STABLE HETERO-ACENE ANALOGS OF HEPTACENE: THE SYNTHESIS AND STUDY OF THEIR CONDUCTIVE PROPERTIES IN ORGANIC TRANSISTORS

AND

THE PHOTO-INDUCED FORMATION OF QUANTUM DOT – CONDUCTIVE POLYMERS (QD:CP) FOR APPLICATION IN PHOTOVOLTAICS

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ABSTRACT

PART I: STABLE HETERO-ACENE ANALOGS OF HEPTACENE: THE SYNTHESIS AND STUDY OF THEIR CONDUCTIVE PROPERTIES IN ORGANIC TRANSISTORS.

The surge of organic electronics in the last two decades has augmented the necessity for the development of high performance devices with superior and less expensive processability. Polycyclic Aromatic Hydrocarbons (PAHs) have been widely investigated for this purpose. With advancement in this field, PAH-based organic semiconductors, in some instances, have superseded Si in performance. They exhibit hole mobilities as high as \(5.5 \text{ cm}^2\text{V}^{-1}\text{S}^{-1}\). Pentacene, for example, has become a benchmark for organic molecular semiconductors. Use of such materials for fabrication of electronic devices, however, is limited due to their extreme lack of stability under ambient conditions. Therefore, efforts have been made to develop materials that exhibit comparable mobilities, and also are air-stable. Heterocyclic aromatic hydrocarbons were first developed as viable materials in this. However, though they are quite stable under ambient conditions, their low hole mobilities as compared to their PAH counterparts are an issue. Recently, heterocyclic aromatic hydrocarbons with high air-stable mobilities have been reported. Dinaptho[2,3-b:2’,3’-f]thieno[3,2-b]-thiophene (DNTT), for example, showed mobilities as high as \(3.1 \text{ cm}^2\text{V}^{-1}\text{S}^{-1}\). It is believed that materials with additional fused rings fused in such systems will allow higher stacking and better molecular packing, leading to higher mobilities. Hence, we propose the synthesis of dianthra[2,3-b:2’,3’-b]thiophene (DAT) for applications in organic electronics. Preliminary theoretical calculations on DAT suggest that such a material will have hole mobilities as high as \(\sim 3 \text{ cm}^2\text{V}^{-1}\text{S}^{-1}\). DAT, therefore, will be promising for applications in organic electronics, namely OFETs, OLEDs, etc. We have synthesized this material,
developed collaboration with a research group at Stanford to make devices with it, and detailed studies on its device performances are underway.

![DNTT](image1.png)  ![DAT](image2.png)

References:

PART II: THE PHOTO-INDUCED FORMATION OF QUANTUM DOT – CONDUCTIVE POLYMERS (QD:CP) FOR APPLICATION IN PHOTOVOLTAICS.

The world’s increasing population and energy consumption has led to a serious issue in dealing with energy supply\textsuperscript{1,2}. A recent study\textsuperscript{3} suggests that, with current world-wide socio-economic growth, the global energy demand increases at a rate of 2\% a year, and an additional 10 terawatts (TW) of energy is needed to sustain the world’s population by 2050. While the present supply of energy is not going to be exhausted in the near future, a shortfall in the supply of energy is impending considering the rapid growth in demand\textsuperscript{4}.

Solar energy stands out as the most viable alternative energy resource available because the amount of sunlight that reaches the surface of the Earth each hour is approximately as much as today's society uses in an entire year. However, the greatest challenge lies in harnessing the sunlight and its conversion to energy\textsuperscript{3}. In order to harness this power, we need to find materials that are both more efficient at converting light into energy and cheap to produce. The solar cells prevalent today are typically made of inorganic semiconductors, mostly silicon. Silicon solar cells are expensive—in both energy and cost—to produce. Therefore, one of the approaches taken toward meeting the clean energy demand combines inorganic semiconductors such as quantum dots (QD) with polymer materials. The inorganic semiconductor in such composites provides high efficiency, and the presence of the polymer ensures both higher conductivity as well as cheap fabrication cost\textsuperscript{5,6}. However, physical blending of the components does not produce the polymer-QD composites because QD aggregation poses a major problem for its preparation\textsuperscript{7}. Hence, achieving a homogeneous dispersion of QD in the polymer matrix is necessary\textsuperscript{8}. There are two popular methods for achieving this: ‘grafting on’ and ‘grafting from’ methods. In the ‘grafting from’ method the polymer chain grows from a QD surface and therefore allows better electronic interaction between QD and the polymer\textsuperscript{9,10}. Such methods
usually involve complex reaction and strategies. Here we discuss the preparation of QD – polymer composites through the photo-induced polymerization process, where no photo-initiator was used. This is the first report of preparing such composites using the photo-induced polymerization method. We used 5-mercapto-2, 2’-bithiophene (BTSH) for surface modification of QD. We observe an efficient hole transfer caused by visible light irradiation from a CdSe quantum dot (QD) core to ligand in BTSH functionalized QD (BTSCdSe); while such hole transfer is ten times slower in 5-(5-mercaptopenyl)-2, 2’-bithiophene functionalized QD (BTC5SCdSe). The interspersing methylene groups inhibit hole transfers in the case of BTC5SCdSe. The radical cation+BTSCdSe+, formed via hole transfer in BTSCdSe, acts as a building block for photoinitiated polymerization, with no conventional photo-initiator required. The three dimensional composite structure of BTSCdSe and its visible light initiated polymerization is confirmed from the SEM and TEM images. Hole transfer mechanisms are studied using femtosecond and nanosecond transient absorption measurements. Such a polymer-QD composite is expected to be useful in the fabrication of photovolatics such as polymer-inorganic hybrid solar cells.

Reference:


Part I

STABLE HETERO-ACENE ANALOGS OF HEPTACENE: THE SYNTHESIS AND STUDY OF THEIR CONDUCTIVE PROPERTIES IN ORGANIC TRANSISTORS
Chapter 1
Introduction

1.1 Background
Organic Semiconductors are organic materials with semiconductor properties, the discovery of which dates to 1862 when H. Letheby of the College of London Hospital first obtained a partly conductive material, probably polyaniline, by anodic oxidation of aniline in sulfuric acid. However, the use of organic materials as active conductive layers was not known until the twentieth century. In the 1950s researchers discovered that polycyclic aromatic hydrocarbons exhibit semiconductor properties when doped with halogen vapor. In 1977 Shirakawa, MacDiarmid, and Heeger first established the concept of the electrical conductivity in organic materials. This was particularly important as it created a new field of research at the boundary between chemistry, and condensed matter physics, and consequently fostered the emergence of organic electronics. Inspired by this discovery several organic semiconducting materials were designed and synthesized for the application in organic electronics including single molecules, short-chain oligomers, and conductive polymers as organic semiconductors.

![Classification of organic semiconducting materials based on their structural features.](image)

Figure 1.1. Classification of organic semiconducting materials based on their structural features.
1.2. Organic Semiconductors Vs Inorganic Semiconductors

Organic semiconducting materials cannot compete with conventional inorganic semiconductors in terms of their conductivity. Though application of crystalline silicon are limited because silicon is very expensive to produce, crystalline silicon shows conductivity as high as $12 \text{ Cm}^2\text{V}^{-1}\text{S}^{-1}$. Thus hydrogenated amorphous silicon quickly replaced crystalline silicon in the fabrication of semiconductor devices. Hydrogenated amorphous silicon, relatively cheaper to process, exhibits a mobility of $1 \text{ Cm}^2\text{V}^{-1}\text{S}^{-1}$. Therefore, amorphous silicon and several of its derivatives were popularly used in semiconducting devices before the emergence of organic electronics. Inevitably, on the advent of the organic semiconductors a mobility of $1 \text{ Cm}^2\text{V}^{-1}\text{S}^{-1}$ became the benchmark for organic semiconductors. Mutually conductive polymers/oligomers and small molecule polycyclic aromatic hydrocarbons (PAHs) were envisioned to reach this mark, and both types of organic semiconductors have drawn significant attention due to their effectiveness in the field of electronics. Importantly, both of these classes of organic materials eventually surpassed the mobility of amorphous silicon.

1.3. Organic Semiconductors: Advantages

Over the past two decades, thousands of organic semiconducting materials has been designed, synthesized, and used in fabrication of electronic devices. As mentioned earlier, polymers, oligomers, and small molecules were envisaged in this endeavor. Both conductive polymers and small molecule semiconductors offer their own advantages in realizing high performance devices.
As organic semiconductors surpassed the existing amorphous silicon based semiconductors conductivity, it was not surprising that organic semiconductors attracted significant attention in high performance electronic devices. Organic semiconductors are foreseen to be the replacement for the amorphous silicon because of several other advantages. In addition to competitive conductivity, the advantages of organic semiconductors include cheaper cost of production and simple solution based processing. Solution based processing allows for unconventional deposition techniques, such as inkjet, screen, and micro-contact printing alongside the conventional vapor deposition techniques. Organic materials utilize low temperature vapor deposition techniques for processing while inorganic materials can only be processed at high temperatures. This application advantage predictably heralded the use of organic materials in semiconducting devices. Because organic materials are mechanically flexible this offers compatibility with plastic substrates, allowing, also, flexible integrated circuits, electronic-displays, and roll-up materials for modern technologies. In addition, organic semiconductors offer significant mechanical strength, adhesion, thermo-plasticity, and favorable intrinsic rheological properties allowing tolerance for film-processing conditions. This allows for easier fabrication of thin film electronic devices (Fig 1.2).

Figure 1.2. Examples of applications: flexible integrated circuits, roll-up electron display, etc.
Given the advantages over their inorganic counterparts, several organic semiconducting materials were designed. Initially conductive polymers\(^\text{43-46}\) alone were envisioned as the organic semiconducting material. This was inspired by the work of MacDirmid, Shirakawa, and Heeger’s. (Fig 1.3). However, it was soon observed that anthracene, when doped with iodine, also exhibits conductivity.\(^\text{47}\) This triggered an entirely new field of research – investigation of small molecular polycyclic aromatic hydrocarbons (PAHs) for application in organic electronics.

![Figure 1.3. Examples of some conductive polymers: (1) poly-thiophenes\(^\text{41}\), (2) polyindolocarbazole\(^\text{44}\), (3) polyfluorenes\(^\text{45}\), and (4) poly-arylamines\(^\text{46}\).](image)

### 1.4. Polymer / Oligomer and Poly-cyclic Aromatic Hydrocarbons

Although conductive polymers and PAHs both have their own advantages, there are two key aspects of PAH application that set them apart. First, their scale-up is more manageable because it's easier to maintain the high purity and reproducible quality of the product.\(^\text{48}\) Second, the controllable and rigorously defined structure allows for structure – property correlations.\(^\text{49}\) Therefore, the opportunities for simpler structural tailoring of such materials lead to broader families of species with different superiorities.\(^\text{32-36}\) In addition, PAHs have lower molecular weights and high solubility- allowing vacuum sublimation and solution processing at low cost. Furthermore, inherent poly-dispersity and only limited purification techniques are available for the production of polymers on an industrial scale causing limitations to the use of polymer materials.\(^\text{50}\)
Several PAHs, acenes and hetero-acenes, have been designed and synthesized for use as organic semiconductors over the years (Fig 1.4). These materials were used in the fabrication of organic field effect transistors (OFETs) and organic thin film transistors (OTFTs) to estimate their effectiveness in the electronic industries.

![Figure 1.4](image-url)

**Figure 1.4.** Evolution of OFET performances with time for various p-channel and n-channel semiconducting materials based on single organic molecules, oligomers, and polymers; V: vapor deposition, S: solution deposition, SC: single crystal.

### 1.5. Polycyclic Aromatic Hydrocarbons: Acenes

There are several types of polycyclic aromatic hydrocarbons (PAHs) based on their structural features. Acenes or poly acenes are PAHs made up of linearly fused benzene rings (Fig 1.5).
Acenes, particularly pentacene, one of the earliest small molecule organics to be used as a semiconductor, has drawn recent attention and its performance is continually improving. This is due to more researchers currently focusing on the engineering involved in the device fabrication of acenes in organic transistors (Fig 1.6).\textsuperscript{51-55}

Figure 1.5. Structure of acenes- from benzene to nonacene, with increasing oligomeric length.

Figure 1.6. High mobilities in OFETs based on acenes/heteroacenes; all measurements were done for OFETs fabricated by vacuum deposition of the materials.
1.6. Acenes: Incentives

As can be seen in Figure 1.6, pentacene shows mobility as high as 3 Cm²V⁻¹S⁻¹. Therefore, it is no surprise that the acenes have received extensive attention as potential organic semiconductors. One of the more fascinating aspects of the properties of the acenes is the rapid evolution of electronic properties as the oligomer length is increased. For example, acenes have low lying HOMO energy levels and the HOMO-LUMO energy gap decreases with increasing oligomeric length. Oligomeric acenes have smaller HOMO-LUMO gaps than any other hydrocarbons having identical numbers of aromatic rings. Most importantly, the two-dimensional electronic interactions in the solid state of acenes increases with an increase in the of the oligomer, so the charge carrier mobility increases with an increasing number of fused aromatic rings in the acene. A series of other electronic properties also scale with the size of the acene, such as decreasing reorganization energy, exciton binding energy and increasing band width. All of these electronic properties suggest use of larger acenes in various opto-electronic applications, including as photovoltaics.

1.7. Origin of conductivity in Acenes

Conductivity in organic semiconductors results from the delocalization of π-electron density through a conjugated chain of organic molecules. Given that the sigma electrons remain localized, the π-electrons behave as a particle in a one dimensional box. Conduction of charge involves charge hopping between the localized state and carriers. The hopping mechanism is assisted by phonon, which leads to the formation of the solitons. The soliton’s effective length in the π-conjugated oligo-ene system is about 14 carbon atoms according to the Su-Schrieffer-Heeger model. Therefore, it is theoretically feasible for a heptacene (15 π – conjugated carbon
atoms) to produce two parallel oligo-ene solitons. Due to charge transport through the hopping mechanism, the mobility of acenes increases with temperature, although typically it remains low overall.\textsuperscript{61,62}

Oligoacene based semiconductors typically produce polycrystalline or disordered films. The individual molecules inside the film weakly interact through van der Waals, hydrogen bonding, and \(\pi-\pi\) interactions. Therefore, while the charge delocalization along the conjugated backbone of a single molecule is possible, transport between the adjacent molecules is inhibited. Therefore, charge transport in such materials is thought to rely on the intermolecular order adopted by the individual molecules in the solid state and charge hopping from these localized states, which can be thought of as an electron transfer between a charged oligomer and an adjacent neutral oligomer. Good electronic performance requires strong electronic coupling between adjacent molecules in the solid state. There are two common packing motifs adopted by acenes – herringbone and \(\pi\)-stacking - to allow intra-molecular electronic coupling. In the classic “herringbone” packing, the aromatic edge-to-face interaction dominates, yielding two-dimensional electronic interactions in the solid state.\textsuperscript{21} Alternatively, the molecules can also adopt a coplanar arrangement and stack through their \(\pi\)-electron cloud, typically with some degree of displacement along the long and short axes of the molecules (Fig. 1.7). The strong interaction between the \(\pi\)-electron-rich faces (\(\pi\)-faces) of the molecules in these \(\pi\)-stacked arrays yields strong electronic coupling, and further interactions with adjacent stacks can yield strong two dimensional electronic coupling. It is recognized that long-range molecular ordering in the solid state is highly important in order to obtain high charge carrier mobilities in organic semiconductors.\textsuperscript{63}
1.8. Challenges with Acenes

Unfortunately, with increasing acene length the stability of acenes tends to decrease significantly. Consequently, while small acenes, such as naphthalene and anthracene are readily available being isolated from petroleum resources, larger acenes – tetracene, pentacene, hexacene, etc are much less stable and must be synthesized. Because they are more available and cheaper, naphthalene and anthracene, have been tested in large scale devices, and their charge carrier mobility has been measured. Karl and co-workers demonstrated their significant electronic properties, as well as the exceptional level of purity needed to utilize these properties. The detrimental effect of a small amount of impurities has also been studied.

In contrast larger acenes are not isolated from petroleum derivatives, and the synthesis of the largest known acenes becomes increasingly more challenging because of the decreased stability and solubility as the size of the acenes increases. The unstable nature of larger acenes can be explained by Clar’s empirical method, known as the Sextet rule. According to Clar’s method, acenes whether benzene, anthracene, pentacene, or higher analogs, have only one π-electron sextet (Fig 1.8). Therefore, higher acenes share the lone sextet over a large number of rings, and larger assemblies consequently become increasingly unstable.
In terms of molecular orbital theory the same observation is explained through the sequential loss of benzenoid character.\textsuperscript{69}

According to valence band theory, acenes can be represented by several valence bond structures, including undistorted, \textit{cis}-distorted, and \textit{trans}-distorted structures.\textsuperscript{70} Valence band theory suggests that all of the three structures are degenerate (same energy).\textsuperscript{71} However, when long range Coulomb’s interactions are considered, the \textit{cis}-distorted form is expected to be more stable than the \textit{trans}-form. The non-interacting model, on the other hand, indicates that the \textit{trans}-distorted form will be most stable, while the MP2/6-311 G** (a non-interacting Gaussian model) suggests that the undistorted form is preferred (Fig 1.9).\textsuperscript{71} Houk et al.\textsuperscript{70} suggested that acenes consist of two fully conjugated non-alternating ribbons joined by relatively longer bonds. The energy levels for particular acenes are discrete, and the HOMO-LUMO gap (\(\Delta E\)) decreases for higher acenes. The energy gap, \(\Delta E\), near the Fermi level for a chain of \(N\) monomeric acenes are given by:

\[\Delta E \sim \frac{W}{N^2}\]

where, \(W \approx 10\) eV, the \(\pi\)-band width.\textsuperscript{72} From this equation it is also evident that with an increasing number of rings the band gap narrows. An increasing number of rings in the acene backbone does not only reduce the band gap, it also reduces the ionization energy. Low ionization energies are responsible for exceptionally low stability in the acenes given that easy
ionization makes the compounds highly prone to oxidation and other reactions even under ambient conditions.

Figure 1.9. Valence band theory proposed structures of acenes, and (bottom) B3LYP simulated model showing conjugated no-alternating ribbons joined through long chain.

1.9. Probable Solutions

It is important to develop new organic semiconducting materials that achieve both high charge carrier mobility and are highly stable under ambient conditions. Thug efforts have been made to synthesize the larger acenes.\textsuperscript{73-74} The introduction of a heteroatom (e.g. sulfur, nitrogen, and oxygen) into a fused ring system (namely heteroacene) has been one of the primary approaches attempted to improve stability. The introduction of heteroatoms leads to low lying HOMOs in heteroacenes, and also induces a larger band gap giving oxidative stability to the heteroacenes compared to regular acenes.
1.10. Heteroacenes

Several heteroacenes have been synthesized over the last decade (Fig 1.10). Most exhibit field effect mobilities in the order of 0.1-2 cm²V⁻¹s⁻¹. The heteroacenes can contain different heteronuclear aromatic rings, such as thiophene, pyrrole, etc.⁷⁵-⁸⁰

![Heteroacenes](image.png)

**Figure 1.10.** Examples of some heteroacenes.

Among all the heteroacenes, thiophene containing heteroacenes have attracted tremendous attention. Such heteroacenes are believed to combine the stability of thiophene ring with the planarity of the linear acene, In addition to this, these thiophene containing heteroacenes preserve the characteristics of highly conductive oligothiophenes, while limiting the deviation from planarity that restricts the conjugation and potentially affects the band gap in its solid state (Fig 1.11).⁸¹

Neckers and co-workers⁸² reported the synthesis and characterization of thioenobis(benzothiophene), ¹¹, and its crystallographic analysis showed that the molecule
crystallizes in a co-planar arrangement.\textsuperscript{21} Field effect transistor mobilities for such molecules are 0.1-0.2 cm\textsuperscript{2}V\textsuperscript{-1}S\textsuperscript{-1}. Katz and co-workers synthesized one of the most widely studied heteroacenes, anthradithiophene (ADT), 5. This also exhibits a moderate FET mobility of 0.09cm\textsuperscript{2}V\textsuperscript{-1}S\textsuperscript{-1}.\textsuperscript{83}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure11.png}
\caption{Examples of crystal structure showing the effect of planarization induced by ring fusion: (a) perfluorothiophene shows inter-ring torsional angle restricting the conjugation, while (b) dibenzothienothiophene adopts a planar structure.}
\end{figure}

Relatively low charge carrier mobility along with exceptionally low switching speed (I\textsubscript{on}/I\textsubscript{off}) creates challenges in the practical application of heteroacenes. However, due to their high stability under ambient conditions heteroacenes have drawn significant attention, and researchers are focused on designing heteroacenes that retain their stability, but at the same time exhibits as high mobility as pentacene.\textsuperscript{84}

\section*{1.11. Objective}

As discussed earlier, pentacene and other larger acenes are known to be highly conductive. However, the exceptionally poor stability of such materials restricts their practical application in electronic devices. Therefore, our objective in this project is to design stable large acenes that will be highly conductive while still demonstrating supreme stability towards ambient conditions.
We designed a synthesis of a heteroacene analog of heptacene containing thiophene as the heteronuclear aromatic ring. We initially designed the synthesis of an TMS-substituted heptacene analog containing thiophene ring, 1, 6,8,15,16-tetrakis-(trimethylsilyl)-dianthra [2,3-b; 2’,3’-d] thiophene (tetakis-TMS-DAT). The TMS-substituted DAT, 1, assumes a linear symmetric structure. To compare the effect of the molecular structure on the crystal packing of these materials in the solid state, and hence on the mobility of these materials in the OFET devices we designed the synthesis of an isomer of the heteroacene analog of heptacene containing thiophene ring. The isomer is comprised of an unsubstituted non-linear analog of heptacene, 2, Dianthra [1,2-b; 1’,2’-d] thiophene (DAT-b,d). We attempted several synthetic strategies for their synthesis, and we were finally able to successfully design unique synthetic routes for both, one of these involved a photochemical route. The successful schemes for their syntheses and their characterization will be discussed in this dissertation.

Figure 1.12. Structures of the target compounds 1 and 2.

1.12. Overview of the Project

While designing the target compounds for this project two key attributes were considered- the conductivity and the stability. The oligomeric length of the acene is crucial in guiding the mobility of the material. At the same time, introduction of a suitable heteroatom with-out inhibiting the two-dimensional interactions in the solid state is important for the stability of the material. Therefore, two major questions need to be answered about the design of 1 and 2 –
(a) Why heptacene?

(b) What benefits do we get from sulfur substitution?

As mentioned earlier the electronic properties change of the acenes favorably with an increase in the oligomeric lengths. Heptacene contains seven linearly annulated benzene rings that presumably will allow extended conjugation as well as suitable intra-molecular interaction in the solid state, leading to higher conductivity. A heteroacene analog of a heptacene can potentially be a prototype of a highly conductive stable PAHs.

In introducing sulfur as the hetero atom a number of molecular factors have been taken into account: the chalcogen effects, the frontier MO energy levels, high stability, and ready accessibility. Chalcogen effects include short intermolecular contacts between chalcogen molecules, influencing molecular packing geometry in many electroactive materials. At the same time, the presence of polarizable sulfur atoms should enhance intermolecular orbital overlap, which will facilitate intermolecular charge transfer. It is also noted that the terminal or internal thiophene rings in the heteroacenes help to form a “kinked” substructure, which increase the benzenoid character of the conjugation in such systems, thus stabilizing the HOMO levels and increasing the HOMO–LUMO band gap.\textsuperscript{85} Therfore, compounds 1 and 2 are expected to be stable under ambient conditions.

![Figure 1.13](image_url). Chalcogen effect: showing the inter-molecular interactions between the sulfur atoms.
Preliminary theoretical calculations on compound 1 and 2 suggested very high mobility in such materials. We believe these materials will exhibit mobility as high as 2-3 Cm²V⁻¹S⁻¹. Our goal of this project is to fabricate organic field effect transistor devices and test the mobility of 1 and 2. On successful device fabrication observation of high mobility in these materials will be a significant improvement in the field of organic semiconductors.⁸⁵

1.13. Organic Transistors

Organic field effect transistors or OFETs adopt the architecture of thin film transistors (TFT). There are two common types of device configurations used in thin film transistors, (i) top contact, and (ii) bottom contact. Source and drain electrodes are placed onto the organic semiconducting layer in the top contact TFTs, while the organic semiconducting layers are deposited onto source and drain electrodes in a bottom contact configuration. Then a thin film of insulator is deposited between the semiconducting layer and the metal gate contact. This structure ensures that there is no depletion layer to separate the device from the substrate. At zero bias, the electrons are expelled from the surface due to the Fermi-level energy difference of the semiconductor and the metal, which leads to band bending of the semiconductor. In this case, there is no carrier movement between the source and drain. When a positive charge is applied, the accumulation of electrons on the interface leads to the bending of the semiconductor in an opposite way. This also leads to the lowering of the conduction band with regards to the Fermi-level of the semiconductor, which then forms a highly conductive channel at the interface.⁸⁶-⁹⁰
Figure 1.14. Schematic diagram of top-contact and bottom-contact thin film transistors (top), and schematic graph of band-bending in a transistor device.
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Chapter 2

Synthesis and Characterization of a Stable Heptacene Analog

2.1 Motivation.
As one of the most important families of semiconducting materials, thiophene containing heteroacenes have attracted tremendous attention. Thiophene containing heteroacenes combine the stability of the thiophene ring with the planarity of the linear acenes such as pentacene/heptacene. Additionally, such systems retain the desirable properties of poly- or oligothiophenes, while limiting deviations from planarity that disrupt conjugation and potentially affect the band gap in the solid state. Unsurprisingly, many synthetic methods have been developed, which included generally two different strategies - insertion of sulfur atoms into the conjugated skeleton and direct annulation of thiophene units.

2.2 General Synthetic Approaches for Synthesis of Thiophene Containing Heteroacenes.
2.2.1. Insertion of sulfur atoms into the conjugated skeleton.

2.2.1.1. Synthesis via sulfur-bridge formation.

Sulfur containing aromatic compounds can be synthesized via the sulfur-bridge formation. Such reactions are usually carried out through the acid-catalyzed reduction of aryl-sulfoxide; e.g. phenyl methylsulfoxide (1), in the presence of trifluoromethanesulfonic acid (triflic acid) give methyl(4-phenylthio) phenylsulphonium cation (2) as an active species, eq1, Scheme 2.1. The S=O bond in 1 is polarized as S+--O- due to the presence of the d empty orbital in S; the electrophilic attack, therefore, occurred at the negatively charged oxygen atom. The formed sulfonium cation
could be isolated quantitatively as a stable salt. The activated sulfoxide, now, can act as an electrophile (Swern method). The active species, 2, can therefore react electrophilically with the benzene ring (3) to eliminate water as a byproduct (eq2, Scheme 2.1). Finally, the demethylation proceeded quantitatively in presence of pyridine as a nucleophile (eq3, Scheme 2.1).

Scheme 2.1. Mechanism of the super acid induced electrophilic substitution leading to the S-bridge formation.

When the intermolecular substitution is applied to intramolecular reactions, a sulfur bridge can be formed between two adjacent aromatic rings. Due to the easy availability of the Ar-methylsulfoxide (1) and the straightforwardness of the reaction, intramolecular acid catalyzed S-bridge formation from Ar-methylsulfoxides has been a powerful tool to construct sulfur containing ladder type polymers and oligoacenes. In 1999, Tsuchida et. al. first reported the triflic acid induced intramolecular ring closure, from which were obtained oligoheteroacene dibenzo[b,b']thieno[2,3-f:5,4-f']bis[1]benzothiophene (DBTBT) as a potential OFETs material. However, due to the nature of the precursor, three isomers (6-8) were present in the final product, scheme 2.2a. Another fluorine based heteroacene (9) synthesis using this strategy has been reported recently for OLED applications, scheme 2.2b.[63]
Scheme 2.2. Two examples of the acid catalyzed intramolecular ring closure reaction for the synthesis of thiophene fused heteroacenes.

There are two disadvantages with this method. The first one is the low functional group tolerance. Functional groups like halogen atoms (Br or I), trimethylsilyl, carbonyl groups and α-H of thiophene etc can react with triflic acid activated sulfoxide and lead to significant side reactions. The second drawback is that longer alkyl groups (CnH2n+1, n > 10) will degrade in the triflic acid. This means that under some conditions, one can not achieve enough solubility due to the limited length of the alkyl groups.
2.2.1.2. Introduction of thiophene rings by aromatic nucleophilic substitution (SNAr) reaction. Benzo[b]thiophene and its related fused-aromatic compounds are attracting current interest as promising electronic materials. Hence, much work has been done to develop new and convenient synthetic approaches to benzo[b]thiophenes. In particular, the use of phenylacetylene-based precursors in cyclization reactions affording fused-thiophene or selenophene moieties has emerged: Sashida et al. first reported that o-alkynylbromobenzenes (10) react with elemental chalcogene (sulfur, selenium, or tellurium) upon lithium-halogen exchange to afford benzo[b]chalcogenophenes in good yields.[64] Later on, Takimiya et al. employed the same method and successfully applied it to 2-fold cyclization reactions to give benzo[1,2-b:4,5-b']dithiophenes and benzo[1,2-b:5,4-b']diselenophenes (11, Scheme 2.3).7,8

Scheme 2.3. Synthesis of benzodichalcogenophenes

Furthermore, Yamaguchi et al. developed the intramolecular triple cyclization of bis(o-haloaryl)-diacetylenes (12) to produce heterole-1,2-dichalcogenin-heterole (13) fused tricyclic skeletons. Then the subsequent dechalcogenation with copper metal affords a series of thiophene- and selenophene-based heteroacenes (14, Scheme 2.4).9-14
Based on the result of Shvartsberg et al., Takimiya and his colleagues further developed the nucleophilic cyclization reaction using inorganic sulfur sources, such as sodium sulfide (Na₂S), as reagent and o-alkynylbromobenzenes (15), from which they realized a 3-fold cyclization reaction to get benzo[1,2-b;3,4-b';5,6-b'']trithiophenes (16) in one pot procedure. However, despite the accessibility of the precursors and the easy experimental operation and reasonable yields of the products, this method is limited to the synthesis of nonlinear benzothiophenes, scheme 2.5.
Furthermore, Watson et al. employed a very clever route that involves nucleophilic aromatic substitution (SNAr) to synthesize fluorinated benzobisbenzothiophenes (17, scheme 2.6). The reaction is so efficient that the dealkylation and ring closure are allowed to be finished in one-pot. There are two limitations to this synthetic strategy: firstly, the reaction could only be performed efficiently in highly electron deficient systems which are also sustainable in strong base, and secondly, it can be employed for the synthesis of ladder type heteroacenes only.

2.2.1.3. Introduction of thiophene rings by electrophilic cyclization reaction.

Larock et al. developed synthesis of 2,3-disubstituted benzo[b]thiophenes (19) involving electrophilic cyclization of o-alkynylthioanisol (18) catalysed by I₂, Br₂, NBS, and sulfur and selenium electrophiles, scheme 2.7. The high yield of this reaction makes it quite promising to
other chemists. Pei and his colleagues used this method in a two fold structure to construct C2-symmetric ladder-type heteroacenes.$^{18,19}$

![Image]

**Scheme 2.7.** Intramolecular electrophilic cyclization reaction.

Recently, Takimiya et al. designed and synthesized dinaphtho[2,3-b:2’,3’-f]- chalcoge[3,2-b]chalcogenophenes (21, scheme 2.8) with six fused aromatic rings. In the presence of excess iodine (Lewis acid), the olefin intermediates (20) forms the thienothiophene (21a) or selenophenosenlenophene (21b) moieties in good yields. It should be noted that the present method is much shorter than the previously reported one$^{13}$ and is a versatile tool to obtain various novel heteroacenes.

![Image]

**Scheme 2.8.** Synthesis of DNTT and DNSS via intramolecular electrophilic cyclization.

2.2.2. Direct annulation of thiophene units.

2.2.2.1. Friedel-Crafts-type alkylation and acylation reactions.
Scheme 2.9. Example of thiophene unit containing heteroacenes by Friedel-Crafts alkylation.

Benzothiophene substituted aryl groups containing carbonyl groups (22) can be converted into thiophene containing ladder type heteroacenes (23) via Friedel-Craft’s alkylation followed by ring closure, scheme 2.9. The application of such reaction for the synthesis of heteroacenes is limited due to lack of ready availability of the starting materials, and the yields of such reactions are significantly low. Intramolecular Friedel-Crafts acylation is on the other hand can be a convenient way to construct n-channel semiconducting materials. Wang et al. resynthesized indeno[1,2-b]fluorine-6,12-dione (24) using sulfuric acid induced Friedel-Crafts acylation in high yield. The reaction was performed much more easily than the alkylation reaction and left two electron withdrawing ketone groups, scheme 2.10.

Scheme 2.10. Wang’s synthesis of ladder-type oligoacenes.

To combine thiophene rings into the conjugated system through the Friedel-Crafts acylation, the reaction condition needs to be modified in order to preserve the thiophene system, scheme 2.11.
2.3. Attempted routes for the synthesis of 6,8,15,16-tetrakis-(trimethylsilyl)-dianthra [2,3-b; 2’,3’-d] thiophene (tetrakis-TMS-DAT).

The synthetic approaches, described above, for the synthesis of thiophene containing heteroacenes gave reasonable yields. However, use of such methodologies was limited to the synthesis of nonlinear and ladder type heteroacenes. As a result, there are very few linear heteroacenes reported to the date. Anthra-[2,3-b]-thiophene (25) and tetracenothiophene (26) are examples of such linear thiophene containing heteroacenes, scheme 2.12.²¹

The synthesis of 25 involved the aldol type condensation between thiophene-2,3-carboxaldehyde and naphthohydroquinone. The synthesis of 26, on the other hand, is carried out via the formation of diene type intermediate on the 2,3-positions of thiophene followed by Diels-Alder type reaction of that intermediate with 1,4-anthraquinone.
Based on the synthetic strategies used for the synthesis of 26, we attempted the synthesis of dianthra [2,3-b; 2’,3’-d] thiophene (DAT, 30) via the formation of 28. Several synthetic strategies were employed for the synthesis of 28. To be able to synthesize 28, we attempted the synthesis of 4,5-dimethyl-anthra-[2,3-b]-thiophene (27) first, scheme 2.13. The H at the 1 position of anthra-[2,3-b]-thiophene (25) is sufficiently acidic for lithiation with butyl-lithium (BuLi). Therefore, first methylation at the 1-position of anthra-[2,3-b]-thiophene can be enabled through lithiation followed by treatment with methyl iodide (MeI). The H at the 2-position of 25, is however not acidic enough for successful lithiation using BuLi. Therefore, we attempted introducing bromo-group at the 2-position, using bromine in chloroform, prior to the lithium-halogen exchange using BuLi. The treatment of MeI with the 2-lithio-anthra-[2,3-b]-thiophene would produce 27. The bromination on the methyl substituents on aromatic systems is wellknown. So formation of 28 from 27 would be simple. However, while we were successful in introducing bromo-group at the 2-position of 25, the lithium-halogen exchange on it was not successful. It was inferred that the rate of the lithium-halogen exchange equilibrium in this step of the reaction did not favor the product formation. Therefore the synthesis of 30 using this synthesis scheme was futile.

Therefore, we wanted to introduce diene type intermediates at the 2,3- and 4,5- positions of thiophene, scheme 2.14. So our primary goal was to be able to synthesize 32. Two consecutive Diels-Alder reaction on 32 in presence of NaI and naphthaquinone would produce 33, which upon reduction can be converted to 30. Although, the synthesis and tetra-bromination of 2,3,4,5-tetramethylthiophene was successful, the conversion of the 32 to 33 involving domino Diels-Alder type reaction was unsuccessful. The failure of such reaction can be attributed to the complications concerning the performance of two consecutive Diels-Alder reactions.


As the synthetic strategies involving the formation of diene type intermediates on the thiophene systems were failure, we wanted to follow the synthetic strategy used for the synthesis of 25. Considering the strategy used for the synthesis of 25, we decided to synthesize anthra-[2,3-b]-thiophene-4,5-dicarboxaldehyde (34). Aldol type condensation of 34 with 1,4-naphthohydroquinone in presence of pyridine would enable 29. It (29) could then easily be reduced to 30 using lithium aluminum hydride (LiAlH₄). So, our intial goal was to synthesize
anthra-[2,3-b]-thiophene-4,5-dicarboxaldehyde (34). We attempted modified Swern type oxidation on dibromo-dianthrathiophene using BuLi in presence of dimethylformamide (DMF). However, such attempt was not successful. As an alternative, we attempted to synthesize 34 in stepwise manner, i.e. stepwise formylation. The attempted Swern type oxidation to get mono-formylated product was again unsuccessful. Then we tried to employ Vielsmayer-Haack type of formylation using phosphonyl chloride (POCl₃) in DMF solvent. The first formylation at the 2-position of anthrathiophene worked. However, we were unable to successfully perform second formylation on it. This can be attributed to the deactivation of the aromatic system in presence of first –CHO group.

Scheme 2.15. Synthesis of 30 via formation of 34.

So, instead of using formyl derivatives of the anthrathiophene we wanted to utilize 2,3-naphthalene-dicarboxaldehyde, scheme 2.16. But this scheme was not successful either. We modified this approach in various ways, but none of them were successful, scheme 2.17.

Scheme 2.16. Synthesis of 30 via dibromo-dianthrathiophene.
Finally, we decided to utilize a multi-step procedure involving multiple Fridel-Craft’s acylation steps, scheme 2.18. A Fridel-Craft’s acylation of thiophene with 2,3-naphthoic anhydride in presence of Aluminiumtrichloride (AlCl₃) enabled the formation of 35. It was then cyclized in presence of concentrated sulfuric acid. The yield at the cyclization step was significantly low (40%). The product obtained after the cyclization (36) was further reduced to get anthrathiophene. The Fridel-Craft’s acylation of anthrathiophene with 2,3-naphthoic anhydride was carried out in presence of AlCl₃. The product from the acylation was cyclized into 29, at a very poor yield (>25%), in presence of concentrated sulfuric acid. The final product 30 was successfully prepared at low yield under reductive conditions. This scheme overall, as stated above, gave very poor yield. At the same time, it was hard to scale –up the synthesis. So, we sought for another reaction scheme to enable the production of 30 at a reasonable yield.

Scheme 2.17. Scheme for the synthesis of 30 using reductive conditions.

Scheme 2.18. Synthesis of 30 using multiple Fridel-Craft’s acylations steps.
Meanwhile, Ni et al.\textsuperscript{22} showed a novel technique for the synthesis of anthrathiophenes using zirconia catalyst. We utilized this idea for our synthesis to successfully obtain 30 with reasonable yield, scheme .

\textbf{Scheme 2.19.} Novel synthesis strategy for the synthesis of anthrathiophene.

Commercially available o-Xylenedibromide was treated with BuLi to perform lithium-halogen exchange. It was then reacted with trimethylsilyl-acetylene (TMS-acetylene) in presence of Cu(I)Cl to obtain 39. Utilizing the chemistry published by Ni et al., 39 was then treated with tetrabromo-thiophene in presence of zirconocene-dichloride to enable the synthesis of 40. It was then aromatized using dichlorodicyanoquinone (DDQ) to obtain 41. We attempted the removal of the TMS group using tetrabutylammonium fluoride (TBAF) to produce 30. This scheme finally provided the desired yield and it was easy to scale-up the synthesis of 30 using this scheme.

\textbf{Scheme 2.20.} Strategy for the successful synthesis of 30.
This was the first example of the synthesis of unsubstituted dianthra-[2,3-b; 2',3’-d]-thiophene to the best of our knowledge. This is linear heteroacene analogous to the structure of heptacene. The X-ray crystal structure confirms its structure.

Figure 2.1. Perspective view of the crystal structure of dianthrathiophene.

Preliminary theoretical calculations, based on the crystal structure, predicted high mobility for this material. Therefore, we wanted to study the mobility of this material in an organic thin film transistor (OTFT). The fabrication of OTFT device using dianthrathiophene (DAT), and study of the mobilities in the device is currently ongoing.

2.4. Experimental Section.

2.4.1. Synthesis of 40: To a solution of Cp₂ZrCl₂ (702 mg, 2.4 mmol) in 10 mL of Toluene was added n-BuLi (1.6 M hexane solution, 3.05 mL, 4.8 mmol) at -78 °C, and the mixture was stirred at -78 °C for 1 h. 1,2-bis-trimethylsilylethynylbenzene (600 mg, 2.0 mmol) was added and the mixture was warmed to room temperature by removal of the cooling bath. After stirring for overnight, CuCl (392 mg, 4.0 mmol), DMPU (0.87 mL, 7.2 mmol), and tetraiodothiophene (294 mg, 0.5 mmol) were added and the mixture was stirred for 1 h at 110 °C. The mixture was quenched with 3 M aqueous HCl solution, and extracted with ethyl acetate. The combined organic phase was washed with water, saturated aqueous NaHCO₃ solution, brine, and dried over anhydrous MgSO₄. After removal of the solvent, the resulting black viscous oil was purified by a
flash chromatography (silica gel, hexane: toluene = 5:1 as eluent) to afford the title compound **40** as yellow solid (242 mg, 79% yield).

**40**: 1H NMR (CDCl$_3$, Me$_4$Si) $\delta$ 0.70 (s, 18 H), 4.02 (s, 8 H), 7.18-7.25 (m, 4 H), 7.32-7.39 (m, 4 H); 13C NMR (CDCl$_3$, Me$_4$Si) $\delta$ 13.9, 126.08, 126.12, 126.90, 126.92, 129.8, 133.4, 133.6, 134.0, 134.1, 137.6, 137.8, 138.4. HRMS calcd for C$_{44}$H$_{52}$S: 612.3790. Found: 612.3796.

**2.4.2. Synthesis of 41:** A mixture of tetrahydrodianthrathiophene **40** (89 mg, 0.15 mmol) and DDQ (72.4 mg, 0.32 mmol) in toluene (3 mL) was heated to 75 °C for 1 h. After cooling to room temperature, the mixture was filtered through a pad of Celite. The filtrate was concentrated *in vacuo*, and the residue was purified by a silica gel chromatography (hexane: toluene = 10:1 as eluent) to afford a red solid, which was further purified by recrystallization from hexane. After drying *in vacuo*, the title compound **12** was obtained as red crystals (77 mg, 87% yield). **41**: 1H NMR (CDCl$_3$, Me$_4$Si) $\delta$ 0.59 (s, 18 H), 7.45-7.52 (m, 4 H), 8.05-8.09 (m, 4 H), 8.56 (s, 2 H), 8.76 (s, 2 H); 13C NMR (CDCl$_3$, Me$_4$Si) $\delta$13.7, 121.1, 124.9, 125.3, 125.6, 126.8, 128.1, 128.4, 130.2, 130.3, 130.7, 131.4, 133.7, 134.5, 136.2. HRMS calcd for C$_{44}$H$_{48}$S: 608.3477. Found: 608.3474.

**2.4.3. Synthesis of 30:** To a mixture of **41** (60 mg, 0.10 mmol) in toluene, a solution of tetrabutylammonium fluoride in ethanol was added. The mixture was then heated to 65°C for 3 h to obtain 30. The resulting reaction mixture was filtered through celite and the filtrate was dried under vacuum. The solid was then purified through column chromatography to obtain red crystalline solid (50 mg, 90%). **30**: 1H NMR (CDCl$_3$, Me$_4$Si) $\delta$ 7.45-7.52 (m, 4 H), 8.05-8.09 (m, 4 H), 8.56 (s, 2 H), 8.76 (s, 2 H); 13C NMR (CDCl$_3$, Me$_4$Si) $\delta$ 121.1, 124.9, 125.3, 125.6, 126.8, 128.1, 128.4, 130.2, 130.3, 130.7, 131.4, 133.7, 134.5, 136.2. HRMS calcd for C$_{44}$H$_{48}$S: 384.3477. Found: 384.3384.
References


Chapter 3

Photo-generation of a Stable Heptacene Analog: Synthesis and Characterization

3.1. Motivation.

Thieno-containing heteroacenes composed of linearly fused benzene and thiophene rings have been mostly studied heteroacenes to date.\textsuperscript{1-13} Thiophene containing non-linear heteroacenes, however, will be interesting as they will have different crystal packing in the solid state, and hence, rationale between the crystal structure and their electronic conductivity in the solid state can be established. The nonlinear counterparts provide additional advantages due to their versatile non-linear optical properties.\textsuperscript{14-22} Two types of non-linearly fused systems are known-phenacenes and helicenes.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure31.png}
\caption{Structures of phenacenes (left) and helicenes (right).}
\end{figure}
Phenanthrene, the prototype of phenacenes, is commonly synthesized via \([4+2]\) photo-cyclization of stilbene. In 1971, Wynberg established this common method of photocyclization of stilbene and their analogs.\(^{23}\) Such photo-cyclization reactions are used extensively for the syntheses of numbers of polycyclic aromatic hydrocarbons, including helicenes, aza-helicene, thia-helicene, and several complex heterocyclic compounds.\(^{24}\)

**Figure 3.2.** Mechanism for phenanthrene cyclization.

The oxidative conversion involves the isomerization of trans- stilbene (A) into its cis- form (B). The photo-cyclic conversion of B to C is guided by a \([4+2]\) electrocyclization step, commonly known as Wynberg cyclization. The conversion of C to D is accompanied by reduction of iodine to produce two moles of hydrogen iodide. The photolysis is usually carried out in the presence of excess of propylene oxide or ethylene oxide. The strong acid byproduct, HI, is thus neutralized in the opening of the epoxide ring of these reagents. Alternatively, the photocyclization can be carried out in the presence of oxygen with good results.\(^{25}\) It is reported that when a primary amine is used as the scavenger of this HI, the cyclization favors an ionic mechanism and gives dihydro derivative.\(^{26}\) Other bases have been used as acid scavengers in this type of photocyclization with some success.\(^{27, 28}\) An analogous reaction of photochemical cyclization of stilbazole salts within a Nafion membrane micro-reactor has been reported, without using any base nor iodine.\(^{29}\)

3.2.1. Synthesis of Coronenes.

There are reports of use of such photocyclization for synthesis of a wide range of polycyclic aromatic hydrocarbons. They have been used for the synthesis of π-conjugated coronene derivatives, that are known to have high degree of conductivity. A facile route has been developed for the preparation of a new family of contorted 1.2.3.4,7.8,9.10-tetrabenzo coronenes (TBCs). A two-step cyclization reaction, i.e., oxidative photocyclization followed by FeCl₃-mediated intramolecular cyclodehydrogenation, was carried out on the olefin precursors to obtain the final TBC compounds. These new TBC molecules have contorted conformation due to steric overcrowding as disclosed by single-crystal crystallographic analysis. Nevertheless, they showed extended π-conjugation compared with coronene and exhibited strong aggregation in solution.

![Synthesis of coronene derivatives](image)

**Figure 3.3.** Synthesis of coronene derivatives.

3.2.2. Synthesis of Photochromic Materials.

Such photocyclization reactions have been exploited for the synthesis of photo-chromatic compounds that cyclizes in presence of a specific wavelength of light, and decyclizes at a
different wavelength of light. Such processes are reversible, and therefore, used in the preparation of molecular switches.\textsuperscript{31-35}

![Diagram of photochromic behavior]

\textbf{Figure 3.4.} Photochromic behavior.

\textbf{3.2.3. Biological Applications.}

Such processes have applications in both organic electronics and biological sciences. Photochromic nucleosides were designed that combine the structural features and molecular recognition properties of nucleic acids with the light-sensitivity of diarylethenes. Target compounds 1a-c consist of a 7-deazaadenosine unit that is linked to a thiophene as the second aryl functionality via a 1,2- cyclopentenyl linker. These nucleoside analogues undergo a reversible electrocyclic rearrangement, generating strongly colored closed-ring isomers upon irradiation with UV-light, while exposure to light in the visible range triggers the cycloreversion to the colorless opened-ring form. UV-vis spectroscopy, HPLC, and 1H NMR measurements revealed recognition of complementary thymidine and up to 97\% conversion to the thermally stable closed-ring isomers after illumination with UV-light. The required wavelength for ring closure was found to vary depending on the substituents attached to the thiophene moiety. These
new photochromic nucleosides represent useful building blocks for the generation of light-sensitive nucleic acids for biological applications.\(^{36}\)

![Photochromic Nucleoside](image)

**Figure 3.5.** Biological applications of photochromic compounds.

### 3.2.4. Synthesis of Helicenes.

Such photocyclization methods are used in planning the synthesis of helicenes as well. The helicenes are very important for their optical properties and for the wide applications in optoelectronics. Helicenes\(^{[1]}\) are very interesting helical-shaped aromatic systems, and they possess great potential for the use in the development of new materials with optoelectronic properties.

In fact, theoretical and experimental studies conducted both on carbo- and heterohelicenes pointed out that they possess peculiar characteristics related to their optical and electronic properties. Heterohelicenes,\(^{[1b,1g,2]}\) in which heteroaromatic units are incorporated into an extended aromatic \(\pi\) system, have received less attention than carbohelicenes, but they can provide some advantages due to the presence of heterocyclic rings, which may allow regioselective functionalization of the aromatic system.\(^{[2e,2g,3]}\) Among the various heterohelicenes known, tetrathia\(^{[7]}\)helicene (1, \([7]\)TH, Scheme 1) is one of the most interesting owing to the alternate presence of thiophene and benzene rings. In this system, the regioselective
functionalization of the terminal thiophene rings should, in principle, be easy and versatile, allowing, through the introduction of different functional groups, the tuning of specific properties, such as the nonlinear optical (NLO) response or the entry to new chiral ligands for catalysis.\textsuperscript{37}

![Figure 3.6. Synthesis of helicenes.](image)

3.2.5. Non-linear Heterocyclic Aromatic Hydrocarbons.

Hu et al used such concept for the synthesis of a non-linear polycyclic heter-aromatic hydrocarbons containing thiophene ring as heterocyclic ring.\textsuperscript{38} Such materials have been known to have high degree of conductivity and wide range of applications due to their high thermal and photostability. Photocyclization of stilbene-like olefins followed by in situ oxidation using iodine is a crucial step in the synthesis of higher numbered helicenes.\textsuperscript{39,40} This reaction requires dilute solutions and is typically carried out in toluene. Application to higher helicenes and heterohelicenes is limited due to their poor solubility, the small scale of the synthesis, and the fact that the products act as filters for incident radiation. Decomposition products were detected by NMR spectroscopy during photochemical cyclization.

[4+2] photo-cycloaddition, therefore, can be a useful method for the synthesis of nonlinear longer heteroacenes. This method will allow a facile route for the synthesis of long stable acenes that are otherwise hard to synthesize. Herein, we discuss the facile synthesis of stable non-linear analog of heptacene, 2, using photo-cyclization method.

Commercially available bromo-methyl naphthalene was substituted with tri-phenyl phosphine followed by the elimination with butyllithium. Thus the Wittig reagent was prepared, and it was further reacted with thiophene-2, 5-dicarbaldehyde to synthesize the precursor for 2. The precursor for the synthesis of the 2 was irradiated with light (> 300 nm) in presence of oxygen for 6 hours before the compounds 2 was isolated through preparatory chromatography.
3.4. Photophysical Properties.

The absorption spectra in different solvents for the compound 2 were recorded. The absorption spectra show absorption up to 450 nm. As expected, the absorption spectra in relatively non-polar solvent, such as cyclohexane, is more structured than in polar solvents, such as dimethylformamide. This compound was highly stable under ambient conditions.

3.5. Experimental Procedure

Commercially available reagents were used as received from the chemical suppliers unless otherwise noted. Reactions that required anhydrous conditions were carried out under an inert atmosphere of argon in flame-dried glassware. Toluene, DCM, and THF were dried using a Solvent Purification System. The rest of solvents used for synthetic purposes were purified according to conventional protocols. All reactions were monitored using F250 silica gel 60 M analytical TLC plates with UV detection ($\lambda = 254$ and 365 nm). Hanessian’s stain and iodine
vapors were also used as developing agents depending on the nature of the material. Silica gel (60 Å, 40–63 µm) was used as stationary phase for column chromatography.

NMR experiments were acquired with working frequencies of 300.0 MHz for $^1$H, and 75.5 MHz for $^{13}$C experiments for characterization purposes. The shifts were reported in parts per million (ppm) and referenced to the residual resonance signal of commercially available CDCl$_3$ ($\delta = 7.26$ ppm) and CD$_2$Cl$_2$ ($\delta = 5.32$ ppm).\textsuperscript{24} Low resolution mass spectra were recorded on a quadrupole mass analyzer instrument equipped with a direct insertion probe (ionization 70 eV), and coupled to a gas chromatograph. MALDI–TOF MS were recorded using dithranol as matrix for compound ionization when measurements of neat compounds were unsatisfactory.

The starting materials 5,5’-Dibromo-2,2’-bithiophene and 3,6-Di-tert-butyl-9H-carbazole were synthesized from commercially available compounds according to reported procedures.

3.5.1. Synthesis of triphenylphosphinyl methylenynaphthyl: Bromomethylnaphthyl (1.00 g, 3.50 mmol), triphenylphosphine (3.65 g, 10 mmol) were transferred to a clean and dry Schlenk flask. The flask was then evacuated and refilled with argon three times. Afterwards, the solids were suspended in Argon-saturated toluene (100 mL), and the reaction mixture was heated to reflux, and allowed to react overnight under Argon atmosphere with constant stirring. Upon completion, the reaction mixture was cooled to room temperature, and was filtered to remove the tri-phenyl phosphobromide. The filtrate was collected, and the organic phase was finally dried over MgSO$_4$. The filtrate was evaporated to dryness affording a bright yellow solid. (Yield 96 %). It was further treated with butyllithium in toluene overnight to get the final product at 80% yield.
3.5.2. Synthesis of 2,5-di-naphthylethenyl thiophene: To a dry three neck round bottom flask fitted with thermometer, was added a suspension of thiophene-2,5-dicarboxaldehyde (522 mg, 1.0 mmol) and triphenylphosphinyl methyl naphthalene. The suspension is then constantly stirred at room temperature under argon atmosphere. The mixture was then allowed to stir at room temperature for overnight. A bright yellow solid is obtained (yield 75%). M.P. 148-150 °C.

$^1$HNMR (300MHz, CD$_2$Cl$_2$): δ(ppm) 8.1 (s, 2H), 7.5 (d, 2H, $J=1.0$ Hz), 7.47 (d, 2H, $J=0.5$ Hz), 7.27 (d, 1H, $J=1.2$ Hz), 7.22 (d, 1H, $J=1.2$ Hz), 7.10 (d, 2H, $J=1.57$ Hz), 1.51 (s, 18H).

$^{13}$CNMR (CDCl$_3$, 75.5 MHz): δ(ppm) 31.9, 32.0, 34.8, 109.6, 116.3, 122.3, 123.6, 123.9, 124.0, 124.8, 127.9, 138.6, 138.7, 140.1, 143.9. MALDI-MS 521 (M$^+$). HRMS (EI) calcld for [C$_{28}$H$_{29}$NS$_3$] 475.1462, found m/z 475.1463.

3.5.3. Synthesis of 2: 2,5-dinaphthylethenyl thiophene was transferred into a dry three-necked round flask containing toluene. The flask is then set in a photo-reactor and irradiated with visible light (<300 nm) for 6 hours. The solution turns red. The solvent is then evaporated to dryness. The resulting dark red solid is purified through column chromatography, to get pure bright yellow solid. Yield (65%). $^1$HNMR (300MHz, CD$_2$Cl$_2$): δ(ppm) 10.32 (s, 1H), 10.2 (s, 1H), 9.3 (s, 1H), 9.12 (d, 1H, $J=1.2$ Hz), 8.42 (s, 1H), 7.7 (dd, 1H, $J_1=1.57$ Hz, $J_2=2.2$ Hz), 7.6 (dd, 1H, $J_1=2.2$ Hz, $J_2=1.2$ Hz). $^{13}$CNMR (CDCl$_3$, 75.5 MHz): δ(ppm) 109.6, 116.3, 122.3, 123.6, 123.9, 124.0, 124.8, 127.9, 138.6, 138.7, 140.1, 143.9. MALDI-MS 384 (M$^+$). HRMS (EI) calcld for [C$_{28}$H$_{16}$S] 384.2482, found m/z 384.1463.
References


THE PHOTO-INDUCED FORMATION OF QUANTUM DOT – CONDUCTIVE POLYMERS (QD:CP) FOR APPLICATION IN PHOTOVOLTAICS
Chapter 1
Introduction

1.1. Background
The supply of and demand for energy determine the course of global development in every sphere of human activity. In the twentieth century, the world’s increasing population and energy consumption lead to a serious issue in dealing with its energy supply. A recent study suggests that, with current world-wide socio-economic growth, the global energy demand increases at a rate of 2% a year, and an additional 10 terawatts (TW) of energy is needed to sustain the world’s population by 2050.\(^1\) While the present supply of energy is not going to be exhausted in the near future, a shortfall in the supply of energy is impending considering the rapid growth in demand.\(^2\) The reserves of fossil fuels that currently power society will fall short of this demand over the long term. Besides, the continued use of fossil fuels causes harmful side effects- pollution and greenhouse gas emission. The air-pollution and greenhouse gas emission, caused by the enhanced rate of burning fossil fuel, threatens human health as well as has adverse effect on the global climate.\(^3-5\) Therefore, a clean energy source has to be found promptly in order to meet the global requirement of an additional 10 terawatts (TW) of energy that is needed to sustain the world’s population.

Unfortunately, alternative renewable fuels are at present far from being competitive with fossil fuels in cost and production capacity. Without viable options for supplying double or triple today’s energy, the world’s economic, technological, and political horizons will be severely limited.\(^6\) Provided this shortfall to the global energy supply is accurately predicted, today’s concern is – what could be a viable solution?
1.2. **Solar Energy**

The sun deposits 120,000 TW of radiation on the surface of the Earth. This far exceeds the demand of energy even in the most demand scenarios. A calculation suggests that the production of 20 TW of power would require covering 0.16 % of Earth’s land with 10%-efficient solar panels.¹ This could, therefore, provide nearly twice the world’s consumption rate of fossil energy and is equivalent to constructing one new electric nuclear fission plant of 1 GW (gigawatt) of production ability somewhere on this planet everyday till 2050.⁷ These comparisons illustrate the extraordinary magnitude of the solar resource; it provides an energy flow far more effective than existing technologies can achieve. However, to tap this enormous amount of energy is far from being simple. It requires a concerted world-wide effort employing our most advanced scientific and technological capabilities.

1.3. **Background of Solar Energy Research**

Edmund Becquerel fist observed the photovoltaic (PV) effect in 1839, when he found that a “voltage and a current were produced when a silver chloride electrode immersed in an electrolytic solution and connected to a counter metal electrode was illuminated with white light.”⁸ However, the onset of the modern era of PV solar cells did not occur until in the mid-twentieth century, when D. Chapin, C. Fuller, and G. Pearson at Bell Laboratories demonstrated solar cells based on p-n junctions in single crystal Si with efficiencies of 5–6%.⁹ This original single-crystal Si based photo-voltaic cells still dominates the commercial PV market.

From the mid 1950s to the early 1970s, PV research and development (R&D) was directed primarily toward space applications and satellite power. In 1973, the oil embargo in that year caused serious concern about energy supply and the demand. This attracted several researchers, muti-national companies, and governmental organizations to initiate the research and
development focused in solar energy quest. The establishment of U.S. Department of Energy (DOE), along with its Photovoltaics Program, is one of those initiatives triggered by the crisis in the energy supply and the demand in the late 1900s. These organizations started to support solar energy research and their development and the “terrestrial solar cell industry quickly evolved”. As a result, the annual PV power production has seen exponential increase in last two decades (Figure 1); and the current total global PV installed capacity is about 3 GWp, where Wp stands for “peak watt”. The “peak watt” (Wp) rating is the power (in watts) produced by a “solar module illuminated under the standard conditions: 1,000 W/m2 intensity, 25°C ambient temperature, and a spectrum that relates to sunlight that has passed through the atmosphere when the sun is at a 42° elevation from the horizon (defined as air mass [or AM] 1.5; i.e., when the path through the atmosphere is 1.5 times that when the sun is at high noon). Due to the varying sun light intensity depending on the different time of the day or the season and clouds over the sky, the average electrical power produced by a solar cell over a year is about 20% of its Wp rating.

Figure 1.1. World photovoltaic cell power production per module production (in MWp) Vs time.
1.4. Challenges and Current Status in Solar Energy

Although, solar energy production incurs no fuel expenses, it involves tremendous capital costs for installation, and the efficiency of the solar cells are far from being competitive to conventional fossil fuels. A typical single-crystalline Si solar cell, with an efficiency of 10%, costs ~ $3.50/Wp which is much higher than a standard $0.10/Wp for the fossil fuel generated energy supply.\textsuperscript{11} The cost for the electricity produced by the cell is calculated by amortizing the capital cost over the lifetime of the cell and considering the total electrical output energy produced over the cell lifetime. The efficiency of solar cells, thus, directly impacts the overall electricity cost as solar cells with higher-efficiency will produce more electrical energy per unit of cell area over the cell lifetime. Figure 2 depicts the cost per peak watt (Wp) of electricity against the efficiency of the solar cells. The area labeled I in Figure 2 represents the first generation (Generation I) of solar cells and covers the range of module costs and efficiencies for these cells. Evidently, second and third generation of solar cells with much higher efficiencies has to be devised to reach the goal of producing electricity at a standard cost of ~ $0.10/Wp.\textsuperscript{12,13}

Researchers have investigated the scope of different types of solar cells to meet this goal. The efficiencies of the solar cells have definitely made significant progress in last few decades, but it is still far from realizing its benchmark. A plot of improvements in solar cell efficiencies versus time (figure 3) shows that the solar cells efficiencies have progressed to as high as 15-16%, at least under the laboratory conditions. The plot includes the various PV technologies of single-crystal Si, thin films, multiple-junction cells, and emerging technologies — such as dye sensitized, nano-crystalline TiO2 cells, and organic compounds based solar cells.
The emerging technologies, such as multi-junction solar cells that utilize the multi-photon absorbing capabilities of the solar cells, show efficiencies in the order of 50-60%. However, none of the solar cells have yet practically reached the desired efficiency, at least not at the industrial level.
More than 99% of today’s PV production is Si based, and the efficiencies of solar cells depend on the extent of purity of the Si crystals. Due to the inherent costs of making and handling Si wafers the production cost is unusually high. Furthermore, the improvements in performance of the Si based solar cells are presently limited because researchers do not yet understand the mechanisms of this improvement. Therefore, efforts have been made to replace Si crystals with other organic, inorganic, polymeric, and mixtures of both to reduce the cost of production of the materials for solar cells. Such materials are inexpensive as compared to the Si crystals, and they provide additional advantages over the conventional solar cells in the form of flexibility, and durability. However, such materials have not yet showed the desired efficiencies, and researches are at present focused on designing novel materials in this endeavor.

1.5. How do the Solar Cells Work?

All routes for utilizing solar energy exploit the functional steps of capture, conversion, and storage. The sun’s energy arrives on Earth as radiation distributed across the color spectrum from infrared to ultraviolet. The energy of this radiation must be captured as excited electron-hole pairs in a semiconductor, a dye, or a chromophore. Excited electrons and holes can be tapped off for immediate conversion to electrical power, or transferred to biological or chemical molecules for conversion to fuel.

Photovoltaic cells generally consist of a light absorbing molecule that will only absorb solar photons above certain minimum photon energy. This minimum threshold energy is called the “energy gap” or “band gap” (Eg); photons with energies above or below the band gap pass through the absorber, while photons with energies equivalent to the band gap are absorbed. The light absorber in PV cells can be either inorganic semiconductors, organic and polymeric molecular structures, or a combination of both. In inorganic semiconductor materials, such as Si,
electrons (e-) have energies that fall within certain energy ranges, called bands. The energy ranges, or bands, have energy gaps between them. The band containing electrons with the highest energies is called the valence band. The next band of possible electron energies is called the conduction band; the lowest electron energy in the conduction band is separated from the highest energy in the valence band by the band gap. When all the electrons in the absorber are in their lowest energy state, they fill up the valence band, and the conduction band is empty of electrons. This is the usual situation in the dark. When photons are absorbed, they transfer their energy to electrons in the filled valence band and promote these electrons to higher energy states in the empty conduction band. There are no energy states between the valence and conduction bands, which is why this separation is called a band gap and why only photons with energies above the band gap can cause the transfer of electrons from the lower-energy-state valence band into the higher-energy-state conduction band. When photons transfer electrons across the band gap, they create negative charges in the conduction band and leave behind positive charges in the valence band; these positive charges are called holes (h+). Thus, absorbed photons in semiconductors create pairs of negative electrons and positive holes. In a PV cell, the electrons and holes formed upon absorption of light separate and move to opposite sides of the cell structure, where they are collected and pass through wires connected to the cell to produce a current and a voltage — thus generating electrical power.
1.6. **Types of Solar Cells.**

Photovoltaic cells can be classified into three categories based on the types of materials used in them – (1) inorganic solar cells, based on solid-state inorganic semiconductors; (2) organic solar cells, based on organic semiconductors; and (3) photoelectrochemical (PEC) cells, based on interfaces between semiconductors and molecules. The organic, polymer, and photoelectrochemical solar cells have drawn recent attention due to their low cost of production. An organic or polymer solar cell (Fig 1.6) typically consists of an active light absorbing material sandwiched between metallic contact cathode layer (usually Ag, Au, Al) and a conducting layer followed by a transparent anode layer. The sandwich, called a p-n junction, allows the photogenerated electrons and holes to be separated and transferred to external wires for electrical power production.
1.7. **Organic/Polymer Solar Cells: Advantages and Challenges.**

Solid-state PV cells based on carbonaceous (organic and polymer) matter were first discovered 20 years ago. Early work on organic photovoltaics using molecular-based systems demonstrated the concept; however energy conversion efficiencies were low. Considerable excitement in this area was generated by reports published in the early-1990s, when Gratzel et. al. showed 1.6% efficient dye-sensitized solar cells, and in the mid-1990s, when Yu et. al. published 2.9%-efficient cells based on conducting organic polymers mixed with derivatives of C60 (fullerene). During the past two decades, refinements in the chemical components of the cells, improvements in cell physics and device engineering have led to solar cells that demonstrate solar-to-electrical-power conversion efficiency as high as 5%. The advantages and motivations for potential improvement here are significant: low-cost, clean, lightweight, large-
area, flexible, high-efficiency solar cells. The basic research goal is to develop ample understanding of such materials and structures to improve their conversion efficiency by a factor of 2–5, and thus obtain robust, scalable efficiencies of 15–25% in cheap, plastic-type solar cells.

The basic principle of operation in an organic PV cell is that illumination of a mixture of electron-rich (donor) and electron-poor (acceptor) species leads to separation of (+) and (-) charge carriers. Collection of these carriers at electrodes produces an electrical current that can do work on a load in an external circuit. Although the basic principles behind the operation of organic PV cells and conventional p-n junction cells are similar, the details of key events, such as charge carrier generation and charge transport, are very different in the organic cells. Consequently, the basic understanding of the physics and chemistry of organic PV systems lags behind that of conventional p-n junction devices. The molecules and materials from which these devices are made vary considerably, with polymers, organic molecules, inorganic molecules, quantum dots, and other nanostructures all contributing equally to the field. The large array of options provides ample scope for researchers to develop novel solutions for improving device performance.

Despite the promise of organic solar cells, significant challenges must be overcome to develop molecular structures and cells that operate efficiently and are stable for long-term operation under one-sun solar conditions. Four key aspects need to be addressed to improve the efficiencies of organic solar cells:

Photon Energy Management in Organic and Hybrid Photovoltaic Devices: Current state-of-the-art organic and hybrid PV cells produce a photovoltage that is considerably less than 32%, the thermodynamic limit calculated by Shockley and Queisser (1961). Solving this problem should lead directly to a threefold increase in overall cell efficiency. Although recent investigations have
shed some light on the reasons for the low photovoltage, researchers lack a clear understanding of the factors that control this parameter.

Organic and Hybrid Photovoltaic Layers and Cell Architectures: Organic-inorganic hybrid layers will provide opportunities for the use of different building blocks in the fabrication of PV cells, allowing researchers to combine the best properties of organic and inorganic structures. The fabrication methods developed could allow the assembly of high-efficiency tandem device structures to extract energy from the different wavelengths of sunlight, thereby leading to a substantial improvement in solar-to-electrical energy conversion. The light-absorbing and semiconducting properties of quantum structures (e.g., nanoparticles, nanorods, and more complex structures), combined with the range of properties accessible with organic semiconducting polymers, afford new active layers for PV cells that could enhance efficiency.\textsuperscript{23}

Chemical Discovery and Synthesis: Improved molecular, polymer, and nanocrystal building blocks are needed to address such issues as (1) light harvesting across the visible and near infrared spectrum, (2) electron donor and acceptor properties, (3) electronic (semiconducting) properties, (4) charge transport in the solid state, and (5) nonlinear optical properties.\textsuperscript{24,25} While many materials are already available, systematic chemical discovery and synthesis are needed to broaden the scope of materials and to allow the development of improved synthetic methods to lower costs and improve purity.\textsuperscript{6}

Properties of Organic and Hybrid Photovoltaic Structures: Many basic science questions need to be addressed to better understand the fundamental steps involved in energy conversion in organic and hybrid systems. First, the morphology of the solid-state PV film needs to be defined, then researchers need to develop an understanding of the relationship between the morphology and the structure of the building blocks, the nature of the substrate, and the deposition method used to
fabricate the film. Physical methods are needed to elucidate the thermodynamics and dynamics of the fundamental steps of light absorption and exciton generation, charge carrier generation, and charge carrier diffusion to the collector electrodes. To obtain cells that are durable enough for long-term use, photostability and photochemical degradation pathways need to be improved.\textsuperscript{26}

*Charge Carrier Annihilation at the Interface:* An intrinsic feature of the organic solar cell is the diversity of interfaces; either between dissimilar organic materials acting as the photoconversion layer; with the contact electrodes, where transparency and good ohmic contact are essential; or between multiple layers in a tandem design, where carrier annihilation must be facilitated. These features provide additional challenges that can be met through molecular design and an understanding of electronic interactions at an interface.\textsuperscript{6}

1.8. **Should Nanotechnology be a Viable Alternative?**

During the last two decades, nanomaterials have been studied extensively in developing new strategies for light energy conversion. It is well established that quantum confinement of an electron by the potential wells of nanoscopic assemblies provides a powerful and versatile means to control the electrical, optical, magnetic, and thermoelectric properties of solid state functional materials.\textsuperscript{27} Consequently, several organic and inorganic nanoscopic materials have been envisaged for their potential application in effective next generation solar energy conversion devices. This regime of nanoscopic materials includes the study of metal semiconductor clusters, metal-organic nano-composites, and many other novel materials. Recent efforts in developing well defined geometrical shapes over the 0-dimention to 3-dimentional nano architecture have widened the scope and span of this science.
Three major approaches\(^7\) (Fig.3) have been envisioned that utilize nanoscopic materials for solar energy conversion. These approaches are based on the nature’s cue obtained from photosynthesis. In photosynthetic organisms, light is harvested by an antenna system consisting of pigment protein complexes. The excitation energy captured therefrom, is transferred to the reaction center protein which converts that excitation energy into electrochemical potential energy through an excited state electron transfer mechanism.\(^1\) The nano-technological approach involves similar light harvesting and electron transfer processes. However, nano-technological approaches so far are not as efficient as natural photosynthesis.

![Diagram showing different solar energy conversion methods](image)

**Figure 1.6.** Technology Vs Nature’s cue.

Among the three major approaches for solar energy conversion, the first basically mimics the photosynthetic process with electron transfer occurring in the donor-acceptor assemblies and clusters. The second involves semiconductor assisted photocatalysis producing fuels such as hydrogen. The third, and probably the most promising category is the nano structured semiconductor based solar cell—the Photochemical Solar Cell. Various promising strategies have been developed in recent years to construct photochemical solar cells. Using quantum dots has been one of them. The use of semiconductor quantum dots in solar cells has attracted much
recent attention because of specific advantages. The most important aspect of quantum dots is that their size quantization that offers a tunable visible response and variable band offset to modulate the vectorial charge transfer across different sized particles.\textsuperscript{27}

1.9. **Quantum Dots (QDs).**

Quantum Dots are zero-dimensional (0D) nanostructured semiconductors with excitons being confined in all the three spatial dimensions.\textsuperscript{27} These can also be viewed as an ordered assembly of low band gap semiconductor nanostructures. Endowed with the quantum confinement of the exciton, QDs have properties that are between bulk semiconductors and those of discrete molecules. An exciton is a Coulomb correlated electron-hole pair; excited by a photon, the electron at the valence band of a semiconductor hops into the conduction band leaving a hole (electron deficiency) at the valence band (Fig.4). This pair, the electron (at the conduction band after excitation) and the hole (generated at the valence band) is called an exciton; it is short-lived and the electron-hole pair is held by Coulomb’s force.

![Figure 1.7. Exciton formation upon excitation with photon.](image)

1.10. **Scopes and Goals of this Dissertation**

There are many advantages of inorganic materials being used in electronic devices, e.g. solar cells. The advantages are actually attributed to the high intrinsic charge carrier mobilities associated with inorganic semiconductors.\textsuperscript{28} However, there are certain disadvantages that cause
some limitations to the widespread expansion in the use of inorganic semiconductors. The high costs imposed by processing that involves elevated temperature, high vacuum, and several costly lithographic techniques being one of them. Organic Solar Cells that use polymers have been investigated as a low cost alternative to their inorganic counterparts.\textsuperscript{29} Unfortunately, the charge carrier mobilities for most of the organic polymers are extremely low,\textsuperscript{30} typically below $10^{-4}$ Cm$^2$V$^{-1}$S$^{-1}$. Again the charge carrier mobility of such materials depends on inefficient charge hopping mechanisms, which can often be trapped by the presence of oxygen and by several other factors.\textsuperscript{31,32} So, the use of organic polymers for solar cell fabrications is far from being practical. Hence, one way to overcome this limitation of charge carrier mobility is to combine polymers with an inorganic semiconductor.\textsuperscript{28} Charge transfer now becomes favored between high electron affinity inorganic semiconductor and relatively low ionization potential organic molecules or polymers.\textsuperscript{33,34} Charge transfer rates are found to be remarkably faster for the organic compounds bound to the nanocrystalline or bulk inorganic semiconductors; e.g. quantum dots which have high densities of electronic states.\textsuperscript{35} Besides, the nanoscale nature of light absorption and photocurrent generation in the solar energy conversion, the advent of methods for controlling inorganic materials in the nanometer scale has opened new opportunities for the development of new generation solar cells. So, essentially conductive polymer-QD organic-inorganic hybrid composites have attracted significant attention.

The goal of this dissertation is to prepare novel conductive polymer-QD organic-inorganic hybrid composites to study and elucidate the thermodynamics and kinetics of the fundamental steps of light absorption and exciton generation, charge carrier generation in a hybrid solar cell to contribute towards a better understanding of the solar cell system, and hence to improve their performances.
References


Chapter 2

Photo-induced Hole-transfer Forming Polymer: Quantum Dot Composites

2.1. Motivation.

Utilizing solar energy involves three key steps: capture of photons, conversion into a functional form of energy, and storage of that energy. Use of nano-structured quantum dots (QD) has attracted attention in devising photo-electrochemical solar cells for this purpose. The most important aspect in the use of semiconducting QDs is due to its size quantization of the absorption of solar radiation can be adjusted by varying the size of the QD particles.\textsuperscript{1} This allows easy modulation of the photon capture and efficiency. However, the high cost and complex technologies associated with the processing of such materials into a photo-electrochemical device limits their use. Use of polymers, on the contrary, alleviates these complexities, but only at the cost of charge carrier mobilities.\textsuperscript{2-5}

Combining polymers with semiconducting QDs can, therefore, be a potential solution in this issue.\textsuperscript{6} The charge transfer between high electron affinity inorganic semiconductors and relatively low ionization potential polymers facilitates the charge transport though the composites.\textsuperscript{7-9} Processing becomes cheaper as it does not require elevated temperature, high vacuum, or complex technologies.

Charge transport in such composites is, in fact, higher than in inorganic semiconductors alone, due to the electronic coupling between the nano-crystalline inorganic semiconductors and
polymers. However, charge transport in these composites depends on their morphologies and interactions at the bulk hetero-junctions of the composites. Understanding and ensuring a suitable morphology at the interface of the QD and the polymer is extremely important. Besides, comprehension of the charge transfer mechanism within the composite material is crucial as it potentially affects the photon *capture* and hence, the efficiency of the solar cell devices.\textsuperscript{10-12}

Therefore, the focus of this project will be:

(i) To prepare the nano-composites using QD and conductive polymers.
   a. We chose cadmium selenide (CdSe) as the semiconducting QD, and polythiophene as the polymer in this case.

(ii) To ensure suitable electronic interaction between the CdSe QD and polythiophene we have adopted a photo-induced hole transfer assisted polymerization mechanism from the surface of the QD.
   a. Thus, we designed a new method for preparing polymer: QD composites that will have suitable electronic interaction between the QD and the polymer through proper chemical linkage.

(iii) To Study the kinetics of the electron transfer mechanism in the composite materials in order to further understand the mechanisms involved in solar cells, and hence, to be able to improve the performances of solar cells.

2.2 Overview.

Conductive polymer–QD composites possess dual properties- those of the polymer and of the QD.\textsuperscript{13-16} Given that interfaces between polymer and QDs have a substantial effect on the electronic interaction, and QD aggregation poses a major problem in preparations of composite
materials, mere physical blending of the components does not produce products with the desired properties.\textsuperscript{17,18} Instead, blending just produces a mixture without substantial electronic interactions between QD and the polymer. Hence, achieving a proper dispersion of the QD particles in the polymer matrix is necessary.\textsuperscript{19} There are two popular methods for achieving proper dispersion: ‘grafting on’ and ‘grafting from’ methods. In the ‘grafting on’ process, pre-synthesized ligands are attached to the QD surface by ligand exchange or are directly used as surfactants during the reduction stage in the formation of nanomaterials.\textsuperscript{20-22} In contrast, the ‘grafting from’ method involves polymer chain growth from a QD surface.\textsuperscript{23,24} Both techniques have been investigated exclusively and proved to be viable methods for solar cell fabrication; e.g. CdSe/poly(3-hexylthiophene) with an amino terminus has been prepared by ‘grafting on’ method and is reported to show improved performance, while the ‘grafting from’ method was successfully used to prepare CdSe/poly(\textit{para}-phenylenevenylene) composites.\textsuperscript{23-25}

In this chapter we discuss the preparation of conductive polymer – QD composites by visible light photopolymerization. Efficient hole transfer from the QD core to the ligand is observed and the charge separated state initiates the polymerization without the use of a conventional photoinitiator. The mechanism and kinetics of the hole transfer process was studied using steady-state and transient absorption spectroscopic techniques.

\textbf{2.3. Preparation and Characterization of CdSe Quantum Dots.}

CdSe nanocrystals were synthesized from CdO and elemental Se using a kinetic growth method where particle size depends on the reaction time.\textsuperscript{26,27} The samples were, therefore, collected at different time spans. By doing this, we obtained a colloidal suspension of CdSe quantum dots of increasing size. When viewed under long wavelength UV illumination, CdSe quantum dot
suspensions fluoresce with colors varying from blue to red (Fig.2.1). The UV absorption and emission are also recorded for these quantum dots (Fig.2.2).

Figure 2.1. A representative picture of CdSe quantum dot suspensions under long wavelength UV illumination. The color of the dots varies from green to yellow. (Several other quantum dots fluorescing at ranging from blue to red were also prepared).

Figure 2.2. Absorption (left) and emission (right) spectrum of quantum dots; the quantum dots are excited at 470nm for the emission spectra. (The numbers are in the order the samples are collected, with higher number signifying larger size).
2.4. Surface Modification. Two ligands, 5-mercapto-2,2'-bithiophene (BTSH) and 5-(5-mercaptopentyl)-2,2'-bithiophene (BTC₅SH) were chosen as the surface modifiers for this study. BTSH was synthesized according to literature procedures, while we synthesized BTC₅SH (Scheme 2.1).²⁸,²⁹

![Scheme 2.1. Synthesis of BTSH and BTC₅SH.]

BTSH and BTC₅SH functionalized CdSe QDs (BTSCdSe and BTC₅SCdSe) (Fig. 2.3) were prepared by ligand exchange reactions. TOPO modified CdSe QD were mixed with BTSH or BTC₅SH in toluene and stirred for three hours. The mixture was then kept in the dark for two days after which the solution was triturated with methanol and the QD isolated by centrifugation. The precipitates were washed with methanol several times to remove all the displaced TOPO, unreacted ligands, and the final residues dissolved in toluene.

![Figure 2.3. Structures of ligands and functionalized QD discussed in this chapter.]

Figure 2.3. Structures of ligands and functionalized QD discussed in this chapter.
The characteristics of the ligand’s absorption are evident in the UV absorption and emission spectra of BTSCdSe and BTC₅SCdSe (Fig. 2.4). Electronic interaction between ligand and the CdSe QD core in the ground state is weak. The number of BTSH or BTC₅SH attached on the surface of CdSe QD is estimated based on the absorption spectra and extinction coefficients ($\varepsilon$) ($\varepsilon_{560}$: $\sim 2.0 \times 10^5$ M⁻¹cm⁻¹ for CdSe QD, $\varepsilon_{320}$: $\sim 8.5 \times 10^3$ M⁻¹cm⁻¹ for BTSH and $\varepsilon_{310}$: $\sim 1.0 \times 10^4$ M⁻¹cm⁻¹ for BTC₅SH. The $\varepsilon_{320}$ and $\varepsilon_{310}$ values were calculated using 9,10-diphenylanthracene as a reference) and found to be $\sim 100$. The emission spectra of BTSCdSe and BTC₅SCdSe are similar to that of the CdSe QD with greater quenching observed in case of BTSCdSe. This suggests that some energy or charge transfer occurs between the ligand and the CdSe QD core.

![Image](90x300 to 522x456)

**Figure 2.4.** UV absorption spectra (a) of CdSe QD (black line), BTSCdSe (red line), BTC₅SCdSe (blue line), BTSH (red short dash line) and BTC₅SH (blue short dash line) and emission spectra (b) of CdSe QD (black line), BTSCdSe (red line) and BTC₅SCdSe (blue line), excitation at 478 nm.

### 2.5. Kinetics of Hole Transfer and Suggested Mechanism.

Since the ligand has no absorption at ≥ 450 nm, only the CdSe core will be excited when either BTSCdSe or BTC₅SCdSe are irradiated at 478 nm. Besides, BTSH and BTC₅SH have higher singlet state energies (estimated from the absorption and/or emission spectra) and lower oxidation potentials [BTSH and BTC₅SH have similar oxidation values $\sim +1.1$ V vs NHE,
measured by cyclic voltammetry (EC epsilon, BASI) with silver chloride electrode as reference electrode and platinum as working electrode (Fig. 2.5)] than do the CdSe QD (+1.2 ~ +1.7 V vs NHE),30-32 hole transfer from the CdSe QD core to BT ring is possible.

Figure 2.5. Cyclic voltammogram of BTSH (ferrocene used as reference).

Femtosecond and nanosecond time-resolved transient absorption measurements indicate that hole transfer from the CdSe QD core to BT occurs efficiently in BTSCdSe but not in BTC$_5$SCdSe. Hence, BTSH is linked on the QD surface through its thiol (-SH) and the holes produced during excitation of QD are transferred into the bithiophene moiety leading to the formation of charge separated state; and thus a radical cation ($^+\text{BTSCdSe}$) is formed (scheme 2.2).

Scheme 2.2. A schematic presentation of the hole transfer in BTSCdSe.
Femtosecond transient absorption measurements (excitation at 478 nm and spectra obtained at 800 ps) and the decay (a relative slow decay in case of BTSCdSe) show (Fig.2.6) the formation of charge separated state, the radical cation (\textsuperscript{+}BTSCdSe\textsuperscript{−}).

![Figure 2.6. Femtosecond transient absorption spectra (a) CdSe QD (black line), BTSCdSe (red line) and BTC\textsubscript{5}SCdSe (blue line); and the decay (b) of CdSe QD (black line), BTSCdSe (red line) and BTC\textsubscript{5}SCdSe (blue line), excitation at 478 nm.](image)

A nanosecond transient absorption measurement was also carried out to confirm the formation of radical cation (\textsuperscript{+}BTSCdSe\textsuperscript{−}). A new transient absorption peak around 620 nm (\(\tau = 415 \pm 70 \text{ ns}\)), which is not quenched by oxygen (Fig. 2.7), is assigned to the charge separated state of BTSCdSe (\textsuperscript{+}BTSCdSe\textsuperscript{−}). As a result of the strong ground state absorption of CdSe QD around 570 nm, absorption of \textsuperscript{+}BTSCdSe\textsuperscript{−} is observed only in the longer wavelength region. Kinetic decay at 620 nm is found similar to the literature\textsuperscript{33-38} and hole transfer from the CdSe QD core to the ligand occurs in a few picoseconds (Fig. 2.7 inset). Rapid decay within 10 ps (Fig. 2.7 inset) is likely due to hole migration in BTSCdSe\textsuperscript{33,34}.
Figure 2.7. Nanosecond transient absorption measurements, excitation at 532 nm and kinetic decay of BTSCdSe measured at 620 nm, in air (black line), oxygen (red line) and nitrogen (blue line). The bold black line is fit by first order exponential decay. Inset shows the kinetic decay measured at 620 nm in picosecond time scale.

The average hole transfer rate \( k_{ht} \) is calculated to be \( 1.57 \pm 0.08 \times 10^8 \) s\(^{-1}\) for BTSCdSe and \( 1.56 \pm 0.05 \times 10^7 \) s\(^{-1}\) for BTC\(_5\)SCdSe respectively, based on the average emission lifetimes using equation \( k_{ht} = 1/\tau_{av'} - 1/\tau_{av} \), where \( \tau_{av'} \) is average lifetime of BTSCdSe or BTC\(_5\)SCdSe, and \( \tau_{av} \) is the average lifetime of CdSe QD (Table 2.1). Methylene groups between the BT ring and CdSe QD core inhibit hole transfer with the average hole transfer rate of BTC\(_5\)SCdSe being ten times less than that of BTSCdSe.

<table>
<thead>
<tr>
<th>QD</th>
<th>Emission lifetimes(^{[a]})</th>
<th>Average lifetime(^{[b]})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \tau_1 / \text{ns} )</td>
<td>( \tau_2 / \text{ns} )</td>
</tr>
<tr>
<td>CdSe</td>
<td>6.30 (21%)</td>
<td>31.98 (79%)</td>
</tr>
<tr>
<td>BTSCdSe</td>
<td>1.05 (30%)</td>
<td>7.24 (70%)</td>
</tr>
<tr>
<td>BTC(_5)SCdSe</td>
<td>5.02 (29%)</td>
<td>25.81 (71%)</td>
</tr>
</tbody>
</table>

Table 2.1. Average Lifetimes. (a) The emission decay was analyzed using the expression \( F(t) = a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2) \), where \( \tau_1 \) and \( \tau_2 \) are the lifetimes. The values in the parentheses indicate the fraction (\%) of the corresponding lifetime component. (b) The average lifetime value was calculated using the expression \( \tau_{av} = \Sigma a_i \tau_i^2 / \Sigma a_i \tau_i \).
2.6. Observation.

Since BT radical cation coupling is known to produce polythiophene and polymerization of BTSH modified gold nanoparticles has been previously reported,\textsuperscript{39,40} the reaction of `BTSCdSe` coupling to produce a polymer-QD composite is likely. The UV absorption changes of BTSCdSe and BTC\textsubscript{5}SCdSe after ≥450 nm irradiation for 30 minutes is shown in Fig. 2.8. The spectrum of BTSCdSe increased and shifted from 323 nm to 315 nm. The shoulder absorption around 390 nm is decreased and absorption around 450 nm is increased indicating possible polymerization of BTSCdSe.\textsuperscript{39} No obvious changes are observed in the case of BTC\textsubscript{5}SCdSe.

![Figure 2.8](image.png)

*Figure 2.8. UV absorption spectra of BTSCdSe before (black line) and after (red line) and BTC\textsubscript{5}SCdSe before (blue line) and after (green line) exposure to light [≥450 nm]*

Polymerization of BTSCdSe was confirmed by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) measurements (Fig. 2.9). Three dimensional nano structures are observed in the case of BTSCdSe, but not in the case of BTC\textsubscript{5}SCdSe. The emission
intensity is different before and after the irradiation of BTSCdSe, but little change is observed in the case of BTC$_5$SCdSe (Fig. 2.9 d). The photos are taken under the long wavelength UV lamp (UVGL-58, Mineralight Lamp, Multiband UV-254/366 nm, US Entela).

![Figure 2.9. TEM images of BTSCdSe before (a) and after (b) irradiation. SEM image of BTSCdSe after irradiation (c). Photos taken (d) under a 366-nm UV lamp, A: CdSe QD; B: BTSCdSe before irradiation; C: BTSCdSe after irradiation; D: BTC$_5$SCdSe before irradiation; E: BTC$_5$SCdSe after irradiation.]

2.7. Conclusion.

We observe efficient hole transfer from a CdSe QD core to ligand in BTSCdSe caused by visible light irradiation. The average hole transfer rate constants are $1.57 \pm 0.08 \times 10^8$ s$^{-1}$ in BTSCdSe and $1.56 \pm 0.05 \times 10^7$ s$^{-1}$ in BTC$_5$SCdSe respectively. Since, interspersing methylene groups inhibit the reaction, hole transfer with BTC$_5$SCdSe is ten times slower than is that of BTSCdSe and does not initiate polymerization. $^+$BTSCdSe$^-$ ($\lambda \geq 415 \pm 70$ ns) acts as a building block and initiator for thiophene polymerization, and no conventional photoinitiator is needed.

Hence, as QD are covalently linked to the polythiophene, there is no loss in conformational entropy caused by the polymer chain stretching around the nanoparticle, and a
good QD distribution within the matrix is expected. In addition, since QDs are pre-synthesized, the particle size can be controlled. The number of ligands on the QD surface can be adjusted by changing the ligand concentration and exchange reaction time, and formation of a QD chain or QD network is possible. Hence, this is a facile method for the preparation of conductive polymer-QD composites using visible light irradiation. The following scheme represents the process.


2.8. Experimental Section.

2.8.1. Preparation of CdSe Quantum Dots.\textsuperscript{26,27}

A stock solution of Se is prepared by combining 30mg of Se and 5ml of octadecene (tech., 90%) in a 10ml round-bottom flask clamped over a stirrer hot plate. To this mixture, trioctylphosphine (0.4ml) is added, with stirring. The solution is warmed to 40°C to accelerate the dissolution of
Se. The solution is then stored at room temperature in a moisture free stoppered round bottom flask.

To prepare the Cd precursor, CdO (13mg) is taken in a 25ml round-bottom flask clamped in a heating mantle. To the same flask, 0.6ml of oleic acid and 10ml of octadecene are added. The mixture is then heated to 225°C. Once the mixture reaches 225°C, 1ml of Se stock solution is added quickly. Since the crystal growth rate is very fast initially, samples are quenched at frequent time intervals. About 0.5-1 ml of resulting mixture is simply removed each time from the round-bottom flask using pasteur pipettes to quench the sample and to get quantum dots of different sizes. The first sample is collected within 10 seconds from the time when Se was added to the hot Cd precursor. Initially a few other samples (about 4-5) are also collected within a time span of 1 minute. Considering that crystal growth slows as they grow in size, the time intervals between sample collections are next increased to 30 seconds to 1 minute.

2.8.2. Synthesis of 5-(5-mercaptopentyl)-2,2’-bithiophene (BTC$_5$SH).

Dry, distilled tetrahydrofuran (20 ml) and 2,2’-bithiophene (1 mmol) were added in a dry round bottom flask. The mixture was flushed with argon for 15 minutes and cooled to 0 °C with ice. To this mixture tert-butyllithium in hexanes (1.2 mmol) was slowly added while stirring vigorously. The mixture was warmed to room temperature while stirring for five hours. 1,5-Dibromopentane (1.3 mmol) in tetrahydrofuran was added and the mixture refluxed for five hours after which it was cooled and ammonium chloride solution was added. The mixture was separated using ethyl acetate, dried and the solvent evaporated. A green, oily product [5-(5-bromopentyl)-2,2’-bithiophene] was obtained (70 %). The HRMS (EI) measured mass value is 313.9796 and calculated mass value is 313.9799. The 5-(5-bromopentyl)-2,2’-bithiophene (0.7 mmol) was mixed with thiourea (1.5 mmol) in dry ethanol and the mixture refluxed for 24 hours. The
mixture was then cooled to room temperature, sodium hydroxide solution added and the resulting mixture refluxed for another five hours. Subsequently the mixture was neutralized with hydrochloric acid, extracted with ether, washed with water several times and dried over MgSO₄. After evaporation of the solvent, crude product was subjected to silica gel column (20% dichloromethane in hexanes) producing pure white powder (90 % yield). ¹H NMR (300 MHz, CDCl₃) δ 1.35 (1H), 1.5 (2H), 1.7 (4H), 2.5 (1H), 2.7 (1H), 2.8 (2H), 6.7 (1H), 6.95 (2H), 7.05 (1H), 7.15 (1H); ¹³C NMR (300 MHz, CDCl₃) δ 24, 27, 30, 31, 33, 122.5, 123, 123.2, 128, 135, 138, 145; The HRMS (EI) measured mass value is 268.0415 and calculated mass value is 268.0414.

2.8.3. Electron Microscopy.

TEM images were taken on a ZEISS EM10 transmission electron microscope operating at 80 kV. The nanoparticles were dropcast from toluene solutions onto formvar-carbon coated 300-mesh copper grids and air-dried before viewing under the TEM. SEM images were recorded on a Hitachi S-2700 electron microscope at 15 kV. Samples for SEM were prepared by placing a few drops of the nanoparticle solution onto a glass cover slip placed on an aluminum stub. The samples were allowed to dry before viewing under the electron microscope. To enhance contrast and the quality of the SEM images, samples were sputter-coated with gold/palladium.

2.8.4. Ultraviolet-Visible Absorption, Excitation and Fluorescence Spectroscopy.

Ultraviolet-Visible (UV) absorption spectra were measured using MultiSpec-1501 (Shimadzu). The excitation spectra, emission spectra and emission lifetimes were measured using a SPEX Fluorolog-3 (Jobin Yvon Inc.) equipped with Time Correlated Single Photon Counting (TCSPC).

2.8.5. Femtosecond Transient Absorption Measurements.
The femtosecond time-resolved apparatus at the Ohio Laboratory for Kinetic Spectrometry at Bowling Green State University, USA, has been described elsewhere. A Spectra-Physics Hurricane system was used as the laser source. The pump beam 478 nm was focused into the sample cell where it was overlapped with the probe beam white light continuum (effective useful range, 460–800 nm) at an angle of ca. 5°. The probe light was coupled into a 400 µm optical fiber connected to a CCD spectrograph (Ocean Optics, PC 2000). The delay line and the CCD spectrograph were computer-controlled by a LabVIEW (National Instruments) software routine developed by Ultrafast Systems, LLC. The sample was flowed through a quartz cell with an optical path of 2 mm that was connected to a solution reservoir and a pump system (Micropump Corp.). All measurements were carried out at room temperature, 20 ± 2 °C.


Nanosecond transient absorption measurements were performed on a kinetic spectrometric system previously described. The excitation pulse (532 nm, 12-19 mJ/pulse) is the second harmonic of a Q-switched Nd:YAG laser. The excitation pulse width is ~7 ns. Transients produced are followed temporally and spectrally by a computer-controlled kinetic spectrophotometer. The sample solutions were adjusted with absorbance of 0.15-0.33 at the excitation wavelength in 1-cm² quartz cuvettes. Fresh samples were used for obtaining each kinetic trace. All measurements have been made at room temperature.
References


Chapter 3

Poly-thiophene CdSe Quantum Dot Carbon Nanotube Composite Formation under Visible Light Irradiation

3.1. Motivation.

Silicon solar cells are expensive to make, install and maintain and polycrystalline semiconductor thin films, though less expensive, are inefficient; the search for the ideal solar cell continues.\(^1\) Polymer-based solar cells have the potential to deliver higher efficiency at a lower cost and can be easily made into flexible plastics.\(^2\)-\(^4\) Though polymer-based solar cells exist, cheap, stable and safe materials which can capture and efficiently transport photogenerated electrons/holes to external electrodes are still being sought.\(^5\)-\(^9\)

The advantages of using semi-conducting quantum dots (QDs) as solar energy conversion materials are their tunable bandgap and high absorption coefficients,\(^5\),\(^25\) multiple excitons (electron/hole pairs) generation with single photon absorption,\(^26\),\(^27\) easy formation of different forms - sheets or three-dimensional arrays - and finally their low cost. QDs can be produced in bulk via chemical manufacturing techniques. The crucial step to achieve high power conversion efficiency in QD based-solar cells lies in the rapid trapping of the exciton, or transfer of the electron or hole formed in the QD by absorption of a photon, to the external electrode before the exciton undergoes recombination. Efforts have been focused on the efficient electron or hole transfer from QD to acceptors. Conductive polymers such as polypyrrole, polyaniline, poly(paraphenylene vinylene) and polythiophene have \(\pi\) electrons in their backbone and are therefore good charge carriers. QD-conductive polymer inorganic-organic hybrid composites having dual properties, those of the QD and the conductive polymer, are expected to be suitable materials for
photovoltaic cells. Additionally, carbon nanotubes (CNT) with their high electronic conductivity, elasticity, and optical transparency are also considered to be efficient exciton trappers and transporters of charges. Two approaches for forming CNT-nanoparticle composites have been used. One method attaches presynthesized nanoparticles to the CNT; the other grows nanoparticles directly on the CNT. The preparation of conductive polymer-QD or CNT-QD composites is a complicated chemical procedure. There are few reports of fabrication of conductive polymer-QD-CNT composites. Herein we discuss the functionalization of CNTs using 5-mercapto-2,2'-bithiophene functionalized metal nanoparticles. A crosslinked polymer nanostructure is formed around the CNT under UV light irradiation. Furthermore, we investigate the morphology of the conductive polymer-QD-CNT composites to understand their behavior in photovoltaic cells.

3.2 Scope of the Project.

As mentioned earlier, we will discuss herein the formation of thiophene-QD-CNT composites by visible light irradiation. First, two kinds of bithiophene modified CdSe QDs - BTSCdSe and BTC$_5$SCdSe - were prepared. These bithiophene functionalized QDs were then mixed in with CNTs to prepare a heterogeneous mixture of functionalized QDs and CNTs. Photo-induced polymerization of 5-mercapto-2,2'-bithiophene functionalized QDs on the CNT surface was observed under light ($\geq$450 nm) irradiation onto the heterogeneous mixture of BTSCdSe and CNTs. The polythiophenes were attached on the CdSe surface via thiol (-SH) linkage, and the polythiophene chain wrapped around the CNTs upon light irradiation to form Polythiophene-QD-CNT composites. However, in case of BTC$_5$SH modified QDs, no polymerization was observed. Transmission electron microscopy (TEM), scanning electron microscopy (SEM),
energy dispersive X-ray (EDX), and an inverted confocal microscope were used to investigate the morphology of the polythiophene-QDs-CNTs composites.

3.3. Preparation of the Composite.

5-Mercapto-2,2′-bithiophene (BTSH) was synthesized according to literature procedures\textsuperscript{19,20} and 5-(5-mercaptopentyl)-2,2′-bithiophene (BTC\textsubscript{5}SH) was synthesized according to the synthetic procedure developed in our lab.\textsuperscript{21,22} Trioctylphosphine oxide (TOPO) modified CdSe QDs (~3.5 nm) were synthesized following the directions in previous reports.\textsuperscript{23,24} BTSH and BTC\textsubscript{5}SH functionalized CdSe QDs (BTSCdSe and BTC\textsubscript{5}SCdSe) were prepared by ligand exchange reactions. TOPO modified CdSe QDs were mixed with BTSH or BTC\textsubscript{5}SH in toluene and stirred for one day under argon. The solution was then triturated with methanol and the QDs isolated by centrifugation. The precipitates were washed with methanol several times to remove all displaced TOPO and unreacted ligands. The final residues were dissolved in toluene. Exchange reactions and subsequent procedures were carried out in the dark. Single wall CNT (SWCNT) (Pure HiPco, <15% Ash content) or multiwall CNT (MWCNT) (O.D. 10-30 nm, I.D. 5-10 nm, length 0.5-50 μm) (<1% w/w) were added into the BTSCdSe or BTC\textsubscript{5}SCdSe solution and sonicated for at least 15 minutes to ensure good dispersion of the CNTs and QDs. The solution was then was irradiated using a Xe lamp (ORIEL Corp. Model, 68805) equipped with a light filter (≥450 nm) for 30 minutes. After centrifugation, the precipitates were washed with methanol and toluene several times. The final precipitate was dispersed in toluene by sonication for product characterization. All solvents were ACS grade.

3.4. Observation.

Cai et al. recently reported\textsuperscript{21,22} efficient charge transfer from the bithiophene ligand to the nanoparticle core in 5-mercapto-2,2′-bithiophene (BTSH) functionalized nanoparticles upon
photo-irradiation of the ligand. As a result, the BTSH functionalized nanoparticles formed polythiophene-CdSe QD composites. Therefore, the heterogeneous mixture of CNTs and nanoparticles, when excited with visible light, undergoes photoinduced polymerization of BTSH modified nanomaterials from the excitation of the ligand with visible light; the polythiophene-nanoparticle composites then wraps around the CNTs.\textsuperscript{21,22} Hence, polythiophene-nanoparticle-CNT composites were prepared in this process, Figure 1. BTC\textsubscript{5}SH functionalized nanoparticles with CNTs, even after long irradiation with visible light, showed no polymerization as the electron transfer from the BTC\textsubscript{5}SH ligand to the nanoparticle core is not fast due to the separation of the aromatic bithiophene unit from the nanoparticle surface by five methylene groups.\textsuperscript{22}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{diagram.png}
\caption{The structures of BTSM, BTC\textsubscript{5}SM, and schematic drawing showing polymerization of BTSM upon UV irradiation (for metal nanoparticles) or visible light irradiation (for CdSe QDs). Insets show TEM images of BTSCdSe QD before (a) and after (b) ≥450 nm light irradiation.}
\end{figure}

Since bithiophene is $\pi$ electron rich, it is expected that BTSCdSe or BTC\textsubscript{5}SCdSe will attach to the surface of the CNT through $\pi-\pi$ interactions.\textsuperscript{1,10} The wrapping of polythiophene-nanoparticles on the surface of CNTs is likely. Figure 2 and 3 show the UV absorption spectra and TEM image
changes of BTSCdSe and BTC$_5$SCdSe in toluene solution before and after ≥450 nm light irradiation in the presence of CNTs.

**Figure 3.2.** UV absorption changes of BTSCdSe (a) and BTC$_5$SCdSe (b) toluene solution before (short dashed lines) and after (solid lines) ≥450 nm light irradiation in the presence of SWCNT (blue) and MWCNT (red). The inset in (a) show enlarged absorption region of 550 - 650 nm.
Obvious changes were observed in the UV absorption spectra and TEM images of BTSCdSe, Figure 2a and Figure 3a and b, but no such changes were observed in the case of BTC₅SCdSe, Figure 2b and Figure 3c and d. The UV absorption changes near 350 nm after irradiation suggests the polymerization of BTSCdSe.²¹,²² Quantum confinement in the CdSe nanoparticle core remains though the absorption of CdSe is slightly blue shifted and decreases after irradiation, Figure 2a inset. TEM images show clear morphological differences between the BTSCdSe modified CNT in the non-irradiated sample (smooth, hollow, only a few QDs on the surface, and QDs dispersed equally around the CNT) and the irradiated sample (rough, solid, and polymerized QDs are observed around the CNT), Figure 3a and b. Such morphological differences are not seen in the case of BTC₅SCdSe modified CNT, Figure 3c and d.

SEM and EDX analysis provides further proof that BTSCdSe is polymerized on the CNT surface. When excited on the CNT part of the composite (Figure 4 a), high surface concentration of Cd (14%), Se (2.3%), and S (1.3%) was observed indicating the wrapping of BTSCdSe on the
CNT surface, Figure 4a. This must have resulted from photopolymerization of BTSCdSe from the CNT surface forming a crosslinked photopolymerized nanostructure of polythiophene-QD composite around the CNT. On the contrary, when the background in the SEM plate was excited for EDX spectra, extremely low or no Cd, Se, or S concentration was observed on the surface. This is clear evidence supporting the hypothesis of the wrapping of polythiophene-CdSe QD composites around the CNT. Furthermore, it also confirms that the changes in the morphology after light irradiation, as seen in the SEM images, are not due to CNT aggregation merely.
Figure 3.4. SEM images and the EDX elemental analysis results on CNT surface (a) and away from the CNT surface (b) of the irradiated BTSCdSe/MWCNT sample. The sample solution is on a copper film placed on an aluminum stub. X-axis is energy in keV and Y-axis is intensity.

Although the emission of polymerized BTSCdSe was rather weak, under an inverted confocal microscope with excitation laser (532 nm) beam, the fluorescence images of polythiophene-CdSe-CNT composites were clearly observed with a laser focus scanning speed
of 4 ms/pixel, Figure 5d. The bright intensities in the confocal microscope images revealed the shape of the composites, Figure 5d A, B and C. Control experiments using BTC₂SCdSe and CNTs under identical conditions were also carried out. No photopolymerization was detected on the surface of CNT due to the absence of polymerization of BTC₂SCdSe. This again, further confirms the formation of composites in case of BTSCdSe and CNT mixture.

Figure 5. SEM images [(a), (b), and (c)] of the irradiated BTSCdSe/SWCNT sample, the EDX element analysis results at twisted CNT surface (a) and at the background (b) of the irradiated sample, and the inverted confocal microscope images of the irradiated BTSCdSe/MWCNT sample (d) [A, B, and C show the enlarged regions in (d)].
CdSe QDs are considered as a viable candidate for application as solar energy conversion materials. Figure 2a shows that polythiophene-CdSe-CNT retains the broad absorption originating from the CdSe QDs. Since the CdSe QDs are connected via chemical bond and linked to at least a $\alpha$-quatrathiophene unit, Scheme 1, the electron/hole formed in QD by absorption of a photon can be very efficiently transported to thiophene rings as has been proven by Cai et. al. in a previous report.\textsuperscript{22} Considering the photo-induced polymerization of BTSCdSe on the CNT surface, CNT will capture and transport charges to the external electrode efficiently.\textsuperscript{5,28} Therefore, thiophene-CdSe-CNT composite is a promising material for fabrication of solar cells. Construction and testing the film solar cell using thiophene-CdSe-CNT composite as an active material is going on. The method to prepare thiophene-CdSe-CNT composite discussed here is a facile way to produce ideal materials for the third generation solar cells.

3.5. Conclusion.

A thiophene-QD-CNT composite was successfully produced using visible light irradiation of BTSCdSe in the presence of CNTs. The formation of the composite is based on a photoinduced hole transfer between ligand and the QD core which forms polymeric QDs. TEM, SEM, EDX, and an inverted confocal microscope show clear evidence of successful formation of polymerized BTSCdSe wrapping around the CNT. As this composite has a broad absorption in the spectrum of the sun, together with the flexibility of conductive polythiophene and the efficient charge transfer of CNT, it is a promising material for making a hybrid polymer solar cell. As a comparison, no polymerization of BTC\textsubscript{5}SCdSe on the surface of CNT is observed.

3.6. Instrumentation.

**Electron Microscopy** TEM images were taken on a ZEISS EM10 transmission electron microscope operating at 30 to 80 kV. The sample was dropcast from toluene solutions onto
formvar-carbon coated 300-mesh copper grids and air-dried before viewing under the TEM. Samples for SEM, recorded on a FEI Inspect F (SN- D8580) electron microscope at 5 kV, were prepared by placing a few drops of the sample solution onto a copper film placed on an aluminum stub. The samples were allowed to dry before viewing under the electron microscope. EDX were carried out using the same equipment with an EDX detector. An inverted confocal microscope (Axiovert-200, Zeiss) with an excitation laser (532 nm CW, Crystalaser) beam was used to take fluorescence image (50 µm × 50 µm) of CP-QD-CNT composites. The laser focus scanning speed was 4 ms/pixel.

**Ultraviolet-Visible Absorption and Fluorescence Spectroscopy.** Ultraviolet-Visible (UV) absorption spectra were measured using MultiSpec-1501 (Shimadzu). The emission spectra and emission lifetimes were measured using a SPEX Fluorolog-3 (Jobin Yvon Inc.) equipped with Time Correlated Single Photon Counting (TCSPC).
References


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Synthesis of Carbazole Substituted Bithiophenethiol and Fluorescence Enhancement

4.1. Motivation.

Nanoparticle enhanced emission has attracted significant interest because of its wide application in chemistry, biology, medicine, and the material sciences.\(^1\)\(^-\)\(^13\) Coupling of the fluorophore with the plasmon resonance of the nanoparticles enhances the emission.\(^11\)\(^,\)\(^14\)\(^-\)\(^16\) The electronic interaction between the ligand molecule and the nano core may form a new emissive excited state.\(^17\) On the other hand, molecular structure restriction on the nanoparticle surface has also been observed. The structure restriction inducing unusual fluorescence enhancement of a carbazolyldiacetylene is also reported on gold nanoparticles.\(^16\) Recently, we found such structure restriction of 5-mercapto-2,2’-bithiophene (BTSH) on the surface of a metal nanoparticle and enhanced emission.\(^19\) The bithiophene ring isomer restriction is dependent on particle size and its distance from the surface. However, the emission is quenched under UV irradiation because of thiophene radical cation coupling and photopolymerization or aggregation of the nanoparticles.\(^19\) To further understand isomer restriction on a particle surface, we wanted to investigate the scope of the emission enhancement on the quantum dot (QD) surface. Therefore, we synthesized 5-\((3,6\text{-di-tert-butyl-9-carbazol})\)-2,2’-bithiophene-5’-thiol (CBTSH) containing a carbazol group substituted on the terminus of the bithiophene ring. Use of CBTSH as a ligand overcomes the limitations of the BTSH as no photopolymerization or aggregation occurs under the UV irradiation. We found that isomer restriction not only occurs on a metal nanoparticle surface, but also on the surface of a CdSe quantum dot. Herein we report the first observation of isomer
restriction and emission enhancement on the CdSe QD surface. Primary theoretical calculations and emission measurements provide us strong evidence.

4.2. Synthesis.

The scheme designed for the synthesis of CBTSH (2) involves two major steps — a Ullman type coupling of 3,6-di-tert-butyl-9-carbazole with 5,5'-dibromo-2,2'-bithiophene to obtain 1 and then organo-lithiation followed by introduction of the thiol group (scheme 1).

![Scheme 4.1](image_url)

Scheme 4.1. Synthesis of 3,6-di-tert-butyl-9-carbazole with 5,5'-dibromo-2,2'-bithiophene (CBTSH)

5,5'-Dibromo-2,2'-bithiophene was synthesized from commercially available 2,2'-bithiophene in the dark using N-bromosuccinamid. The product is recrystallized from absolute ethanol to remove any impurities from whence one obtains white needle shaped crystals. Carbazole was alkylated at the 3 and 6 positions by standard aromatic electrophilic substitution reactions using tert-butyl chloride in presence of zinc chloride as catalyst. The products are recrystallized from a mixture of dichloromethane and hexane (1:10) to obtain white crystals.

Coupling of 3,6-di-tert-butylcarbazole with 5,5'-dibromo-2,2'-bithiophene was carried out using an Ullman type coupling method. Obtaining the mono-coupled product is the key; 5,5'-dibromo-2,2'-bithiophene was, therefore, taken in much excess (~ 3 equiv.). The product
obtained from this reaction was purified through column chromatography, and shiny needle shaped crystals were obtained as product.

The introduction of a thiol group to 1 is highly moisture sensitive. Lithiation of 1 was performed using n-butyllithium (BuLi), with the temperature of the reaction mixture maintained below -78°C at all times. The addition of BuLi must be slow, and inert atmospheric conditions maintained. Commercially available sublimed sulfur was used for the introduction of the thiol group. The product was purified using column chromatography, under a constant flow of nitrogen gas to avoid the dimerization of CBTSH. The final product is obtained as shiny yellow crystals.

4.3. Theoretical Calculations.

DFT calculations of CBTSH at the B3LYP/6-31G* level shows that the carbazole group is almost perpendicular with the neighboring thiophene ring, and the energy of cis-CBTSH in the ground state with optimized geometry is ~0.8 kcal mol⁻¹ higher than that of trans-CBTSH (Figure 1). HOMOs of both conformers are located in the carbazole units while the LUMOs are localized in the bithiophenethiol (BTSH) unit. The vertical transitions calculated using TDDFT (B3LYP/6-31G*) result in two major absorption bands of CBTSH around 320 and 380 nm. The trans-CBTSH conformer presents slightly lower energy transitions than the cis-CBTSH. Interestingly, when computing the vertical transitions using a conformation such that the carbazole unit is parallel to that of bithiophene, it was found that the oscillator strength of the low energy transition is increased regardless of the conformation of the bithiophene unit (Figure 1).
4.4. Photophysical Properties.

There are two major absorption bands of CBTSH around 320 and 380 nm which correspond to the UV absorption of CBTSH in toluene. Based on this theoretical calculation, one can assign the UV absorption at the longer wavelength side (~380 nm) and emission at the longer wavelength side (~450 nm) mainly to the trans-CBTSH (Fig. 1, left).

CBTSH modified CdSe QDs (~2.5 nm) were prepared (experimental section). The characteristic UV absorption of CBTSH in QD indicates the successful attachment of CBTSH on the QD surface, Figure 2.
Figure 4. UV absorption spectra of CdSe QD, CBTSH, and CBTSCdSe; and the schematic structure of CBTSH modified CdSe QD, inset.

The emission intensity at the longer wavelength side increases in the case of the CBTSCdSe, spectral characteristics remain the same as that of CBTSH, Figure 3A. CBTSCdSe also has similar lifetime to that of CBTSH (~1.8 ns), Figure 3B. This indicates that the emission comes from the ligand on the QD surface. Using 9,10-diphenylanthracene with a quantum yield of 91% in non-polar solvent as a reference, the quantum yield of CBTSH and CBTSCdSe was calculated to be 2.5% and 11.4%, respectively. The emission quantum yield of CBTSH alone is slightly low, but in the case of CBTSH modified QD the emission is enhanced by almost 5 times to that of CBTSH. The emission intensity of CBTSCdSe is also 2.5 times to that of CBTSH.
Figure 4.3. (A) Excitation (dotted line) and emission spectra (solid line) of CBTSQD (blue) and CBTSH (red). The inset shows photo taken under 366-nm UV lamp irradiation, the emission of CBTSQD is higher than that of CBTSH. (B) Emission decay of CBTSQD (blue) and CBTSH (red).

4.5. Fluorescence Enhancement.

Such an emission enhancement of the CBTSH modified QDs can be attributed to isomer restriction of the CBTSH on the QD surface. Cai et al\textsuperscript{18} previously showed that emission enhancement on a nanoparticle surface is due to isomer restriction in the bithiophenethiol molecule. 2, 2’-Bithiophenethiol (BTSH) was synthesized and used to functionalize nanoparticle surfaces where the electronic interaction between the ligand and the nanoparticle core restricts the cis-trans isomerization. This causes a higher trans/cis ratio in the equilibrium mixture. The higher ratio of the trans-isomer in the equilibrium mixture was found responsible for the enhanced emission from the surface of the nanoparticles. The isomer restriction of BTSH on the surface of the nanoparticle was established with experimental evidence obtained from \textsuperscript{1}H- NMR and UV-vis spectroscopy. Therefore, considering the ligand trans- and cis- isomer character in CBTSH, it is suggested that the two thiophene rings are in a trans- configuration where, in the case of CBTS\textsubscript{CdSe}, they avoid steric interactions.
The excitation spectra indicate emission of CBTSCdSe is mainly from \textit{trans}-CBTSH on the surface because the shoulder absorption at the longer wavelength side is much higher, Figure 3A. The high \textit{trans}-CBTSH/\textit{cis}-CBTSH ratio can be estimated from the peak intensity at 365 and 340 nm compared to that of CBTSH [peak intensity ratio of 365 nm/340 nm, CBTSCdSe (0.90), and CBTSH (0.75)] in Figure 3A. The \textit{trans}-CBTSH or \textit{cis}-CBTSH on the QD surface is, therefore, restricted by the interaction between the ligand and the QD surface.

Considering the high energy barrier (as high as 21-29 kJ mol\(^{-1}\)) for rotation between the carbazole ring and the neighboring thiophene ring, we propose that QD nano core has no or little effect on the angle between carbazole and the neighbor thiophene ring. The emission enhancement in CBTSCdSe is mainly due to the isomer restriction of the two thiophene rings near to the CdSe surface.

Since CBTSH has a lower oxidation potential value \([\sim +1.2 \text{ V vs NHE}],\) measured by Cyclic Voltammetry (EC epsilon, BASI) with silver chloride electrode as reference electrode and platinum as working electrode] than the CdSe QD \([\sim +1.7 \text{ V vs NHE}],\) an electron transfer from the CBTSH to the CdSe QD core is expected, resulting in an emission quenching to the QD core.
4.6. Explanation.

However, femtosecond transient absorption measurements show that the electron transfer rate in CBTSH modified QD is significantly slow. Therefore, the electron transfer from the CBTSH to the QD core does not interfere with the emission enhancement.

Figure 4.4. Emission spectra of CBTSH modified CdSe QD (blue line) and CdSe QD only (black line) in toluene ($\lambda_{\text{exc}}=470$ nm).

Figure 4.5. Femtosecond transient absorption spectra (left) taken at 50 ps and kinetics profile (right) at 30 ps time scale of CBTSCdSe (blue) and QD only (black).
In summary, *trans*- and *cis*- isomer restriction of CBTSH on the surface of a CdSe QD was successfully observed by UV absorption, emission, and excitation spectra measurements. Theoretical calculations provide strong support to the structure restriction on the QD surface postulate. The *trans*-CBTSH/*cis*-CBTSH ratio on the QD surface is responsible for the emission enhancement of CBTSH on the QD surface. Although CdSe QD core emission is significantly quenched, emission from the ligand molecule on the surface is enhanced. Understanding the interaction between QD and its ligand on the surface is very important for QD applications as a sensor or solar energy collector.

Figure 4.6. A schematic representation of the isomer restriction and emission enhancement.

4.7. Experimental Section.

Commercially available reagents were used as received from the chemical suppliers unless otherwise noted. Reactions that required anhydrous conditions were carried out under an inert atmosphere of argon in flame-dried glassware. Toluene, DCM, and THF were dried using a Solvent Purification System. The rest of solvents used for synthetic purposes were purified according to conventional protocols. All reactions were monitored using F250 silica gel 60 M
analytical TLC plates with UV detection (λ = 254 and 365 nm). Hanessian’s stain and iodine vapors were also used as developing agents depending on the nature of the material. Silica gel (60 Å, 40–63 µm) was used as stationary phase for column chromatography.

NMR experiments were acquired with working frequencies of 300.0 MHz for \(^1\)H, and 75.5 MHz for \(^{13}\)C experiments for characterization purposes. The shifts were reported in parts per million (ppm) and referenced to the residual resonance signal of commercially available CDCl\(_3\) (δ = 7.26 ppm) and CD\(_2\)Cl\(_2\) (δ = 5.32 ppm).\(^{24}\) Low resolution mass spectra were recorded on a quadrupole mass analyzer instrument equipped with a direct insertion probe (ionization 70 eV), and coupled to a gas chromatograph. MALDI–TOF MS were recorded using dithranol as matrix for compound ionization when measurements of neat compounds were unsatisfactory.

The starting materials 5,5’-Dibromo-2,2’-bithiophene and 3,6-Di-tert-butyl-9H-carbazole were synthesized from commercially available compounds according to reported procedures.\(^{25,26}\)

4.7.1. Synthesis of 5-bromo-5’-(3,6-di-tert-butylcarbazol-9-yl)2,2’-bithiophene (1): 3,6-di-tert-butylcarbazole (1.00 g, 3.50 mmol), 2,2’-dibromo-5,5’-bithiophene (3.65 g, 10 mmol), activated Cu powder (160 mg, 2.40 mmol),\(^{27}\) 18-crown-6 (330 mg, 1.20 mmol), and K\(_2\)CO\(_3\) (1.93 g, 14.0 mmol) were transferred to a clean and dry Schlenk flask. The flask was then evacuated and refilled with argon three times. Afterwards, the solids were suspended in Argon-saturated 1,2-Dichlorobenzene (100 mL), and the reaction mixture was heated to gentle reflux, and allowed to react overnight under Argon atmosphere with constant stirring. Upon completion, the reaction mixture was cooled to room temperature, filtered through a pad of silica gel, and eluted with 1:1 mixture of DCM/Pentane. The filtrate was collected, and the volatile solvents were then evaporated. 2-Chlorophenol (100 mL) was added to the mixture and the formed azeotrope was
then evaporated to dryness. The solid mixture was redissolved in DCM, washed with 1 M NaOH (3x), water (2x) and finally brine. The organic phase was finally dried over MgSO\textsubscript{4}, filtered and evaporated to dryness affording a dark yellow solid. The crude product was then purified by column chromatography using 10% DCM/Hexanes as eluent (Yield 76 %). Yellow oil. \textsuperscript{1}\textsuperscript{1}HNMR (CDCl\textsubscript{3}, 300MHz): δ(ppm) 8.12 (dd, \(J_1=0.6\) Hz, \(J_2=1.8\) Hz, 2H), 7.50–7.55 (dd, \(J_1=1.8\) Hz, \(J_2=8.7\) Hz, 2H), 7.44–7.49 (dd, \(J_1=0.6\) Hz, \(J_2=8.4\) Hz, 2H), 7.16–7.18 (d, \(J=3.9\) Hz), 7.08–7.10 (d, \(J=3.9\) Hz, 1H), 7.01–7.04 (d, \(J=3.9\) Hz, 1H), 6.95–6.98 (d, \(J=3.9\) Hz, 1H), 1.48 (s, 18H).

\textsuperscript{13}CNMR (CDCl\textsubscript{3}, 75.5 MHz): δ(ppm) 31.9, 32.0, 34.8, 109.6, 11.3, 116.3, 122.6, 123.6, 123.9, 124.7, 130.7, 134.0, 138.6, 138.7, 140.1, 143.9. DIP-MS (EI) 521 (M\textsuperscript{+}). HRMS (EI) calcd for [C\textsubscript{28}H\textsubscript{28}NS\textsubscript{2}Br] 521.0847, found m/z 521.0850.

4.7.2. Synthesis of 5'(3,6-di-tert-butylcarbazol-9-yl)-5-mercapto-2,2'-bithiophene (CBTSH, 2): To a dry three neck round bottom flask fitted with thermometer, was added a suspension of 1 (522 mg, 1.0 mmol) dry ether. The suspension is then constantly stirred at −78 °C under argon atmosphere. To the stirred suspension of 1, n-BuLi (0.62 mL of 1.6 M solution in hexane, 1.0 mmol) was added slowly. The mixture was then allowed to stir at −78 °C for 30 minutes. To the solution was added sublimed S\textsubscript{8} powder (32mg, 1.0 mmol). The solution was constantly stirred for another hour at −78°C and then allowed to warm up to room temperature for an hour. The resulting reaction mixture was hydrolyzed by adding 1M NaOH solution. The layers were separated and the aqueous solution was neutralized by slow addition of 1M HCl solution, and finally extracted with DCM. The extracts and the mother liquor were then combined, and evaporated to dryness to obtain a yellowish solid. The crude product was purified through column chromatography using 10% DCM/Hexanes as eluant. A bright yellow solid is obtained (yield 75%). M.P. 148-150 °C. \textsuperscript{1}\textsuperscript{1}HNMR (300MHz, CD\textsubscript{2}Cl\textsubscript{2}): δ(ppm) 8.1 (s, 2H), 7.5 (d, 2H,
\[ J=1.0 \text{ Hz}), \quad 7.47 \text{ (d, 2H, } J=0.5 \text{ Hz),} \quad 7.27 \text{ (d, 1H, } J=1.2 \text{ Hz),} \quad 7.22 \text{ (d, 1H, } J=1.2 \text{ Hz),} \quad 7.10 \text{ (d, 2H,} \]
\[ J=1.57 \text{ Hz),} \quad 1.51 \text{ (s, 18H).} \]

13CNMR (CDCl3, 75.5 MHz): \( \delta \text{(ppm)} 31.9, 32.0, 34.8, 109.6, 116.3, \]
\[ 122.3, 123.6, 123.9, 124.0, 124.8, 127.9, 138.6, 138.7, 140.1, 143.9. \]
MALDI-MS 521 (M\(^{+}\)).

HRMS (EI) calcd for \([C_{28}H_{29}NS_3] 475.1462\), found \( m/z 475.1463\).

4.7.3. Preparation of CBTSH modified CdSe QDs: Trioctylphosphine oxide (TOPO) modified CdSe QDs (~2 nm, ~2.3 nm, and ~2.5 nm) were synthesized according to previous reports.\(^{28,29}\) CBTSH functionalized CdSe QDs (QD1, QD2, and QD3) were prepared by ligand exchange reactions. TOPO modified CdSe QDs were mixed with CBTSH in toluene and stirred for one day under argon. The solution was then triturated with methanol and the QD isolated by centrifugation. The precipitates were washed with methanol several times to remove all the displaced TOPO and unreacted ligands and the final residues were dissolved in toluene for photophysical measurements.

4.7.4. UV-Vis absorption and emission measurements: All the spectrophotometric measurements of compounds, QDs, and composites were done in degassed toluene of spectrophotometric quality. UV-Vis absorption spectra were recorded using a single beam spectrophotometer, accurate to ± 0.5 nm. Steady-state and time-resolved excitation and fluorescence measurements were performed on a single-photon-counting spectrofluorimeter equipped with pulsed NanoLEDs for emission lifetime measurements. Solutions with optical densities below 0.1 at the wavelength of excitation were prepared. The fluorescence quantum yields of the luminophores were measured against 9,10-diphenyl anthracene as standard (\( \Phi_F=91\% \) in cyclohexane), using the well-known comparative method. The time resolved ultrafast UV-vis spectroscopy was done using standard kinetic spectroscopic measurement technique.\(^{30}\)
References


To activate Cu-powder the following procedure was followed: Commercial Cu-powder (3.0 g) was suspended in a 2% iodine solution in acetone (50 mL), swirled for 5 min and sonicated for another 5 min. Afterwards, it was vacuum filtered, washed with abundant water, then acetone and finally diethyl ether. The dry powder was then suspended in a 1:1 concentrated HCl/acetone solution, which was swirled and sonicated in a similar way as
the previous step. The mixture was again filtered, washed with abundant water until it
gave a negative AgNO₃ test, then acetone and finally diethyl ether. This copper powder
was used immediately for the Ullman coupling reaction.

Appendix

1. Synthesis of Dianthra-[2,3-b; 2’,3’-d]-thiophene:

Scheme 1. Outline of the strategy for the synthesis of dianthra-[2,3-b; 2’,3’-d]-thiophene.

Figure 1. $^1$H NMR spectra for 35.
Figure 2. Expansion and assignment of the $^1$H NMR spectra for 35.

Figure 3. Mass spectra for 35, showing the molecular ion peaks and respective fragments.
Figure 4. $^1$H NMR spectra for 36.

Figure 5. Expansion and assignment of the $^1$H NMR spectra for 36.
**Figure 6.** Mass spectra for 36, showing the molecular ion peaks.

**Figure 7.** $^1$H NMR spectra for 37.
Figure 8. Expansion and assignment of the $^1$H NMR spectra for 37.

Figure 9. MALDI-MS spectra for 37 showing the molecular ion peak.
Figure 10. $^1$H NMR spectra (expansion of the aromatic region) and its assignment for 38.

Figure 11. Mass spectra for 38, showing the respective fragment from the molecular ion.
Figure 12. $^1$H NMR spectra (expansion of the aromatic region) and its assignment for 29.

Figure 13. MALDI-MS for 29, showing the respective molecular ion peak.
Figure 14. $^1$H NMR spectra (expansion of the aromatic region) and its assignment for 30.

Figure 15. MALDI-MS for 30, showing the molecular ion peak.
**Scheme 2.** Synthesis of 30 using zirconocene catalyst.

**Figure 16.** $^1$H NMR spectra and its assignment for 39.
Figure 17. $^1$H NMR spectra and its assignment for 40.

Figure 18. MALDI-MS for 40, showing the molecular ion peak.
Figure 19. $^1$H NMR spectra and its assignment for 41.

Scheme 3. Outline of the strategy used for the synthesis of dianthra-[1,2-b; 1',2'-d]-thiophene.
Figure 20. MALDI-MS showing the differences in the molecular weights before and after the photocyclization.

Figure 21. 1H NMR spectra (expansion of the aromatic region) and its assignments for dianthra-[1,2-b; 1’,2’-d]-thiophene.
400 Hz $^1$H NMR spectra of BTSH in D-acetone at 298, 243, 223, and 203 K.

![NMR spectra diagram]
Figure S5. 400 Hz $^1$H NMR of BTSH in D-acetone at 298, 243, 223, and 203 K, respectively. The spectra shifted to the low field side with the decreasing of temperature. The distance between 3(H) and 3'(H) peaks increased with the decreasing of temperature due to the twist angle of two thiophene rings changes from 34 ($cis$-BTSH) to 158 ($trans$-BTSH) degree.

Explanation:

If we consider that the two peaks under consideration (between 7.2 and 7.3) are peak 3 and 4 - it will apparently make sense, because both 3 and 4 are expected to show a doublet in their NMR spectra.

However, the following observations favor the assignment:

1. There are significant changes in the coupling constant values with temperature: the coupling constant changes from 0.020 ppm at 298K to 0.032, 0.034, and 0.040 ppm at 243, 223, and 203 K respectively. If we assign the two peaks under consideration to be 3 and 4 - there will be no reason that they will show temperature dependent changes in the coupling constant values.

2. The –SH group moves the peak 4 downfield to >7.5. The following literatures support the NMR assignment. This gives the NMR spectra of 5-Mercapto-2,2’-bithiophene (BTSH) itself.
