was thoroughly washed with water, saturated solution of sodium bicarbonate and brine. Upon evaporating the solvent and followed by drying in vacuo, crude compound containing syn-6,13-dihydro-6,13-dioctylthiopentacene was recovered. After column chromatographic separation using
hexane and dichloromethane (9:1) pure syn-6,13-dihydro-6,13-dioctylthiopentacene (86) was isolated as an white oily liquid (Syn 3: 0.31g, 85%). While same procedure was used with two equivalents of ZnI₂ for 2 hours (monitored by TLC), both two syn and anti diastereomers were detected. A very short column (~1 inch) chromatography using a 15 mL medium fritted glass buchner filtering funnel connected to a round bottom flask with 24/40 joint and a vacuum assembly was used to isolate them using modified procedure of Pedersen et al.¹⁴³ The column initially started with just hexane and then slowly increased to 5% dichloromethane in hexane, to isolate syn-6,13-dihydro-6,13-dioctylthiopentacene (86) in 41% (0.15g) and anti-6,13-dihydro-6,13-dioctylthiopentacene (87) in 23% yield (0.08g). (Comment: Note that both syn and anti was epimerizing during the process of isolation. The epimerization was much pronounced in case of long column. Also, even after isolation pure product was slowly interchanging to other isomer detected by NMR)

syn-6,13-Dihydro-6,13-dioctylthiopentacene (86): ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.87 - 7.83 (m, 4H), 7.80 (s, 4H), 7.51 - 7.47 (m, 4H), 5.35 (s, 2H), 2.70 (t, 4H, J = 7.5 Hz), 1.71 (p, 4H, J = 7.5 Hz), 1.42 (p, 4H, J = 7.2 Hz), 1.35 - 1.32 (m, 16H), 0.99 - 0.78 (m, 6H). ¹³C NMR (125 MHz, CDCl₃) δ (ppm): 135.31, 132.63, 127.68, 127.46, 126.24, 48.11, 33.95, 31.98, 29.43, 29.37, 29.35, 29.31, 22.81, 14.28.

anti-6,13-Dihydro-6,13-dioctylthiopentacene (87): ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.18 (s, 4H), 7.90 - 7.86 (m, 4H), 7.51 - 7.47 (m, 4H), 2.54 (t, 4H, J = 7.4 Hz.), 1.66 (p, 4H, J = 7.4 Hz), 1.47 - 1.33 (m, 4H), 1.31 - 1.13 (m, 16H), 0.89 - 0.85 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 135.18, 132.61, 127.80, 126.52, 126.22, 49.14, 32.02, 31.95, 29.63, 29.37, 29.32, 29.18, 22.80, 14.26.
6,13-Dioctylthiopentacene (96)

To a flame dried, Ar purged 35 mL pressure vessel compound 86 (0.098 g, 0.17 mmol), p-chloranil (0.056 g, 0.23 mmol) and benzene (3.5 mL) was added. The reaction mixture was thoroughly degased and filled with Ar. The vessel was sealed with a Teflon screw cap. The mixture was stirred and heated to 100 °C in an oil bath for 3 hours in the dark. After cooling to room temperature, the reaction mixture was filtered and solvent was evaporated to get crude pentacene. The crude blue solid was re-dissolved in minimum amount of chloroform and methanol was slowly added to the stirred solution to precipitate shiny small blue crystal of 6,13-dioctylthiopentacene (96) (0.044 g, 45.5%). 1H NMR (500 MHz, CDCl3) δ (ppm): 9.71 (s, 4H), 8.08 - 8.04 (m, 4H), 7.42 - 7.38 (m, 4H), 3.02 (t, 4H, J = 7.2 Hz), 1.53 (dt, 4H, J = 14.8, 7.5 Hz), 1.46 - 1.34 (m, 4H), 1.27 - 1.08 (m, 16H), 0.81 (t, J = 7.0 Hz, 6H). 13C NMR (125 MHz, CDCl3) δ (ppm): 132.88, 132.76, 132.11, 129.89, 128.89, 127.02, 125.96, 38.14, 31.87, 30.17, 29.32, 29.24, 29.01, 22.73, 14.20, 0.16.

syn-6,13-Dihydro-6,13-dipheylthiopentacene (88) and anti-6,13-Dihydro-6,13-dipheylthiopentacene (89)

A flame-dried, N2 purged 50 mL round bottom flask was charged with ZnI2 (0.406 g, 1.27 mmol), 6,13-dihydro-6,13-dihydroxypentacene (0.200 g, 0.64 mmol) and 20 mL dry CH2Cl2. To this mixture was added phenylthiol (0.17 mL, 1.40 mmol) and the resulting pinkish reaction mixture was stirred for 30 minutes in the dark. The reaction was TLC monitored. A reaction mixture was filtered and the filtrate was thoroughly washed with water, saturated solution of sodium bicarbonate and brine. Upon evaporating
the solvent and followed by drying *in vacuo*, crude mixture of syn 88 and anti 89 isomer of 6,13-dihydro-6,13-diphenylthiopentacene was recovered in 78% yield (247 mg). Upon trituration using minimum amount of CHCl₃ and 100 mL MeOH, followed by filtration, a portion of major syn isomer 88 was purified as a white solid (127 mg, 40%). The filtrate was dried and contained mixture of both syn and anti diastereomers. A very short column (~1 inch) chromatography using a 15 mL medium fritted glass buchner filtering funnel connected to a round bottom flask with 24/40 joint and a vacuum assembly was used to isolate the diastereomers. Upon chromatographic separation using pure hexane to 5% DCM in hexane, both 88 (66 mg, 20.8%) and anti-6,13-dihydro-6,13-diphenylthiopentacene 89 (24 mg, 7.6%) was isolated. Finally two isolated portions of syn 88 were combined (193 mg, 61%).

**syn-6,13-Dihydro-6,13-diphenylthiopentacene (88):** $^1$H NMR (500 MHz, CDCl₃) $\delta$ (ppm): 7.68 - 7.64 (m, 4H), 7.53 - 7.48 (m, 4H), 7.47 (s, 4H), 7.45 - 7.40 (m, 4H), 7.40 - 7.36 (m, 2H), 7.36 - 7.29 (m, 4H), 5.71 (s, 2H). $^{13}$C NMR (125 MHz, CDCl₃) $\delta$ (ppm): 136.42, 135.57, 133.96, 132.49, 129.03, 128.84, 127.86, 127.64, 126.22, 54.73.

**anti-6,13-Dihydro-6,13-diphenylthiopentacene (89):** $^1$H NMR (400 MHz, CDCl₃) $\delta$ (ppm): 8.00 (s, 4H), 7.77 - 7.73 (m, 4H), 7.46 - 7.42 (m, 4H), 7.29 - 7.25 (m, 4H), 7.20 - 7.15 (m, 6H), 6.01 (s, 2H). $^{13}$C NMR (100 MHz, CDCl₃) $\delta$ (ppm): 134.95, 134.15, 132.58, 132.15, 128.99, 127.80, 127.25, 126.81, 126.29, 53.05.

**6,13-Diphenylthiopentacene (13)**

To a flame dried, Ar purged 15 mL pressure vessel compound 5 (0.2 g, 0.4 mmol), p,p-chloranil (0.2 g, 0.8 mmol) and dry chloroform (10 mL) was added. The reaction mixture
was thoroughly degased and filled with Ar. The vessel was sealed with a Teflon screw cap. The mixture was stirred and heated to 80 °C in an oil bath for 4 hours in the dark. After cooling to room temperature, solvent was evaporated to get crude product (0.234 g). The crude product was thoroughly washed with ethanol, hexanes and diethyl ether to isolate 6,13-diphenylthiopentacene (13) as a dark blue solid (0.119 g, 60%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 9.63 (s, 4H), 7.97 - 7.93 (m, 4H), 7.38 - 7.34 (m, 4H), 7.15 - 7.02 (m, 10H).

**syn-6,13-Dihydro-6,13-naphthylthiopentacene (90) and anti-6,13-Dihydro-6,13-naphthylthiopentacene (91)**

A flame-dried, N\(_2\) purged 100 mL round bottom flask was charged with ZnI\(_2\) (2.24 g, 6.4 mmol), 6,13-dihydro-6,13-dihydroxypentacene (1 g, 3.2 mmol) and 50 mL dry CH\(_2\)Cl\(_2\). To this mixture was added 1-naphthalenethiol (1 mL, 7.04 mmol) and the resulting pinkish reaction mixture was stirred for 2 hours and 20 minutes in the dark. The reaction was TLC monitored. The reaction mixture was filtered and the filtrate was washed with water, saturated solution of sodium bicarbonate and brine. Upon evaporating the solvent and followed by drying *in vacuo*, crude compound containing syn-6,13-dihydro-6,13-naphthathiopentacene and anti-6,13-dihydro-6,13-naphthylthiopentacene was recovered. After trituration using minimum amount of CH\(_2\)Cl\(_2\) then adding excess hexane, pure syn-6,13-dihydro-6,13-naphthylthiopentacene (90) was precipitated and isolated by filtration as an off-white solid (Syn: 1.54 g, 80%). The filtrate was evaporated and dried in vacuo. After column chromatographic separation in silica using CH\(_2\)Cl\(_2\) and hexane (1:3), anti isomer (91) was isolated as an off-white solid (Yield: 27 mg, 1.4%) from the filtrate.
syn-6,13-Dihydro-6,13-naphthylthiopentacene (90): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 8.92 (d, 2H, J = 8.4 Hz), 7.96 (dd, 4H, J = 7.9, 3.0 Hz), 7.70 - 7.59 (m, 4H), 7.59 - 7.54 (m, 2H), 7.54 - 7.50 (m, 4H), 7.39 - 7.35 (m, 4H), 7.35 - 7.32 (m, 2H), 7.23 (s, 4H), 5.69 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 137.05, 135.63, 134.45, 133.77, 132.97, 132.35, 130.29, 128.80, 127.87, 127.50, 126.15, 126.54, 126.36, 126.09, 125.67, 53.69. ESI HRMS: [M$^+$ + Na] 619.1543 (calculated 619.1525, error -2.1 ppm).

anti-6,13-Dihydro-6,13-naphthylthiopentacene (91) $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ (ppm): 8.70 (d, 2H, J = 8.4 Hz), 7.92 (s, 4H), 7.86 (d, 2H, J = 8.1 Hz), 7.69 (d, 2H, J = 8.1 Hz), 7.67 - 7.63 (m, 4H), 7.63 - 7.59 (m, 2H), 7.57 - 7.50 (m, 2H), 7.40 - 7.36 (m, 4H), 7.25 - 7.19 (m, 2H), 7.15 - 7.09 (m, 2H), 6.16 (s, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ (ppm): 134.09, 134.00, 133.73, 132.53, 132.13, 131.20, 128.86, 128.16, 127.72, 126.83, 126.72, 126.34, 126.21, 125.69, 125.18, 52.66. ESI HRMS: [M$^+$ + Na] 619.1504 (calculated 619.1525, error 3.4 ppm).

6,13-Dinaphthylthiopentacene (97)

To a flame dried, Ar purged 15 mL pressure vessel compound 90 (50 mg, 0.085 mmol), P-chloranil (41.75 mg, 0.17 mmol) and dry chloroform (2.5 mL) was added. The reaction mixture was thoroughly degased and filled with Ar. The vessel was then sealed with a Teflon screw cap. The mixture was stirred and heated to 80°C in an oil bath for 4 hours in the dark. After cooling to room temperature, the solvent was evaporated to get crude pentacene. The crude blue solid was washed and filtered with diethyl ether, methanol, hexanes, acetone and dichloromethane. After drying, 6,13-dinaphthylthiopentacene 97 was recovered as a blue solid (18.6 mg, 37.2%). $^1$H NMR (400 MHz, CDCl$_3$, CS$_2$) $\delta$
(ppm): 9.55 (s, 4H), 8.80 (d, 2H, J = 8.5 Hz), 7.85 (d, 2H, J = 8.1 Hz), 7.82 - 7.79 (m, 4H), 7.75 (t, 2H, J = 7.5 Hz), 7.62 (t, 2H, J = 7.6 Hz), 7.50 (d, 2H, J = 8.2 Hz), 7.29 - 7.25 (m, 4H), 6.90 (t, 2H, J = 7.7 Hz), 6.36 (d, 2H, J = 7.3 Hz). $^{13}$C NMR (125 MHz, CDCl$_3$, CS$_2$) $\delta$ (ppm): 136.22, 133.97, 133.39, 132.70, 130.93, 129.62, 128.80, 128.74, 126.84, 126.50, 126.47, 126.31, 126.02, 125.52, 124.19, 124.14. LDI-MS m/z: 593.4 [M$^+$]; ESI HRMS: [M$^+$] 594.1443 (calculated 594.1470, error 4.6 ppm).

**syn-4,4'-(6,13-Dihydropentacene-6,13-diyl)bis(sulfanediyl))bis(butan-1-ol) (92) and anti-4,4'-(6,13-Dihydropentacene-6,13-diyl)bis(sulfanediyl))bis(butan-1-ol) (93)**

A flame-dried, N$_2$ purged 100 mL round bottom flask was charged with 6,13-dihydro-6,13-dihydroxypentacene (200 mg, 0.64 mmol), 20.0 mL dry CH$_2$Cl$_2$ and molecular sieves (about 10 beads, 4A). 4-Mercapto-1-butanol (0.18 mL, 1.28 mmol) followed by ZnI$_2$ (408.6 mg, 1.28 mmol) was added to the reaction mixture. The resulting pinkish reaction mixture was stirred for 40 minutes in the dark and the reaction was TLC monitored. The reaction mixture was filtered and the filtrate was thoroughly washed with water, saturated solution of sodium bicarbonate and brine. Upon evaporating the solvent and followed by drying in vacuo, the crude mixture of syn (92) and anti (93) was recovered in 92% yield. After column chromatographic separation in silica using ethylacetate and hexane (1:1), syn isomer 92 was isolated as an off-white solid (Yield: 205.3 mg, 66%), and anti isomer of 93 was isolated as an off-white solid (Yield: 11.3 mg, 3.6%). The yield of anti isomer 93 was improved to 12% when ZnBr$_2$ was used instead of ZnI$_2$ (6,13-dihydroxy-6,13-dihydropentacene [400 mg, 1.28 mmol]; ZnBr$_2$ [576.5 mg, 168
2.56 mmol]; 4-Mercapto-1-butanol [0.37 mL, 2.56 mmol] in 40 mL CH2Cl2 of to give 61.4 mg anti isomer 10 [12%])
syn-4,4′-((6,13-Dihydropentacene-6,13-diyl)bis(sulfanediyl))bis(butan-1-ol) (92) ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.86 - 7.83 (m, 4H), 7.84 (s, 4H), 7.51 - 7.47 (m, 4H), 5.44 (s, 2H), 3.64 (s, 4H), 2.77 (t, 4H, J = 7.1 Hz), 1.86 - 1.74 (m, 4H), 1.73 - 1.63 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 135.13, 132.68, 127.71, 127.59, 126.39, 62.48, 48.33, 33.64, 32.13, 25.5. ESI HRMS: [M⁺ + Na] 511.1738 (calculated 511.1736, error -0.3 ppm).

anti-4,4′-((6,13-Dihydropentacene-6,13-diyl)bis(sulfanediyl))bis(butan-1-ol) (93) ¹H NMR (500 MHz, CDCl₃) δ (ppm): 8.18 (s, 4H), 7.91 - 7.87 (m, 4H), 7.52 - 7.46 (m, 4H), 5.66 (s, 2H), 3.62 (t, 4H, J = 6.0 Hz), 2.59 (t, 4H, J = 7.1 Hz), 1.83 - 1.71 (m, 4H), 1.71 - 1.63 (m, 4H). ¹³C NMR (125 MHz, CDCl₃) δ (ppm): 135.00, 132.54, 127.75, 126.46, 126.30, 62.38, 49.06, 31.97, 31.78, 25.88. ESI HRMS: [M⁺ + Na] 511.1756 (calculated 511.1736, error -4.0 ppm).

4,4′-(Pentacene-6,13-diylbis(sulfanediyl))bis(butan-1-ol) (98)
To a flame dried, Ar purged 15 mL pressure vessel, 92 (40 mg, 0.08 mmol), Tetrachloro-1,4-benzoquinone (p-chloranil) (26 mg, 0.11 mmol), potassium carbonate (111 mg, 0.8 mmol) and dry benzene (5 mL) was added. The reaction mixture was thoroughly degassed and filled with Ar. The vessel was then sealed with a Teflon screw cap. The mixture was stirred and heated to 100 °C in an oil bath for 2 hours and 30 minutes in the dark. After cooling to room temperature, the reaction mixture was filtered and solvent was evaporated to get crude pentacene. After column chhormatographic separation using
ethyl acetate and hexane (1:1), pentacene 98 was recovered as a dark blue solid (30.7mg, 77%). $^1$H NMR (500 MHz, CDCl$_3$) δ (ppm): 9.71 (s, 4H), 8.10 - 8.04 (m, 4H), 7.45 - 7.39 (m, 4H), 3.49 (s, 4H), 3.07 (t, 4H, $J = 7.1$ Hz), 1.71 - 1.62 (m, 4H), 1.62 - 1.55 (m, 4H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm): 132.87, 132.46, 132.19, 128.87, 126.95, 126.12, 62.43, 37.73, 31.97, 26.56. MALDI-MS m/z: 485 [M$^+$ - 1]; ESI HRMS: [M$^+$ + Na]$^+$ 509.1558 (calculated 509.1579, error 4.3 ppm).
CHAPTER 6

SUMMARY AND CONCLUSION

The development of new organic semiconductors is driven by the desire for portable, flexible and affordable organic electronic devices, including organic field effect transistors (OFETs), organic photovoltaics (OPVs) and organic light emitting diodes (OLEDs). The desired organic semiconductors should have suitable HOMO-LUMO gap for semiconducting properties, good solubility and solution stability allowing solution processability, potentially enabling high-rate fabrication of electronic devices on flexible substrates. In this dissertation, our research has been focused on small molecules organic semiconductors: pentacene derivatives (6,13-bis(organothio)pentacenes) and fullerene derivatives ([60]fullerene-pentacene adduct).

The systematical exploration of the dehydrogenative aromatization reaction using \( p \)-chloranil (or DDQ) in Chapter 5 demonstrated a fast and convenient synthetic method for 6,13-bis(organothio)pentacenes. Numerous dihydropentacenes have been prepared using a ZnI\(_2\)-mediated reaction between 6,13-dihydro-6,13-dihydroxypentacene and organic thiols. Both syn- and anti- 6,13-dihydro-6,13-diorganothiopentacene isomers were formed with the syn- isomers as major products. In most cases, both syn- and anti-dihydropentacene isomers react similarly with \( p \)-chloranil (or DDQ for acetylthio group) to generate the corresponding 6,13-bis(organothio)pentacenes. All 6,13-bis(organothio)pentacenes generated are potential p-type organic semiconductors with relatively small HOMO-LUMO gaps as evidenced by their UV-vis spectra. Those 6,13-bis(organothio)pentacenes with propionic acid or acetyl functional groups, served as
precursors for water soluble pentacene (Chapter 2) and 6,13-dithiopentacene oligomers (Chapter 3), respectively.

The first water soluble pentacene, potassium 3,3’-(pentacene-6,13-diylbis(sulfanediyl)) dipropanoate, has been successfully synthesized and fully characterized as described in Chapter 2. With an optical HOMO-LUMO gap of approximately 1.91-1.97 eV (indicated by UV-vis spectra in several different polar solvents), water soluble pentacene was utilized as donor in an active bi-layer photovoltaic cell with C_{60} as acceptor. Preliminary cyclic voltammetry results also indicated that the water soluble pentacene has potential application as a molecular switch.

Both unsubstituted and t-butylphenyl substituted versions of 6,13-diacetylthiopentacene have been successfully synthesized, as described in Chapter 3. An attempted synthesis of 6,13-dithiopentacene oligomers from 6,13-dimercaptopentacene appears to have been successful. However, due to poor solubility, purification and characterization was limited.

The Diels-Alder reaction between 5,7,12,14-tetraphenylpentacene (TTP) and [60]fullerene to generate mono- and multi- adducts has been studied both experimentally and computationally, as discussed in Chapter 4. A mono-TPP-C_{60} adduct, two regioisomers of a bis-TPP-C_{60} adduct, and a symmetric tetrakis-TPP-C_{60} adduct have all been formed. At the level of B3LYP/6-31G(d,p)//PM6 theory, the adducts have similar HOMO-LUMO gaps as C_{60} indicating their potential application as n-type semiconductors. Among the eight possible regioisomers of bis-TPP-C_{60} adduct, the trans-1, trans-2, trans-3, and e- regioisomers are energetically preferred as compared to cis-1, cis-2, and cis-3 regioisomers. Moreover, the shape-controlled preparation of nano- and
microstructures from the mono-C$_{60}$-TPP adduct have been demonstrated by judicious self-assembly in various solvent systems. Due to the reversibility of the Diels-Alder reaction, the highly symmetric tetrakis-TPP-C$_{60}$ adduct formed could be utilized in the synthesis of trans-1 bis-C$_{60}$ adducts which are otherwise difficult to synthesis directly.
REFERENCES


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APPENDICES

Abbreviation

Spectra
Aq: Aqueous
Ar: Argon
CV: Cyclic Voltammetry
DFT: Density functional theory
DSC: Differential scanning calorimetry
Eq.: Equivalent
OFET: Organic field effect transistors
FTIR: Fourier transform infrared spectroscopy
HOMO: Highest occupied molecular orbital
LUMO: Lowest unoccupied molecular orbital
MALDI-MS: Matrix assisted Laser Desorption Ionisation Mass Spectrometry
MMFF: Molecular Mechanics Force Field
LDI-MS: Laser Desorption Ionisation Mass Spectrometry
OLED: Organic light emitting diode
OSC: Organic solar cell
OPV: Organic photovoltaic
OTFT: Organic thin film transistor
PCE: Power conversion efficiency (%)
PQ: Pentacene quinone
RT: Room temperature
SEM: Scanning electron microscope
TGA: Thermogravimetric analysis
UV: Ultra violet
Pentacene-6,13-dione (24)

$^1$H NMR (400 MHz, CDCl$_3$)
6,13-Dihydroxy-6,13-dihydropentacene (25)
syn-3',3''-((6',13'-dihydropentacene-6,13-diyl)sulfanediyl)(dipropionic acid) (26)

$^{1}H$ NMR (400 MHz, Methanol-$d_4$)
$^{13}$C NMR (125 MHz, Methanol-$d_4$)

syn-3,3'-((6,13-dihydropentacene-6,13-diyl)bis(sulfanediyl))dipropionic acid (26)
$^{1}H$ NMR (400 MHz, DMSO-$d_6$)

Syn-3,3'-((6,13-dihydropentacene-6,13-diyl)bis(sulfanediyl))dipropanoic acid (26)
syn-3',3''-(6',13'-dihydroperpentacene-6,13-diyli(sulfaneidiyli)dipropionic acid (26)

$^{13}$C NMR (100 MHz, DMSO-$d_6$)
Single crystal X-ray structure

syn-3,3'-((6,13-dihydrodipentacene-6,13-diyl)bis(sulfanediyl))dipropionic acid (26)
**189**

**LDI MS**

\[ \text{Molecular Weight: 488.62} \]

\[ \text{syn-3',3''-(6',13'-dihydropentalene-6,13-diylbis(sulfanediyl))dipropionic acid (26)} \]
syn-3,3′-(1,6,13-dihydropentaecene-6,13-diyldiyisulfanediyl)dipropanoic acid (26)
syn-3',3''-((6',13-dihydrooctacene-6,13-diylbis(sulfanediyl))dipropanoic acid) (26)
**syn-3,3'-((6,13-dihydroperylenene-6,13-diyl)bis(sulfanediyl))dipropionic acid (26)**
$^{1}$H NMR (500 MHz, Acetic Acid-$_d_4$)
3,3'-((Pentacene-6,13-diylbis(sulfane-diyi))dipropanoic acid (27))

$\text{H NMR (500 MHz, Methanol-d$_4$)}$
3',3'-((Pentacene-6,13-diylbis(sulfanediyl))dipropionic acid (27)
3.3'(Pentacene-6,13-diylbis(sulfanediyl))dipropionic acid (27)

VT-\textsuperscript{13}C NMR (125 MHz, Acetic Acid-d\textsubscript{4}) at 80 ºC
197

3,3’-(Pentacene-6,13-diylbis(sulfanediyl))dipropionic acid (27)

Molecular Weight: 486.60

M - CH₂CH₂COOH = 413.53

LDI MS
5-(2,6-Dimethylphenyl)-1-benzothiophene 3-carboxylic acid (27)
TGA in N₂

3,3’-(Pentacene-6,13-diylbis(sulfanediyl))dipropanoic acid (27)
TGA in Air

3,3’-(Pentacene-6,13-diylbis(sulfanediyl))dipropanoic acid (27)

Universal V.4A, TA Instrument
UV-vis Spectra (in methanol)

3,3'-(Pentacene-6,13-diylbis(sulfanediyl))dipropanoic acid (27)

$\lambda_{\text{max}} = 527, 570, 612 \text{ nm}$

$E_{\text{opt. gap}} = 1.96 \text{ eV}$
3,3'-{(pentacene-6,13-diylbis(sulfanediyl))dipropionic acid (27)}
Anhydride of 3,3'-{(Pentacene-6,13-diylbis(sulfanediyl))dipropanoic acid (27)
Potassium 3,3'-(pentacene-6,13-diylbis(sulfanediyl))dipropionate (28)

$^{1}$H NMR (400 MHz, D$_2$O)

Potassium 3,3'-(pentacene-6,13-diylbis(sulfanediyl))dipropionate (28)
$^{1} \text{H NMR (500 MHz, Methanol-} d_{4}$)
Potassium 3,3'-(pentacene-6,13-diylbis(sulfanediyl))dipropionate (28)

$^{13}$C NMR (125 MHz, D$_2$O with K$_2$CO$_3$)
Potassium 3,3'-(pentacene-6,13-diylbis(sulfanediyl))dipropionate (28)

$^{13}$C NMR (125 MHz, D$_2$O)
Potassium 3,3'-((pentacene-6,13-diylbis(sulfanediyl))dipropionate (28))

$^{13}$C NMR (125 MHz, Methanol-d$_4$)

CD$_3$OD
Potassium 3,3’-(pentacene-6,13-diylbis(sulfanediyl))dipropionate (28)
Potassium 3,3'-((pentacene-6,13-diylbis(sulfanediyl))dipropionate (28)
TGA in N₂

Potassium 3,3’-(pentacene-6,13-diylbis(sulfanediyldiyl))dipropionate (28)

[Graph showing TGA curve with temperature and weight percentage data points, and chemical structure of the compound.]
Potassium 3,3'-[(pentacene-6,13-diylbis(sulfanediyl))]dipropanoate (28)

TGA in Air

Weight (%)

Temperature (°C)

Universal V.4.5A Instruments

Deriv. Weight (%/°C)

124.46°C 94.65%
257.18°C 90.18%
318.43°C 75.98%
367.21°C 22.04%
373.2°C 33.22%
375.03°C 3.76%
UV-vis Spectra (in Buffer pH=10)

Potassium 3,3'-((pentacene-6,13-diylbis(sulfanediyl))dipropionate) (28)

$\lambda_{\text{max}} = 538, 575, 621 \text{ nm}$

$E_{\text{opt.gap}} = 1.91 \text{ eV}$

$\text{Formula: }$ 

![Chemical Structure](image)
UV-vis Spectra (in H$_2$O)

Potassium 3,3'-(pentacene-6,13-diylbis(sulfanediyl))dipropionate (28)

$\lambda_{\text{max}} = 532, 573, 619$ nm

$E_{\text{opt. gap}} = 1.92$ eV
Potassium 3,3'-((pentacene-6,13-diylbis(sulfanediyl)))dipropionate (28)

$\lambda_{\text{max}} = 526, 565, 611 \text{ nm}$

$\epsilon_{\text{opt}} \text{gap} = 1.97 \text{ eV}$
Potassium 3,3’-(pentacene-6,13-diylbis(sulfanediyl))dipropionate (28)

UV-vis time decay profile (in Buffer pH = 10)

In buffer (K$_2$CO$_3$-K$_3$BO$_3$-KOH, pH = 10): Cap-Off $t_{1/2} = 5786$ min
$^{1}H$ NMR (500 MHz, CDCl$_3$)

13H-spiro[[1,3]oxathiane-2,6'-pentacene]-6,13'-dione (29)
Melting point apparatus calibration

![Melting point calibration graph]

\[
\text{M.P.(measured)} = 1.0562 \times \text{M.P.(theory)} - 13.216 \\
R^2 = 0.99727
\]

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Syn-6,13-dihydro-6,13-diacetylthiopentacene (30)

$^1$H NMR (400 MHz, CDCl$_3$)
Syn-G, 13-dihydro-G, 13-diacetylthiopentacene (30)

$^{13}$C NMR (100 MHz, CDCl$_3$)
Anti-6,13-dihydro-6,13-diacetyltiophentacene (31)

$^{1}H$ NMR (500 MHz, CDCl$_3$)
Anti-6,13-dihydro-6,13-diacetylthiopentacene (31)

$^{13}$C NMR (125 MHz, CDCl$_3$)
6,13-Diacetylthiopentalene (32)

$^{1}$H NMR (500 MHz, CDCl$_3$)
VT $^{13}$C NMR (125 MHz, CDCl$_3$) at 40 °C

6,13-Diacetyltiophosphorocene (32)
$^{1}$H NMR (500 MHz, o-DCB-d$_4$)

6,13-Diaetylthiophenotacene (32)
VT $^{13}$C NMR (125 MHz, o-DCB-$d_4$) at 80 ºC
6,13-Diacetylthiopentacene (32)

MALDI MS

Molecular Weight: 426.55
6,13-Diacetyltiophenanthrene (32)
6,13-Diacetyltiophenanthrene (32)

UV-vis spectra (in CHCl₃)

$\lambda_{\text{max}} = 533 \text{ nm}, 573 \text{ nm}, 621 \text{ nm}$

$E_{\text{opt}}$ gap $= 1.93 \text{ eV}$
UV-vis time decay profile

6,13-Diacetyltiothiopentacene (32)
Solid state UV-vis Spectra

6,13-Diacetyliothiopentacene (32)

$\lambda_{\text{max}} = 584\text{ nm}, 655\text{ nm}, 719\text{ nm}$

$E_{\text{opt gap}} = 1.48$ eV
6,13-Diacetylthiopentacene (32)
6,13-Dithio-6,13-dihydropentacene (34)

$^1$H NMR (400 MHz, CDCl$_3$)
6,13-Dithio-6,13-dihydronaphthacene (34)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

4,5-Dibromo-o-xylene (36)

\[ \text{CHCl}_3 \]

\[ \text{H}_2\text{O} \]
$^{13}$C NMR (125 MHz, CDCl$_3$)

4,5-Dibromo-o-xylene (36)
1,2-Di(4-t-butyphenyl)-5,6-dimethylbenzene (37)

$^1$H NMR (500 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{1}$H NMR (500 MHz, CDCl$_3$)

1,2-Di(4'-t-butyphenyl)-5,6-di(bromomethyl)benzene (38)
1,2-Di(4-t-butyphenyl)-5,6-di(bromomethyl)benzene (38)

$^{13}$C NMR (125 MHz, CDCl$_3$)

CDCl$_3$
$^{1}$H NMR (500 MHz, CDCl$_3$)

2,3,9,10-Tetrakis(t-butyl)phenylpentacenequinone (39)
$^{1}H$ NMR (500 MHz, CDCl$_3$)
2,3,9,10-Tetrakis((t-buty)phenyl)-6,13-dihydro-6,13-diacetylthiopentacene (41)

H NMR (500 MHz, CDCl₃)
$^{13}$C NMR (125 MHz, CDCl$_3$)

2,3,9,10-Tetrakis((t-butyl)phenyl)-6,13-dihydro-6,13-diacetylthiopentacene (41)
$^{1}$H NMR (500 MHz, CDCl$_3$)

2,3,9,10-Tetrakis((t-butyl)phenyl)-6,13-diacylthiopentacene (42)
$^{13}$C NMR (125 MHz, CDCl$_3$)

2,3,9,10-Tetrakis((t-butyl)phenyl)-6,13-diacetyltiothiopentacene (42)

13C NMR (125 MHz, CDCl$_3$)
UV-vis spectra (in CHCl₃)

λ_{max} = 555 nm, 595 nm, 644 nm

E_{opt, gap} = 1.86 eV

2,3,9,10-Tetrakis((t-buty)phenyl)-6,13-diacetylthiopentacene (42)
$^1$H NMR (400 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

5,7,12,14-tetraphenylpentacene (73)
$^1$H NMR (400 MHz, CDCl$_3$)

Mono-Tetraphenylpentacene-C$_{60}$ adduct (74)
$^1$H NMR (500 MHz, C$_6$D$_6$)
C NMR (125 MHz, C$_6$D$_6$)  
Tetrakis-Terphenylpentacene-C$_{60}$ adduct (83)
Crude 6,13-dihydro-6,13-dieethylthiopentacene

$^{1}H$ NMR (500 MHz, CDCl$_3$)

H NMR (500 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

Syn-6,13-dihydro-6,13-diethylthiopentacene (84)
$^{13}$C NMR (125 MHz, CDCl$_3$)

$\text{SYN-G, 13-dihydropenta-6,13-dieithylthiopentacene (84)}$
$^1$H NMR (500 MHz, CDCl$_3$)

Anti-6,13-dihydro-6,13-diethylthiopentacene (85)
Anti-6,13-dihydro-6',13'-diethylthiopentacene (85)
Conversion of 84 to 85 in NMR tube

1H NMR (500 MHz, CDCl3)
Aromatization of Syn-6,13-dihydro-6,13-diethylthiopentacene (84)
Aromatization of Anti-6,13-dihydro-6,13-diethylthiophenacene (85)

$^1\text{H NMR (500 MHz, CDCl}_3$)
Cycloadduct of 6,13-diethylthiopentacene formed during aromatization (99)

\[ \text{H NMR (500 MHz, CDCl}_3\text{)} \]
$^{1}$H NMR (500 MHz, CDCl$_3$)

6,13-diethylthiopentacene (95)
6,13-diethylthiopentacene (95)

$^{13}$C NMR (125 MHz, CDCl$_3$)
Molecular Weight: 398.58

MALDI 6,13-diethylthiopentacene (95)
UV-vis in CHCl₃

6,13-diethylthiopentacene (95)

λ_{onset} = 635 nm

λ_{max} = 529 nm, 569 nm, 617 nm

λ_{max} = 529 nm, 569 nm, 617 nm
Solid State UV-vis

Normalized Absorption (a.u.)

Wavelength (nm)

6,13-diethylthiopentacene (95)

$\lambda_{\text{max}} \approx 558 \text{ nm}, 630 \text{ nm}, 686 \text{ nm}$

$\lambda_{\text{onset}} = 773 \text{ nm}$
Crude 6,13-dihydro-6,13-diethylthiopentacene

$^1$H NMR (500 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

Syn-6,13-dihydro-6,13-dioctylthiopentacene (86)
Syn-6,13-dihydro-6,13-dioctylthiopentacene (86)

$^{13}$C NMR (125 MHz, CDCl$_3$)
Anti-6,13-dihydro-6,13-dioctylthiopentacene (87)

$^1$H NMR (500 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)

Anti-6,13-dihydro-6,13-dioctylthiopentacene (87)
$^{1}H$ NMR (500 MHz, CDCl$_3$)

Aromatization of Syn-6,13-dihydro-6,13-dioctylthiopentacene (86)
Aromatization of Anti-6,13-dihydro-6,13-dioctylthiopentacene

$^1$H NMR (500 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

6,13-dioctylthiopentacene (96)

$\text{CHCl}_3$
$^{13}$C NMR (125 MHz, CDCl$_3$)

6,13-dioctylthiopentacene (96)
6,13-dioctylthiopentacene (96)

UV-vis in CHCl₃

λ<sub>max</sub> = 530 nm, 570 nm, 617 nm

λ<sub>onset</sub> = 639 nm
Solid State UV-vis

Absorption (a.u.)

Wavelength (nm)

6,13-dioctyldithiapentacene (96)

$\lambda_{\text{max}} \approx 556 \text{ nm}, 614 \text{ nm}, 670 \text{ nm}$

$\lambda_{\text{onset}} = 752 \text{ nm}$
Crude 6,13-dihydro-6,13-diphenylthiopentacene

$^1$H NMR (500 MHz, CDCl$_3$)
Syn-6,13-dihydro-6,13-diphenylthiopentacene (88)
$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{1}H$ NMR (500 MHz, CDCl$_3$)

Anti-6,13-dihydro-6,13-diphenylthiopentacene (89)
$^{13}$C NMR (125 MHz, CDCl$_3$)

Anti-6,13-dihydro-6,13-diphenylthiopentacene (89)
\(^{1}\text{H NMR (500 MHz, CDCl}_3\text{)}\)

Aromatization of Syn-6,13-dihydro-6,13-diphenylthiopentacene (88)
Aromatization of Anti-6,13-dihydro-6,13-diphenylthiopentacene (89)
$\text{H NMR (500 MHz, CDCl}_3\text{)}$

6,13-diphenylthiopentacene (13)
6,13-diphenylthiopentacene (13)

UV-vis in CHCl$_3$

Wavelength (nm)

Absorption (a.u.)

$\lambda_{\text{max}} = 536\text{ nm, } 577\text{ nm, } 626\text{ nm}$

$\lambda_{\text{onset}} = 644\text{ nm}$
Solid State UV-vis

Absorption (a.u.)

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Absorption % (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>0.1%</td>
</tr>
<tr>
<td>600</td>
<td>0.3%</td>
</tr>
<tr>
<td>700</td>
<td>0.5%</td>
</tr>
<tr>
<td>800</td>
<td>0.7%</td>
</tr>
<tr>
<td>900</td>
<td>0.9%</td>
</tr>
<tr>
<td>1000</td>
<td>1.1%</td>
</tr>
<tr>
<td>1100</td>
<td>1.3%</td>
</tr>
<tr>
<td>1200</td>
<td>1.5%</td>
</tr>
<tr>
<td>1300</td>
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<tr>
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<td>3.0%</td>
</tr>
<tr>
<td>1500</td>
<td>4.0%</td>
</tr>
</tbody>
</table>

6,13-diphenylthiophenacene (13)

λ<sub>max</sub> = 562 nm, 612 nm, 661 nm
λ<sub>onset</sub> = 781 nm
Crude 6,13-dihydro-6,13-dinaphthylthiopentacene

$^1$H NMR (500 MHz, CDCl$_3$)
Syn-6,13-dihydro-6,13-dinaphthylthiopentacene (09)

$^1$H NMR (500 MHz, CDCl$_3$)

H NMR (500 MHz, CDCl$_3$)
Syn-6,13-dihydro-6,13-dinaphthylthiophentacene (90)

$^{13}$C NMR (125 MHz, CDCl$_3$)

CDCl$_3$
Anti-6,13-dihydro-6,13-dinaphthylthiophenacene (91)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{1}H$ NMR (500 MHz, CDCl$_3$)
Anti-6,13-dihydro-6,13-dinaphthylthiopentacene (91)

$^{13}$C NMR (125 MHz, CDCl$_3$)
Aromatization of Syn-6,13-dihydro-6,13-dinaphthylthiophentacene (90)

$^1$H NMR (400 MHz, CDCl$_3$)
Aromatization of Syn-6,13-dihydro-6,13-dinaphthylthiopentacene (90)

$^1$H NMR (400 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

6,13-dinaphthylthiopentacene (97)
$^{13}$C NMR (125 MHz, CDCl$_3$, CS$_2$)

6,13-dinaphthylthiophenotraceone (97)
Exact Mass: 594.15

6,13-dinaphthylthiolotriphenylene (97)
6,13-dinaphthylthiophenotriene (97)

UV-vis in CHCl₃

λ_{max} = 538 nm, 579 nm, 628 nm

ν_{onset} = 647 nm

Smax = 300% 350% 400% 450% 500% 550% 600% 650% 700% 750% 800%

Anot = 0.5% 0.7% 0.9% 1.1% 1.3% 1.5%
Solid State UV-vis

Absorption (% (a.u.))

Wavelength (nm)

6,13-dinaphthylthiopentacene (97)

$\lambda_{\text{max}} \approx 560 \text{ nm}, 609 \text{ nm}, 660 \text{ nm}$

$\lambda_{\text{onset}} = 740 \text{ nm}$

$\lambda_{\text{onset}} = 740 \text{ nm}$
Crude 6',13'-dihydro-6',13'-dibutylaminophenanthrene

$^1$H NMR (500 MHz, CDCl$_3$)
SYN-6,13-dihydro-6,13-dibutylthiophenanthrene (92)

$^1$H NMR (500 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)

Syn-6,13-dihydro-6,13-dibutanolthiophenacene (92)
$^{1}$H NMR (500 MHz, CDCl$_3$)

Anti-6,13-dihydro-6,13-dibutanolithiopentacene (93)
Anti-6,13-dihydro-6,13-dibutanolithiopentacene (93)

$^{13}$C NMR (125 MHz, CDCl$_3$)
Aromatization of Syn-6,13-dihydro-6,13-dibutanolthiophenacene (92)

\[ ^1 \text{H NMR (500 MHz, CDCl}_3) \]

Chemical shifts and peaks are indicated on the diagram.
Aromatization of Anti-6,13-dihydro-6,13-dibutanolithothiophenacene (93)

$^{1}H$ NMR (500 MHz, CDCl$_{3}$)

- Benzene
- CHCl$_{3}$
- DCM
$^{13}\text{C} \text{NMR (125 MHz, CDCl}_3)$

6,13-dibutanolthiophenacene (98)
MALDI

6,13-dibutylthiophenopentacene

Molecular Weight: 486.69
UV-vis in CHCl₃

6,13-dibutanolthiophenacene (98)

λ<sub>max</sub> = 530 nm, 571 nm, 618 nm

λ<sub>onset</sub> = 638 nm
Solid State UV-vis

Absorption (a.u.)

Wavelength (nm)

Absorption % (a.u.)

200% 300% 400% 500% 600% 700% 800% 900% 1000%

6,13-di-butanolotiothiopentacene (98)

\[ \lambda_{\text{max}} = 548 \text{ nm}, 591 \text{ nm}, 636 \text{ nm} \]
Crude 6,13-dihydro-6,13-dithioacetylpentacene
Aromatization of Syn-6,13-dihydro-6,13-dithioacetylpentacene (30)

$^1$H NMR (500 MHz, CDCl$_3$)
Aromatization of Anti-6,13-dihydro-6,13-dithioacetylpentacene (31)
Epimerization of syn-6,13-dihydro-6,13-diethylthiopentene (84)

Entry 1: Rxn time = 3 h

Benzenel

Epimerization of syn-6,13-dihydro-6,13-diethylthiophenolene (84)
Epimerization of syn-6,13-dihydro-6,13-diethylthiopentene (84)

Entry 2: Rxn time = 6 h

H NMR (500 MHz, CDCl$_3$)
Epimerization of syn-6,13-dihydro-6,13-diethylthiopentencene (84)

Entry 3: Rxn time = 6 h with 10 eq. K₂CO₃

1H NMR (500 MHz, CDCl₃)
H NMR (500 MHz, C$_6$D$_6$)

Aromatization of syn-6,13-dihydro-6,13-diethylthiopentencene (84)

$t = 10$ min
Aromatization of syn-6,13-dihydro-6,13-diethylthiopentene (84)

$t = 20$ min
Aromatization of syn-6,13-dihydro-6,13-dieethylthiopentene (84)

$^1$H NMR (500 MHz, C$_6$D$_6$)

$t = 30$ min
Aromatization of syn-6,13-dihydro-6,13-diethylthiopentene (84)

$t = 45\,\text{min}$
Aromatization of syn-6,13-dihydro-6,13-diethylthiopentencene (84)

$t = 60$ min

$^1$H NMR (500 MHz, C$_6$D$_6$)
Aromatization of syn-6,13-dihydro-6,13-diethylthiopentencene (84)

$t = 80 \text{ min}$
Aromatization of syn-6,13-dihydro-6,13-diethylthiopentencene (84)

1H NMR (500 MHz, C₆D₆)

$t = 100$ min
Aromatization of syn-6,13-dihydro-6,13-diethylthiopentene (84)

$t = 120$ min

$^1$H NMR (500 MHz, C$_6$D$_6$)
Aromatization of syn-6,13-dihydro-6,13-diethylthiopentene (84)

$t = 150$ min

$^1$H NMR (500 MHz, C$_6$D$_6$)
Aromatization of syn-6,13-dihydro-6,13-diethylthiopentencene (84)

$t = 180\text{ min}$
Epimerization of syn-6,13-dihydro-6,13-diphenylthiopentene (88)

Entry 1: Rxn time = 4 h

DCM
Aromatization of syn-6,13-dihydro-6,13-diphenylthiopentencene (88)

$t = 10\text{ min}$
Aromatization of syn-6,13-dihyrdro-6,13-diphenylthiopentencene (88)
Aromatization of syn-6,13-dihydro-6,13-diphenylindenothiopentencene (88)

\[ t = 30 \text{ min} \]
Aromatization of syn-6,13-dihydro-6,13-diphenylthiophenpentene (88)

$^1$H NMR (500 MHz, CDCl$_3$)

$t = 60$ min
$^1$H NMR (500 MHz, CDCl$_3$)

Aromatization of syn-6,13-dihydro-6,13-diphenylthiopentencene (88)

$t = 120$ min
Aromatization of syn-6,13-dihydropenta-1,3-diydroxy-6,13-diphenylthiophenacene (88)

$^{1}H$ NMR (500 MHz, CDCl$_3$)

$t = 180$ min
Aromatization of syn-6,13-dihydro-6,13-diphenylthiopentencene (88)

$^1$H NMR (500 MHz, CDCl$_3$)

t = 240 min