Molecular Designs for Organic Semiconductors: Design, Synthesis and Charge Transport Properties

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MOLECULAR DESIGNS FOR ORGANIC SEMICONDUCTORS: DESIGN, SYNTHESIS AND CHARGE TRANSPORT PROPERTIES

A Dissertation Presented

by

TEJASWINI SHARAD KALE

Submitted to the Graduate School of the University of Massachusetts Amherst in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY

May 2011

Chemistry
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ACKNOWLEDGMENTS

I would like to take this opportunity to express my sincere gratitude to all who made this thesis possible.

Firstly, I thank my Guru, my advisor, Professor Sankaran Thayumanavan, for his constant encouragement and guidance throughout my doctoral work. His patience, support and constructive criticism have immensely helped me in staying on path to completion of this work. His dedication, enthusiasm, critical viewpoint, drive for perfection and scientific integrity have always been inspiring. I thank him for his support and guidance both in scientific context and other professional decisions.

I also thank my dissertation committee members Prof. Lahti, Prof. Barnes and Prof. Tuominen, for their perspectives and suggestions during the course of my work. I also thank you for your help and support during my search for postdoctoral positions.

I take this opportunity to express my gratitude towards past and present Thai group members for providing a friendly, supportive and enthusiastic environment in the lab. I thank you for the many discussions that helped me through testing times when the going got difficult. My special thanks to my collaborators Arpornrat Nantalaksakul, Akamol Klaikherd, Andrea Della Pelle, Bhooshan Popere, Sreedhar Reddy and Ganapathy Balaji. For making me feel at home away from home I thank my roommates and friends here in Amherst, especially Andrea Della Pelle, Sompit Wanwong, Sunita Satav, and Siriporn Jiwpanich in the Thai group. I also thank Dr. Annamalai Chandrashekar for helpful discussions. I would like to thank the entire staff of Chemistry Department for providing excellent facilities during my time here at UMass.
Special thanks are due to Karen Hakala, for helping me with logistics and always bringing us excellent snacks!

My deepest gratitude is to my parents, my sister and my loving husband who have always been there for me. I would not be here without your support and encouragement. My gratitude to you cannot be measured or expressed aptly in words. Thank You!
ABSTRACT

MOLECULAR DESIGNS FOR ORGANIC SEMICONDUCTORS: DESIGN, SYNTHESIS AND CHARGE TRANSPORT PROPERTIES

MAY 2011

TEJASWINI SHARAD KALE, B. TECH., MUMBAI UNIVERSITY INSTITUTE OF CHEMICAL TECHNOLOGY

Ph.D., UNIVERSITY OF MASSACHUSETTS AMHERST

Directed by: Professor Sankaran Thayumanavan

Understanding structure-property relationship of molecules is imperative for designing efficient materials for organic semiconductors. Organic semiconductors are based on π-conjugated molecules, either small molecules or macromolecules such as dendrimers or polymers. Charge transport through organic materials is one of the most important processes that drive organic electronic devices. We have investigated the charge transport properties in various molecular designs based on dendrons, dendron-rod-coil molecular triads, and conjugated oligomers. The charge transport properties were studied using bottom contact field effect transistors, in which the material was deposited by spin coating.

In case of dendrons, their generation and density of charge transporting functionalities were found to play a significant role in influencing the charge transport properties. In case of macromolecules such as dendron-rod-coil molecules, the solid state morphology plays a significant role in influencing the charge transport properties. While these molecules exhibit only electron transporting behavior in field-effect transistor measurements, ambipolar charge transport is observed in the diode configuration.
Short conjugated oligomers, based on donor-acceptor-donor design, provide model systems for conjugated polymers. Effect of varying the donor functionality on optoelectronic and charge transport properties was studied in short donor-acceptor-donor molecules. While donor-acceptor-donor molecules are well known in the literature, the effect of molecular composition on the charge transport properties is not well understood. We designed molecules with 2,1,3-benzothiadiazole as the acceptor and thiophene based donor functionalities. These molecules exhibit a reduced bandgap, good solution processability and charge mobility making them interesting systems for application in organic photovoltaics.

Cyclopentadithiophene (CPD) based materials have been widely utilized as organic semiconductors due to their planar nature which favors intermolecular charge transport. While most CPD based materials are hole transporting, incorporation of electron withdrawing fluorinated substituents imparts n-type behavior to these molecules. This change in charge transport properties has often been attributed to the lowering of the LUMO energy level due to the increased electron affinity in the molecule. We designed CPD based semiconductors in which the bridgehead position was functionalized with electron withdrawing ketone or dicyanomethylene group and the α-positions were substituted with phenyl or pentafluorophenyl groups. Both the phenyl substituted molecules are p-type materials, even though the dicyanomethylene group lowers the LUMO by 500 meV as compared to the carbonyl compound. The pentafluorophenyl substituted molecules are n-type materials even as their LUMO energy levels are about 300 meV higher than the corresponding phenyl substituted molecules. This indicates that charge transport behavior is not an exclusive function of the frontier orbital energy levels.
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CHAPTER 1

INTRODUCTION

1.1 Organic semiconductors

Electronic and optoelectronic devices using organic molecules as active materials, for example, organic light-emitting diodes (OLEDs), organic photovoltaic devices (OPVs), and organic field-effect transistors (OFETs) have recently received a great deal of attention from the standpoint of potential technological applications as well as fundamental science. Organic π-conjugated materials offer advantages because their properties such as band gap, redox potentials and charge transport properties can be tuned easily. Additionally, these materials can be processed by simple solvent processing techniques and therefore, provide the avenue for light weight, potentially low cost, thin-film, large-area and flexible device fabrication. Devices based on organic materials share a common feature: their performance critically depends on the efficiency with which charges (electrons and/or holes) move within the active material, i.e. the π-conjugated material. The charges are either injected into the organic semiconductors from electrodes in the case of OLEDs or OFETs. Charges are generated within the materials in the case of solar cells via photoinduced charge separation at the interface between electron donor and electron acceptor components.

Organic semiconductors are classified based on (i) the nature of charges they transport into hole transporting (HT) and electron transporting (ET) materials, and (ii) their molecular architecture, as small molecules or oligomers, or macromolecules such as polymers or dendrimers. Hole transporting materials are those that accept holes, or donate
electrons, and transport them. On the other hand, electron transporting materials are those that accept electrons and transport them. However, whether a material is a hole transporter or an electron transporter is not determined based on the actual ability of the material to transport charges (i.e., on the actual values of charge mobilities) but rather reflects the ease of charge injection from electrodes traditionally used in devices. Therefore, a material is often referred to as a hole, or electron, transporter when its ionization energy, or electron affinity, closely matches the Fermi level of the electrode. Therefore, conventional wisdom states that materials which have low ionization potentials and low electron affinities are usually HT materials, whereas materials which have high electron affinities and high ionization potentials usually function as ET materials. In other words, charge transporting materials with electron donating and accepting properties usually serve as hole and electron transporting materials, respectively. HT materials are commonly referred to as p-type materials while ET materials are often called n-type materials, as this is the common nomenclature in inorganic semiconductor field, from which the organic semiconductor field is said to have evolved. It should be noted that there are a number of materials that exhibit ambipolar character, that is, materials that can transport both holes and electrons.

1.1.1 Small molecule semiconductors

Small molecules can be synthesized with very high purity and well defined molecular structure. However, their processability can be significantly limited due to their limited film forming capability when cast from solution. This is often attributed to the crystalline nature of these materials.
Some of the common classes of organic crystalline materials used in electronic and optoelectronic devices include polycyclic aromatic hydrocarbons, fused heterocyclic aromatic compounds, oligothiophenes, oligoarylenes, macrocycles such as phthalocyanines, fullerenes, and perylene pigments. Violanthrone, a low-molecular-weight model for graphite, was first studied as an electrically conducting molecular material, and perylene was studied as an electron donor component for conducting charge transfer complexes. Pentacene and related condensed aromatic hydrocarbons have recently attracted attention as a new class of promising materials for use in OFETs. The molecular structures of some of these classes of crystalline materials are shown in Chart 1.1.

![Chart 1.1](image)

**Chart 1.1:** Structures of representative crystalline organic semiconductors (a) pentacene; (b) rubrene; (c) oligothiophenes and (d) perylene diimide

Oligothiophenes (Chart 1.1 (c)) with a well defined structure and high degree of crystallinity are of interest in various opto-electronic applications and serve as model
compounds for polythiophenes. Unsubstituted and alkyl-substituted oligothiophenes with long conjugation lengths, as long as 27-mers have been reported. These have been found to be highly crystalline materials and interestingly, oligomers with greater lengths such as 16-, 20-, and 27-mers, are reported to form molecular wires. Although oligothiophenes are highly crystalline, amorphous molecular materials containing oligothiophenes have also been designed and synthesized. The molecular and crystal structures, optical, electrochemical, and electrical properties of oligothiophenes have been studied extensively.

Organic crystalline materials exhibit larger charge mobilities than organic amorphous materials. Devices using organic single crystals have been reported; however, the single-crystal growth on the plane of a large-area substrate for device applications is not easy. Polycrystalline materials have been used mostly in OFETs and OPVs. The grain size, grain boundaries, and molecular orientations in these materials affect the device performance. For instance, single crystal pentacene exhibits charge mobility as high as 35 cm²/Vs whereas thin films of the same material show mobilities of about 1.5 cm²/Vs. Amorphous materials have advantages over crystalline materials in device fabrication because of their good processability, transparency, and isotropic and homogeneous properties.

Amorphous small molecule based materials are often obtained by recrystallization and form amorphous molecular glasses when the melt samples are cooled. Such glasses show amorphous, homogenous properties without grain boundaries and are characterized by presence of disorder in both molecular distance and orientation. Like polymers, these readily form uniform amorphous thin films by vacuum deposition or spin-coating from
solution. However, unlike polymers, these are pure materials with well defined molecular structure and precise molecular weights. Non-planar molecular structures, which coexist as multiple conformers lead to amorphous glass formation. Commonly used examples of amorphous materials include triarylamines, spiro compounds and 1,3,5-triphenylbenzene or 2,4,6-triphenyltriazine containing molecules. These materials exhibit charge mobilities in the range of $10^{-2}$ to $10^{-5}$ cm$^2$/Vs. Representative amorphous molecular materials are shown in Chart 1.2.

![Chart 1.2: Structures of representative amorphous small molecule organic semiconductors](chart.png)

(a) 4,4',4''-tris(diphenylamino)-triphenylamine; (b) 1,3,5-tris(9,9-dimethylfluoren-2-yl) benzene; (c) $\alpha,\omega$-bis[bis(4-methylphenyl)aminophenyl]bithiophene and (d) 2,4,6-tris[di(2-pyridyl)amino]-1,3,5-triazine
Incorporation of electron withdrawing functionalities such as quinoxaline, benzimidazole, pyridine and oxadiazole at the 1,3,5- positions of the central benzene or triazine core leads to electron transporting materials.\textsuperscript{37, 38} For instance, 1,3,5-tris(9,9-dimethylfluoren-2-yl) benzene\textsuperscript{39} (Chart 1.2 (b)) and 2,4,6-tris[di(2-pyridyl)amino]-1,3,5-triazine\textsuperscript{40} (Chart 1.2 (d)) have both been utilized as electron transporting materials in OLED applications.

1.1.2 Dendritic semiconductors

Dendrimers are monodisperse macromolecules which can be synthesized in a controlled manner with well defined functionalities (based on number of branching points, or generation), their size and molecular weight precisely. This is in contrast to polymers which often suffer from batch-to-batch variations in average molecular weight and its distribution which are known to cause significant variations in device properties. Therefore, relating chemical structure to charge transport properties becomes easier in dendrimers. However, like polymers, dendrimers can be readily cast into thin films by spin-coating from solution and often yield amorphous films.

Dendrimers with charge transporting functionality at the core are known in the literature.\textsuperscript{41-43} The surrounding dendrimer has been utilized to isolate the core from that of the adjacent molecules to understand the photophysical properties as well as charge transport behavior as a function of generation. In one case, phenylenevinylene dendrimers were used to encapsulate a triphenylamine core (Chart 1.3).\textsuperscript{41} The charge mobility in this case was found to decrease by three orders of magnitude from $5.1 \times 10^{-6}$ cm$^2$/Vs for generation zero to $5.5 \times 10^{-9}$ cm$^2$/Vs for third generation dendrimer.\textsuperscript{41} In
another case, [Ru(bpy)_3]^{2+} units were decorated along the periphery of PAMAM dendrimers. The mobility in this case was also found to decrease with increasing generation.\textsuperscript{44}

\begin{center}
\includegraphics[width=\textwidth]{chart1.png}
\end{center}

\textbf{Chart 1.3:} Structure of generation one (a) triphenylamine cored phenylenevinylene dendrimer and (b) Iridium cored dendrimer with carbazole functionalities

Increase in mobility with increasing generation was observed when Iridium cored dendrimers were synthesized with carbazole functionalities in every layer of the dendrimers.\textsuperscript{45} In this case the carbazolyl groups were found to participate in the charge transport leading to an approximately two fold increase in the mobility from $(3-6) \times 10^{-5}$ cm$^2$/Vs for generation one to $(7.3-12) \times 10^{-5}$ cm$^2$/Vs for third generation dendrimer.

\subsection*{1.1.3 Polymeric semiconductors}

Polymers provide advantages in terms of ease of processing and are of interest in making flexible organic electronic devices. Conjugated polymers have been extensively studied for such applications.\textsuperscript{9, 14, 46-53} For instance, organic solar cells based on $\pi$-conjugated semiconducting polymers have attracted widespread interest not only in the
academic, but also in the commercial communities.\textsuperscript{6, 47, 54} However, due to the polydisperse nature of the material, there is often a significant degree of disorder in polymer films. Several approaches have been adopted in the literature to reduce the degree of disorder and improve charge mobility. Self assembling properties of rigid conjugated backbone polymers, such as regioregular P3HT, have been exploited to some advantage. Charge mobility in regioregular P3HT is reported in the range of $10^{-4}$-$10^{-1}$ cm\textsuperscript{2}/Vs depending on the processing conditions such as solvent, annealing time and temperature.\textsuperscript{16, 17, 55} This polymer assembles to form lamellae perpendicular to the substrate with $\pi$-$\pi$ interactions among the 3-hexylthiophene rings being parallel to the plane of the substrate.\textsuperscript{56} Owing to ordered lamellar structure, the polymer exhibits good charge mobility when measured in a plane parallel to the substrate indicating appreciable inter-chain (parallel to the substrate) as well as intra-chain charge transport. However, a significant drop in mobility is observed when measurements are carried out along the plane normal to the substrate,\textsuperscript{57} indicating poor charge hopping.

Due to the high degree of disorder and hence, significant contribution required from charge hopping in the charge transport process in polymers, the charge mobilities in such materials are often moderate, on the order of $10^{-6}$ to $10^{-1}$ cm\textsuperscript{2}/Vs. Poly(arylenevinylene) based polymers have been studied extensively, especially for applications in OPV devices. These, like most other $\pi$-conjugated polymers, exhibit hole transporting behavior and are used as donor components in photovoltaic applications. Poly(thienylenevinylene)s exhibit low bandgap ($\sim$1.6-1.8 eV) and show high hole mobilities on the order of $10^{-1}$ cm\textsuperscript{2}/Vs, making them attractive candidates for OPV applications. Introduction of electron withdrawing side chain functionality (Chart 1.4(c))
improves emission properties, provides a narrower bandgap and a higher mobility as compared to a simple solubilizing alkyl side chain.\textsuperscript{58}

\begin{center}
\begin{tabular}{c c c c}
\textbf{a} & \textbf{b} & \textbf{c} & \textbf{d} \\
\end{tabular}
\end{center}

\begin{center}
\begin{tabular}{c c c c}
\textbf{e} & \textbf{f} & \textbf{g} \\
\end{tabular}
\end{center}

\textbf{Chart 1.4:} Structures of some hole transporting conjugated polymers (a) poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV); (b) poly(3-hexylthiophene) (P3HT); (c) poly(thiophene-3-carboxylic acid hexyl ester); (d) poly(fluorene); (e) copolymer of fluorene and triarylamine; (f) copolymer of benzodithiophene and thienothiophene and (g) copolymer of cyclopentadithiophene and benzothiadiazole

Fused ring systems maximize the $\pi$-orbital overlap and are known to induce face-to-face $\pi$-stacking, facilitating charge transport through intermolecular hopping.\textsuperscript{46} Also, fused aromatic rings make the polymer backbone more rigid and coplanar, enhancing effective $\pi$-conjugation, lowering bandgap and extending absorption. Thus, fluorene, carbazole, indolocarbazole, benzodithiophene, cyclopentadithiophene, dithienopyrrole, and other fused-ring blocks have been introduced into $\pi$-conjugated polymeric systems to
improve the performance in solar cells.\textsuperscript{46} Structures of some conjugated polymers containing fused ring systems are shown in Chart 1.4.

Polyfluorenes possess good thermal and photochemical stability, low-lying HOMO energy level, high mobility, and excellent blue-emitting properties. However, their high optical bandgap (~3.3 eV) is too large to efficiently harvest sunlight. Incorporation of an electron donating and/or accepting unit into the main chain can lower bandgap and extend absorption of the polymers. Copolymer of fluorene and triarylamine (Chart 1.4(e)) exhibited a reduced optical bandgap of 1.9 eV, a low HOMO of -5.3 eV and a FET mobility of 10\textsuperscript{-4} cm\textsuperscript{2}/Vs.\textsuperscript{59}

The planar benzo[1,2-\textit{b}:4,5-\textit{b'}]dithiophene (BDT) unit has emerged as an attractive building block for conjugated polymers. Copolymers of BDT and bithiophene (Chart 1.4(f)) exhibited a high FET mobility of 0.25 cm\textsuperscript{2}/Vs and enhanced stability.\textsuperscript{60} Cyclopentadithiophene derivatives have also attracted considerable attention due to their fully coplanar structure, low bandgap, and strong intermolecular interactions.\textsuperscript{61} Copolymer of 4,4-dihexadecyl substituted cyclopentadithiophene and benzothiadiazole (Chart 1.4(g)) was reported with a high FET mobility of 0.17 cm\textsuperscript{2}/Vs.\textsuperscript{62} A similar polymer with two ethylhexyl groups on cyclopentadithiophene exhibited narrow bandgap (1.4 eV), low HOMO (-5.3 eV), and high mobility (2 \times 10\textsuperscript{-2} cm\textsuperscript{2}/Vs).\textsuperscript{63}

Although fullerenes, particularly the solution processable derivative PCBM, are the most commonly used acceptors in OPVs, perylene diimide (PDI) small molecules and polymers have attracted much interest as alternative acceptor materials since they exhibit large absorptivity, high electron mobilities, and electron affinities similar to those of fullerenes. The first soluble perylene diimide based fully conjugated polymer was a
copolymers of PDI and dithienothiophene (Chart 1.5(a)). This copolymer exhibits broad absorption (300-850 nm), low bandgap (1.7 eV) and high electron mobility \( (1.3 \times 10^{-2} \text{ cm}^2/\text{Vs}) \). Similarly, an alternating copolymer of perylene diimide and phenylenevinylene also exhibits n-type properties. Ladder polymers provide an interesting architecture for conducting materials due to their extensively conjugated backbone. A ladder polymer, similar to perylene diimide polymers (Chart 1.5(c)) was reported to have high electron mobilities of 0.1 cm\(^2/\text{Vs}\).

![Chart 1.5: Structures of some electron transporting conjugated polymers](image)

Installing electron withdrawing functionalities on the backbone has been shown to impart electron transporting character to the material. For instance, replacing vinylene with cyanovinylene in poly[2-methoxy-5-(2’-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) lowers both HOMO and LUMO levels by ~0.5 eV, both increasing the ease of reduction and decreasing the ease of oxidation, and having only minor effects upon absorption and fluorescence spectra and bandgap. Cyano-substituted PPVs (CN-PPVs) (Chart 1.5(d-f)) display relatively high electron affinities and considerable electron-
transport properties as a result of the electron-withdrawing effect of the cyano group. CN-PPVs can function as a suitable electron acceptor in all-polymer solar cells in either bilayer or bulk heterojunction configuration.\textsuperscript{46}

1.2 Figures of merit of organic semiconductors

The figures of merit of charge transporting materials, which define their key properties are solid-state ionization potential (oxidation potential), electron affinity (reduction potential), optical band gap, and charge mobility. While the first three characteristics will be discussed in this section, charge mobility will be discussed in detail in the following sections. Ionization potential and electron affinity of organic materials can be determined by cyclic voltammetry or ultraviolet photoelectron spectroscopy (UPS). The ionization potential or oxidation potential and the electron affinity or reduction potential correspond to the HOMO and LUMO energy levels of a molecule, respectively. The LUMO energy level can also be estimated from the ionization potential or oxidation potential and the optical band gap. The oxidation and reduction potentials are determined by cyclic voltammetry in solution. The solid state ionization potential, which is lowered by the polarization energy (ca. 1.7 eV for organic molecules) relative to the gas phase ionization potential, is related to the oxidation potential as $E_{\text{HOMO}} = -(4.8 + qE_{\text{ox}})$, where $q$ is the elementary charge, and $E_{\text{ox}}$ is the oxidation potential versus Fc (ferrocene)/Fc$^+$ (ferrocenium ion) reference electrode.\textsuperscript{36}

The ionization potential or oxidation potential of materials indicates the strength of electron-donating properties. In other words, it indicates the energy barrier that exists for the injection of holes from the anode into an adjacent HT material. Similarly, the
electron affinity or reduction potential of materials indicates the strength of electron-accepting properties and the energy barriers for the injection of electrons from the cathode into an adjacent ET layer. The HOMO/LUMO energy levels of organic materials are of importance in determining the efficiency of photo-generation of charges and open-circuit voltages in OPVs, and charge injection in OFETs.

Optical bandgap of the material indicates the minimum energy required to promote an electron form the HOMO to the LUMO of the molecule. It therefore gives an estimate of the spectral region covered by the molecule. The wavelength corresponding to the onset of absorption in the absorption spectrum is used to calculate the optical bandgap of the material using the relation \( E (\text{eV}) = \frac{1240}{\lambda_{\text{onset}}} \). Low bandgap materials are desirable for applications in OPVs, since this allows for absorption in the red region of the solar spectrum, which has the highest intensity in the normal solar insolation observed on earth.

### 1.3 Origin of charge transport in organic semiconductors

Unlike in classical inorganic semiconductors such as silicon, in which atoms are held together with strong covalent or ionic bonds forming a highly crystalline three-dimensional solid, organic semiconductors are composed of individual molecules that are weakly bound together through van der Waals forces, hydrogen bonding, and \( \pi-\pi \) interactions and typically produce relatively disordered, polycrystalline films.\(^{19}\) When a large number of individual atoms are gathered together in a three dimensional lattice, the discrete atomic levels widen into bands and the charges move freely in delocalized bands with very high mobilities. In inorganic semiconductors, charge transport occurs in
delocalized states which are limited by the scattering of the carriers, mainly on phonons, that is, thermally induced lattice deformations. In this case, the mobility is limited by phonons that scatter the carriers and thus it is reduced as the temperature increases.

In organic materials, the transport differs from the band transport of inorganic semiconductors. Charge delocalization can only occur along the conjugated backbone of a single molecule or between the \( \pi \)-orbitals of adjacent molecules. Currently, there is a general agreement that charge transport in organic materials occurs via polaron (the deformation of the lattice around the electron or hole) hopping between localized states. In other words, charge transport is thought to rely on charge hopping from localized states and can be thought of as an electron transfer between a charged oligomer and an adjacent neutral oligomer. Hopping is assisted by phonons and hence, the charge mobility increases with temperature in organic semiconductors. However, some organic oligomers have been found to form very ordered crystals, and within these materials, it may be possible that weak bands can form.

### 1.4 Measurement of charge transport

The key parameter that defines charge transport is the charge mobility in a material. In the absence of any external potential, transport is purely diffusive. When voltage is applied to a material sandwiched between two electrodes, charge carriers are transported across the sample under the electric field. The velocity of charges, moving through the material, is a function of the applied field and the drift mobility of the charges through the material. It should be noted that, for organic disordered systems, mobility is a function of the applied electric field. The charge mobilities in organic
materials greatly vary depending on the nature of charge carriers, i.e., whether they are holes or electrons, molecular structure, and morphology of the material.

There are various methods for testing the electrical properties of organic materials including time-of-flight (ToF),\textsuperscript{68, 69} and field-effect transistor (FET) measurements.\textsuperscript{18, 67, 70-72} In ToF devices, charge transport is typically measured perpendicular to the substrate, so these devices are not ideal for measuring mobility in organic semiconductors that typically have the highest $\pi$-orbital overlap parallel to the substrate. Therefore, FET devices, which measure mobility parallel to the substrate, give more relevant estimations of charge mobility in such materials. It must be noted that, organic semiconductors usually form polycrystalline films, and the sample preparation can drastically affect the electrical properties.

1.4.1 Time-of-flight (ToF)

This method is based on the measurement of the time required for a sheet of charge carriers photo-generated near one of the electrodes by pulsed light irradiation to drift across the sample to the other electrode under an applied electric field. This time is denoted as the carrier transit time ($\tau$). The semiconductor sample is sandwiched between the two electrodes, one of which is transparent. Thick films of the sample (1-20 $\mu$m) are prepared using vacuum evaporation, solvent cast from solution, or by pressing melt samples with two ITO electrodes. Relatively thick samples are favorable due to the requirement of a smaller absorption depth of the excitation relative to the film thickness.

The device is first irradiated by a laser pulse in the proximity of one electrode to photo-excite the semiconductor. The exciton is split at the interface of the semiconductor
and electrode to generate charges in the semiconductor layer. Depending on the polarity of the applied bias, and the corresponding electric field (in the $10^4$-$10^6$ V/cm range), the photo-generated charges migrate across the material toward the second electrode. The current at the second electrode is recorded as a function of time. A sharp signal is obtained in the case of ordered materials while in disordered systems a broadening of the signal occurs due to a distribution of transient times across the material. The mobility is calculated using the transient time as $\mu = \frac{d^2}{V\tau}$, where, $d$ is the distance between the electrodes (thickness of the film), $V$ is the applied voltage and $\tau$ is the average transient time.

1.4.2 Field effect transistors (FET)

Field effect transistors can be used to determine the charge mobility in a semiconductor under the effect of applied field. A typical FET consists of a gate electrode on which a dielectric layer, commonly referred to as gate dielectric, is deposited. Semiconductor layer (film thickness in the range of 100-200 nm) is deposited on the gate dielectric by spin coating or vapor deposition. Source and drain electrodes are deposited on the semiconductor layer by vapor deposition to obtain a top contact FET.

![Figure 1.1: Schematic representation of top contact (left) and bottom contact (right) FET devices](image)

A variation in the design can be made by depositing the source and drain electrodes on the gate dielectric followed by deposition of the semiconductor layer. This
configuration is called the bottom contact FET configuration (Figure 1.1). Upon application of voltage to the gate electrode, opposite polarization is observed on the semiconductor layer along its interface with the gate dielectric. In FETs, the charges migrate within a very narrow channel (a few nanometers wide) along the interface between the semiconductor and the dielectric.\(^\text{18, 72}\) Transport is affected by structural defects in the organic layer at the interface and the presence of traps at the interface. The induced charge can be measured in the source-drain circuit and reflects on the charge mobility in the sample. Charge mobility is calculated in the saturation regime as \(I_{ds}^{1/2} = [(W/2L)C_i\mu]^{1/2} (V_g-V_t)\), where, \(I_{ds}\) is drain current, \(W\) is channel width, \(L\) is channel length, \(C_i\) is capacitance of gate oxide per unit area, \(\mu\) is charge mobility, \(V_g\) is gate voltage, and \(V_t\) is threshold voltage.\(^\text{18}\)

The charge mobilities extracted from the FET are generally higher in the saturated regime than those in the linear regime due to different electric-field distributions.\(^\text{67}\) The mobility has also been found to be dependent on gate voltage.\(^\text{73, 74}\) This is often related to the presence of traps due to structural defects and/or impurities (that the charges injected first have to fill prior to establishment of a current) and/or to dependence of the mobility on charge carrier density (which is modulated by \(V_g\)). The dielectric constant of the gate insulator also affects the mobility; for example, measurements on rubrene single crystals\(^\text{75}\) and polytriarylamine\(^\text{76}\) have shown that the carrier mobility decreases with increasing dielectric constant due to polarization effects across the interface.

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1.5 Our molecular designs

In this work, we have focused on developing molecular designs for organic semiconductors for applications in OPV devices. In such devices, the active material (comprising the organic semiconductor) performs important functions such as absorption of light and generation of exciton, charge separation (which occurs only at the interface of HT and ET material) and charge transport. For efficient charge separation, the material must provide the said interface within the diffusion length of the exciton (~10nm). Further, a continuous phase of both HT and ET components must exist so as to allow for efficient charge transport. We hypothesized that, using molecular triads, which consist of HT and ET components bridged via a sensitizer unit can provide (i) high charge separation efficiency, since the interface between HT and ET components will occur within molecular length scales, and (ii) continuous path for charge transport by microphase separation between HT and ET components, enforced by the molecular architecture of the two functionalities.

Our molecular design for such a molecular triad is based on the dendron-rod-coil scaffold, which is known to undergo microphase separation due to the difference in curvature of dendron and coil. A schematic representation of the molecule is shown in Figure 1.2. Additionally, these molecules show excellent photoinduced electron transfer in solution state, indicating high exciton splitting efficiency in the molecules. In order to translate these molecules in materials for OPV devices, we need to understand their solid state morphology and charge transport properties. In Chapter 2, we have discussed the detailed molecular design of the dendron-rod-coil molecules and their charge transport properties.
While there are exhaustive studies on conducting polymers, there is limited understanding on charge transport through dendritic molecules. Dendrimers, or dendrons, are monodisperse macromolecules which can be synthesized with excellent control over molecular structure and size in highly pure form. These can be processed easily like polymers, but much like small molecules, these can be used for structure-property relationship studies due to precise molecular structure and monodisperse nature. Therefore, dendrimers can be said to bridge the gap between small molecules and polymeric materials. In Chapter 3, we discuss the effect of molecular size (generation) and density of charge transport functionalities on charge transport properties of dendrons.

The rod functionality in the dendron-rod-coil molecules is a short oligomeric unit based on donor-acceptor-donor design, utilizing 2,1,3-benzothiadiazole as the acceptor and thiophene based donor functionality. While donor-acceptor-donor molecules are well known in the literature, the effect of molecular composition on the charge transport properties is not well understood. Oligomers, like small molecules, can be obtained in high purity and hence, can be used for structure-property relationship studies. In Chapter 4, we discuss the effect of varying donor functionality on the opto-electronic,
electrochemical and charge transport properties of donor-acceptor-donor based short oligomers.

As discussed previously in section 1.1.3, cyclopentadithiophene based materials are widely used in OPV applications. While this functionality provides a planar backbone, alkylation at the bridgehead position is required in order to impart processability to the materials. In such cases, the bridgehead functionality is not involved in charge transport in the material. We have systematically varied the bridgehead functionality and the functionality at the $\alpha$-position of the cyclopentadithiophene core to understand their effect on the charge transport properties. Solution processable small molecules based on the cyclopentadithiophene core were designed for this purpose. In Chapter 5, we discuss the opto-electronic, electrochemical and charge transport properties of these materials.
1.6 References


CHAPTER 2

CHARGE TRANSPORT IN DENDRON-ROD-COIL MOLECULES

2.1 Introduction

With growing interest in organic photovoltaic devices, the demand for efficient active materials has increased tremendously. Solution processable organic semiconducting materials have garnered tremendous interest due to ease of synthesis, tunability of important material properties such as light absorption, band gap, redox properties and charge transport properties.\textsuperscript{1-5} The efficiency of an OPV device depends upon (i) efficiency of light absorption and generation of exciton; (ii) splitting of exciton into separate hole and electron; (iii) transport of these charges through bulk of the material to the appropriate electrode; and (iv) charge collection at the electrode. While the first three requirements are materials requirements, the last is a device parameter dealing with the properties of the interface between active layer and electrode. The overall efficiency of the device is a direct function of each of these factors and hence optimization of each is required to design efficient OPV devices. An important step in this process is the exciton splitting process which happens only at the interface between the hole transporting (HT) and electron transporting (ET) material. The lifetime of excitons, measured in terms of the diffusion length is \( \sim 10 \text{ nm} \).\textsuperscript{6-8} Hence, it must encounter the said interface within this distance. Various approaches to device fabrication involving mixing the HT and ET materials to yield bulk heterojunction devices have been studied.\textsuperscript{9-14} However, due to limited control of domain size in blend of two components, bulk heterojunction devices often suffer from (i) non-uniform domain sizes: if domain size is larger than \( \sim 20 \text{ nm} \), exciton splitting efficiency may be limited since these may not
always encounter an interface between HT and ET material, and (ii) occurrence of islands of one of the components, leading to charge trapping: such discontinuity in path of charge transport significantly limits the efficiency of the device. Therefore, designing molecules which contain a hole transporting and an electron transporting component provides the advantage of having this interface at molecular length scales, which is significantly less than 10 nm.

Once the charges are separated, it is important that a continuous path be present for these charges to travel through the bulk of the material to the respective electrodes. This can be a significant challenge, since hole transporting and electron transporting materials are essentially electron rich and electron deficient materials which have strong donor-acceptor type interactions. Such interactions make these strongly interacting materials, and hence phase separation of these materials is difficult. One way of driving phase separation among such materials may be by utilization of molecular architecture of the two phases. Block copolymers have been extensively studied in this aspect.\textsuperscript{8, 15-17} Phase separation in block copolymers is dependent upon the volume fraction of each block, the incompatibility parameter and molecular weight of each block. If the two blocks are strongly interacting, phase separation may be limited. Dendrimers are macromolecules which can be obtained with great control on size and structure. These are monodisperse macromolecules which make ideal systems for structure-property relationship studies. Additionally, dendrons are known to phase separate from flexible polymeric chains on account of the difference in curvature of the two phases,\textsuperscript{18-23} making dendron-rod-coil architecture interesting for active materials in OPVs.
We have previously shown that dendron-rod-coil molecules show excellent photoinduced charge separation in solution state and the architecture provides significant advantages over other similar architectures such as dendrimers and dendron-rod molecules.\textsuperscript{24} To effectively translate these molecules into materials for organic photovoltaics, we need to understand their solid state properties of charge transport and morphology. We have studied the charge transport behavior using field effect transistors (FETs). In an FET device, charges move under the influence of the applied field along the interface of gate dielectric and semiconductor material. Hence, mobility is measured along the x-y plane of the device.

A complementary technique to studying the charge transport properties is time-of-flight (ToF) mobility measurement, which determines the mobility in the diode configuration. This system is, therefore, similar in configuration to an organic photovoltaic device and provides insight into the performance of the material in an actual organic photovoltaic cell. In this measurement technique, charges are photo-generated by excitation of the active material using a laser. The exciton is split at the interface of the donor and chromophore into electron and hole. These charges move through the bulk material (in the z-direction) under the influence of the applied field and are measured as photocurrent. The delay time in irradiation with laser and generation of photocurrent (transient time, $\tau$) indicates the time required for the charges to travel through the thickness of the film. Charge mobility can be calculated using this transient time data. This measurement was made in collaboration with Prof. Jayant Kumar, Physics Department, University of Massachusetts, Lowell. Small angle X-ray scattering was used
to obtain an insight into the morphology of these materials in collaboration with Prof. Hayward, University of Massachusetts, Amherst.

2.2 Materials and Methods

2.2.1 Materials

The dendron-rod-coil molecules are designed such that, the dendron contains hole transporting (electron donor) functionalities along the periphery and the coil contains electron transporting (electron acceptor) functionalities as pendent groups. The rod functionality is a sensitizer unit based on a short thiophene based oligomeric chain. Specifically, the electron donor functionality is diarylaminopyrene, the electron acceptor functionality is naphthalene diimide and the sensitizer unit is a donor-acceptor oligomer containing 2,1,3-benzothiadiazole as the acceptor component and a thiophene derivative as the donor component (Chart 2.1).

![Figure 2.1: Photoinduced charge transfer in dendron-rod-coil molecules](image)

The functionalities were so chosen that the electron transfer process ensuing upon excitation of the rod functionality happens spontaneously from the donor to the excited state of the chromophore and from the excited state of the chromophore to the acceptor, as shown schematically in Figure 2.1. The generation of the dendron was varied in the
study to evaluate its effect on the properties of the molecules. These molecules were synthesized following the procedures developed earlier in our laboratory.\textsuperscript{24, 25} Modular synthetic strategy was adopted for the synthesis of these macromolecules allowing us to synthesize all the components individually (Chart 2.1) and assembling the macromolecules in the last stages of synthesis. Briefly, the diarylaminopyrene functionality was synthesized using consecutive Hartwig-Buckwald coupling reactions using bromopyrene, 4-decyl aniline followed by tert-butyldimethylsilyl ether of 3-bromobenzylacohol. Deprotection of the silyl ether yielded the alcohol which was converted to corresponding bromide using mesyl chloride and lithium bromide.

Higher generations of dendrons were obtained by iterative alkylation of 3,5-dihydroxybenzyl alcohol and bromination using conditions. The key step in synthesis of the rod functionality is the palladium catalyzed Stille coupling to form the C-C bond to obtain 4,7-dithienyl-2,1,3-benzothiadiazole. This compound is brominated and subjected to Stille coupling conditions again to obtain the required dihydroxy molecule. This molecule is monoalkylated with propargyl bromide to obtain the appropriately functionalized rod functionality. For synthesizing the coil, the methacrylate ester containing the naphthalene diimide functionality is polymerized using atom transfer radical polymerization to obtain a polymer with low poly-dispersity index.
The dendron-rod-coil molecules were assembled by alkylation of the rod functionality with appropriate dendron to obtain the dendron-rod molecules (Chart 2.2) followed by their coupling with the azide terminated polymer using 1,3-dipolar cycloaddition reaction. The structures of dendron-rod-coil molecules studied here are shown in Chart 2.3. It should be noted that the non-conjugated nature of the dendron and coil, as well as the connectivity between these components, lead to their being no interaction in these components in the ground state. Electron transfer process happens only upon photo-excitation of the chromophore unit. The efficiency of photo-induced electron transfer was studied earlier in our laboratory and found to be ~80% for all generations of dendrons attached in the molecule.
To study the charge transport process, thin films were cast on either prefabricated field effect transistor substrates using spin coating or ITO coated glass by drop casting. All components namely, the dendron, rod, coil and the dendron-rod functionalities were studied independently along with the dendron-rod-coil molecules.

2.2.2 Mobility measurements

2.2.2.1 Field effect mobility measurements

The field effect transistors were constructed using pre-patterned silicon substrates; these transistors were constituted by a heavily n-doped silicon substrate with a 230 nm thermally oxidized silicon dioxide layer with a capacitance of 14.9 nF/cm². Gold
electrodes were deposited on the gate oxide layer to yield the bottom contact FETs. Before deposition of the film, the FET was cleaned with acetone followed by isopropyl alcohol. It was then exposed to hexamethyldisilazane (HMDS) vapor for 1 hour followed by re-cleaning with isopropyl alcohol. After this, thin films (150 ± 5 nm) of the samples were deposited on the surface by spin coating a 1 wt% solution in chlorobenzene (1500 rpm for 45 seconds). The devices were then annealed for 1 hour at 80 °C. The channel width of all transistors was 10 mm while the four different channel lengths, 2.5 μ, 5 μ, 10 μ and 20 μ were used. All measurements were carried out under inert atmosphere using Agilent 4156C precision semiconductor parameter analyzer.

**Chart 2.3:** Structure of dendron-rod-coil molecules
2.2.2.2 Time-of-flight mobility measurements

In a typical experiment, the device is assembled in the ITO/semiconductor/aluminum configuration and irradiated with a laser to photoexcite the semiconductor. The diodes were constructed by depositing thick films of materials by drop casting on indium tin oxide (ITO) coated glass. Aluminum electrode was evaporated on the semiconductor layer to complete the device. In the device ITO acts as the anode while aluminum is the cathode. Film thickness of the semiconductor layer was about 1-2 μm.

2.3 Results and Discussion

2.3.1 Mobility measurements

2.3.1.1 Field effect mobility measurements

In order to obtain a structure-property relationship in the charge transport properties of the dendron-rod-coil molecules, it is necessary that we first evaluate the components individually. Charge transport through polymeric systems has been studied extensively, however, there is limited understanding of charge transport through dendrons. Therefore, it is further interesting to understand this phenomenon. Hence, at the outset, we investigated the charge transport characteristics of dendrons, analog of the rod and coil in the field effect transistor (FET) mode. An example of the typical output and transfer characteristics is shown in Figure 2.2 using the data obtained for the G1 dendron. The hole mobility was calculated from the transfer characteristics using the slope of $I_{ds}^{1/2}$ vs. $V_g$. As expected, the dendron and rod were found to be hole transporting materials while the coil was an electron transporting material. In case of the
dendrons, the hole mobility was found to decrease with increasing generation of the dendron. For instance, mobility in G0 dendron was found to be $2.3 \times 10^{-6}$ cm$^2$/Vs while that in G3 dendron was $8.7 \times 10^{-7}$ cm$^2$/Vs (Table 2.1). This may be due to the increasing rigidity and curvature in the molecule limiting intermolecular packing at higher generations. The hole mobility in rod functionality was found to be $4.4 \times 10^{-5}$ cm$^2$/Vs. In case of the coil, electron mobility of $1.0 \times 10^{-7}$ cm$^2$/Vs was observed. Effect of thermal annealing was studied on all molecules ($80 \, ^\circ$C, 1h). This temperature was selected since the glass transition temperature (Tg) of the molecules was found be about 60 °C. However, no significant effect was observed on the charge mobility.

![Figure 2.2: (a) Output and (b) transfer characteristics of G1 dendron, 2-2, at W/L 500](image)

We further proceeded to measure the charge transport properties of dendron-rod functionalities followed by the dendron-rod-coil molecules. In case of the dendron-rod, significantly higher mobilities as compared to the dendrons were observed (Figure 2.3). This may be due to the participation of the rod functionality in the charge transport.
Interestingly, in this case, the mobility increased at lower generations from $2.4 \times 10^{-6}$ cm$^2$/Vs in G0 dendron-rod to $3.8 \times 10^{-6}$ cm$^2$/Vs in G1 dendron-rod molecule. However, at higher generations, lower mobility was observed which remained fairly constant from G2 to G3 (Table 2.1). G1 dendron-rod molecule exhibits the highest hole mobility indicating that the size of the molecule and density of charge transporting functionalities at this generation are optimum for such a molecular architecture.

**Table 2.1**: Charge mobility in dendron, dendron-rod and dendron-rod-coil molecules measured using field effect transistors

<table>
<thead>
<tr>
<th>Generation</th>
<th>Dendron</th>
<th>Dendron - rod</th>
<th>Dendron- rod-coil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Type</td>
<td>$\mu$ (cm$^2$/Vs)</td>
<td>Type</td>
</tr>
<tr>
<td>0</td>
<td>p</td>
<td>$2.33 \times 10^{-6}$</td>
<td>p</td>
</tr>
<tr>
<td>1</td>
<td>p</td>
<td>$8.00 \times 10^{-7}$</td>
<td>p</td>
</tr>
<tr>
<td>2</td>
<td>p</td>
<td>$6.81 \times 10^{-7}$</td>
<td>p</td>
</tr>
<tr>
<td>3</td>
<td>p</td>
<td>$8.67 \times 10^{-6}$</td>
<td>p</td>
</tr>
</tbody>
</table>

We further investigated the dendron-rod-coil molecules to study the complete molecule containing both p- and n- type components. Interestingly, in these molecules,
only electron transport was observed inspite of the molecule containing two p-type components. The electron mobility decreased with increasing generation of the dendron. As compared to the coil, which exhibits electron mobility of \(1.0 \times 10^{-7}\) cm\(^2\)/Vs, about one order of magnitude lower mobility was observed in case of the dendron-rod-coil molecules (\(3.20 \times 10^{-8}\) cm\(^2\)/Vs for G0 and \(8.98 \times 10^{-9}\) cm\(^2\)/Vs for G3). The lack of hole mobility and lower n-type mobility as compared to that in the coil may be attributed to the morphology of the material (see section 2.3.2).

### 2.3.1.2 Time-of-flight mobility measurements

Films (1-2 \(\mu\)m) were drop cast on ITO coated glass and aluminum electrode was vapor deposited onto the semiconductor layer to obtain the complete device. Each material was tested under this experimental condition to obtain the time-of-flight mobility in the molecules. In this case, both hole and electron mobilities were observed in dendron-rod and dendron-rod-coil molecules, indicating that the photo-generated charges can both be transported through the bulk material.

**Table 1.2:** Time-of-flight mobility in dendron-rod and dendron-rod-coil molecules

<table>
<thead>
<tr>
<th>Generation</th>
<th>Dendron - rod</th>
<th>Dendron- rod-coil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hole mobility (cm(^2)/Vs)</td>
<td>Electron mobility (cm(^2)/Vs)</td>
</tr>
<tr>
<td>0</td>
<td>(2.40 \times 10^{-5})</td>
<td>(2.00 \times 10^{-5})</td>
</tr>
<tr>
<td>1</td>
<td>(2.70 \times 10^{-6})</td>
<td>(2.60 \times 10^{-6})</td>
</tr>
<tr>
<td>2</td>
<td>(7.60 \times 10^{-8})</td>
<td>(1.90 \times 10^{-7})</td>
</tr>
<tr>
<td>3</td>
<td>(9.30 \times 10^{-9})</td>
<td>(2.60 \times 10^{-8})</td>
</tr>
</tbody>
</table>
In case of dendron-rod molecules, mobility decreases with increasing generation of dendron (Table 2.2). Both hole and electron mobilities are observed to drop by about three orders of magnitude from generation zero to three. However, the magnitude of hole and electron mobility in individual molecules is about the same. This suggests that upon photo-excitation of the rod, the exciton is split into hole, resident on the triarylamine, and electron is resident on the rod functionality. These charges are transported with commensurate mobility through the film under equivalent field gradients. In case of dendron-rod-coil molecules, unlike in field effect transistor measurements, both hole and electron transport is observed. Again, both mobilities decrease by about one order of magnitude upon increasing the generation of the dendron from generation zero to three (Table 2.2). This suggests that the morphology of the film in the z-direction may be significantly different from that in x-y direction which is the main participant in field effect transistor measurements. Continuity in the dendron phase in the z-direction is likely to result in the p-type behavior in the molecule. However, as the size of the molecules increases, the packing ability of the dendrons reduces which possibly results in the decrease in the hole mobility with increasing generation. In case of the electron transport properties, as the generation of the dendron increases, the non-contributing volume of the molecule increases. This may affect the packing ability of the coil and also the continuity of the coil phase in the bulk phase leading to a decrease in electron mobility with increasing generation of the dendron.
Figure 2.4: Comparison of charge mobility obtained from FET and time-of-flight measurements in (a) dendron-rod and (b) dendron-rod-coil molecules

A comparison of mobilities measured by field effect transistor measurements (Table 2.1) and time-of-flight measurements (Table 2.2) is shown in Figure 2.4. In case of dendron-rod and dendron-rod-coil molecules, the mobility in generation zero molecules is higher in case of time-of-flight mode as compared to the FET mode. Mobilities at higher generations are comparable from both techniques. The difference likely arises from the difference in packing of the small molecule in the two planes of study. It is also likely that as the generation of the dendron increases, there is no anisotropy in the system due to the increasing globular and amorphous nature of the material. Therefore, no significant difference in hole mobilities is observed at higher generations. Detailed morphological analysis is required to completely understand this system.

2.3.2 Morphology of dendron-rod-coil molecules

The solid state morphology of the molecules has a significant impact on their charge transporting properties. In macromolecules such as dendron-rod-coil molecules, continuity in dendron phase as well as coil phase is required to obtain both hole and electron transport in the molecules. Therefore, studying the morphology of the materials
is important to understand this property. Morphology of the dendron-rod-coil molecules was studied using small angle X-ray scattering (SAXS) experiments. The SAXS profile of the dendron-rod-coil molecules is shown in Figure 2.5 (a). The sole prominent feature in this profile is the peak at 4.2 nm which has varying domain size (calculated as the full width half maximum of the peak) as the generation of the dendron varies. The domain size increases with increasing generation, from 31 nm in case of G0 dendron-rod-coil to 60 nm in case of G3 dendron-rod-coil. Interestingly, the position of the peak matches well with that observed for the rod-coil segment as shown in Figure 2.5 (b).

**Figure 2.5**: SAXS profiles of (a) dendron-rod-coil molecules and (b) rod-coil model compound

This suggests that the principal packing in the dendron-rod-coil arises from the rod-coil segment. Increasing domain size with increasing generation suggests that the size of the dendron plays a role in the packing of the molecule by increasing the distance between the adjacent coil phases. However, no distinct peak is observed that can be attributed to the dendron phase indicating that there may not be a segregated dendron phase in the solid sample. This is possibly the reason for the lack of hole mobility in the FET measurements. However, detailed thin film X-ray reflectivity experiments are required to analyze the difference in morphology in the x-y plane and z-direction to
understand the difference in behavior of the molecules in FET and time-of-flight device configurations.

2.4 Conclusions

Dendron-rod-coil molecules provide an interesting architecture for active materials in organic photovoltaics. These materials have previously shown highly efficient photo-induced electron transfer in solution. The dendron and rod are found to be p-type materials while the coil shows n-type behavior. The charge transport properties of these materials have been studied using two complementary techniques. In field effect transistor measurements only n-type behavior was observed in dendron-rod-coil molecules likely due to the morphology in the x-y plane only consists of continuous coil domains and no continuity is present in the dendron phase. When mobility was measured in the z-direction using time-of-flight mobility measurements however, both p- and n-type behavior was observed. Hole and electron mobilities are of commensurate magnitude in these molecules. This indicates that in the diode configuration which is the device configuration in both time-of-flight mobility measurements and solar cells, the dendron-rod-coil materials exhibit ambipolar charge transport properties with commensurate hole and electron mobilities. Therefore, when used as active materials in solar cells, these molecules will be able to provide good transport of both charges hence avoiding the possibility of one of the charges accumulating due to its lower mobility. Charge accumulation is a significant problem in OPV devices as it limits the efficiency of the device. Therefore, dendron-rod-coil materials provide a promising molecular design for active materials which not only exhibit high exciton splitting efficiency but also ambipolar charge transport properties with commensurate hole and electron mobilities.
2.5 References


CHAPTER 3

CHARGE TRANSPORT IN NON-CONJUGATED DENDRONS: EFFECT OF DENSITY OF CHARGE TRANSPORT FUNCTIONALITY

3.1 Introduction

Solution processable organic semiconducting materials have garnered tremendous interest due to their potential in electronic and optoelectronic applications.\textsuperscript{1-6} Charge transport in these materials is particularly important as it plays a vital role in devices such as organic field effect transistors (OFETs), organic photovoltaics (OPVs) and organic light emitting diodes (OLEDs). Therefore, developing an understanding of key structural features of the molecule that affect its charge transporting ability is important. Organic molecules, designed as charge transporters, can be broadly classified into two categories: small molecules and polymers. In both these classes, owing to the ease in processibility, amorphous forms of the materials are desirable over crystalline forms. Small molecules provide the advantage of being well-defined and are often deposited in their pure form using high vacuum techniques. The well-defined nature of the small molecules allows chemists to carry out the necessary systematic structure-property studies. Polymers, on the other hand, are less-defined due to their polydisperse nature, but can be deposited through a simple spin coating technique. Dendrimers are an interesting class of materials, because these can be achieved in molecular weights comparable to those of polymers and can be deposited by solution processing techniques such as spin coating. In addition, these can also be obtained as monodisperse molecules, especially if synthesized by convergent methods. Hence, dendrimers can be said to bridge the gap between small organic molecules and polymers. For these reasons, it is interesting to investigate
dendritic architectures as potential charge transporting materials. We have studied the effect of generation of dendrimer and density of charge transporting groups in dendrimers on charge carrier mobility.

Dendrimers containing charge transporting functionalities have been previously investigated.\textsuperscript{7-17} In most cases, the charge transporting functionality is incorporated at the core or at the periphery. When a triphenylamine was incorporated at the core of a phenylenevinylene dendrimer, the charge mobilities understandably decrease with increasing generation, because the charge transporting functionalities at the core become more buried with increasing generations.\textsuperscript{7} Interestingly, when the charge transporting moieties based on [Ru(bpy)$_3$]$^{2+}$ were incorporated at the periphery, the mobility was also found to decrease with increasing generation.\textsuperscript{18} More recently, it was observed that iridium-cored dendrimers with carbazole units in every repeat units of the dendrimers exhibit increased charge carrier mobility with increasing generation.\textsuperscript{19}

We were interested in providing complementary insights into these observations together by designing a dendron, where electronically identical charge transporting units are incorporated throughout a dendritic backbone and comparing these with the dendrons where only the periphery is decorated with charge transporting units. In addition, we also imposed that the charge transporting units within the dendrons be connected to each other by an insulating functionality. This feature allows us to isolate the effects of charge transporting group density from the possible complications of charge localization to one part of the dendrimer through a conjugated backbone. Moreover, we have been interested in this type of non-conjugated triarylamine based dendrons as potential charge transporting units, considering our demonstration of dendron-rod-coil type systems as a
potential block copolymer architecture for long lived charge separation and ultimately in photovoltaics.\textsuperscript{20}

In our previously reported dendron-rod-coil structures, the dendron is based diarylaminopyrene as the hole-transporting unit. Therefore, the dendrons designed for the study outlined here are also based on diarylaminopyrene. In one set of dendrons, where the charge transporting units are incorporated only at the periphery, our targeted structures are shown in Chart 3.1 as structures 3-1 - 3-4.

\begin{center}
\textbf{Chart 3.1}: Structure of dendrimers 3-1 – 3-4 containing triarylamine functionality in the periphery
\end{center}

In the fully functionalized dendrons, the two phenolic groups in one of the phenyl rings and the hydroxymethyl group in the other phenyl ring are used as the AB2 functionalities to assemble the dendrimer. Since the resulting benzyl ether linkage does not provide electronic conjugation, the charge transporting functionalities in the
dendrimers do not have any through-bond electronic coupling. Thus, the target dendrons for the fully functionalized dendrons are shown in Chart 3.2 as structures 3-5 – 3-8.

![Chart 3.2: Structure of dendrimers 3-5 – 3-8 containing triarylamine functionality in every layer](image)

3.2 Materials and Methods

3.2.1 Materials

Pyrene, 3-aminobenzyl alcohol, aniline, 3,5-dimethoxybromobenzene, 3,5-dihydroxybenzyl alcohol, methanesulfonyl chloride, lithium bromide, hexamethyldisilazane (HMDS) and other conventional reagents were purchased from Aldrich and used as received. Tris(dibenzylideneacetone)dipalladium(0) and tri-tert-butyl
phosphine were purchased from Aldrich and stored in a glove box. N-bromosuccinimide was purchased from Aldrich and recrystallized from water before use. HPLC grade acetone and isopropyl alcohol were purchased from Fisher and were used as received. HPLC grade toluene and tetrahydrofuran (THF) were purchased from Fisher and dried over sodium and benzophenone. Dry toluene was stored in a Schlenk flask while THF was distilled freshly before use.

3.2.2 Characterization techniques

$^1$H-NMR spectra were recorded on a 400 MHz Bruker NMR spectrometer using the residual proton resonance of the solvent as the internal standard. Chemical shifts are reported in parts per million (ppm). When peak multiplicities are given, the following abbreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet; b, broad. $^{13}$C-NMR spectra were proton decoupled and recorded on a 100 MHz Bruker spectrometer using carbon signal of the deuterated solvent as the internal standard. Molecular weights of the dendrimers were estimated by fast atom bombardment mass spectrometry for small molecules and Bruker Omniflex III matrix assisted laser desorption ionization- time of flight mass spectrometry (MALDI-TOF) using dithreinol as the matrix, for higher generation dendrimers.

3.2.3 Mobility measurements

The transistors were constructed using pre-patterned silicon substrates; these transistors were constituted by a heavily n-doped silicon substrate with a 230 nm thermally oxidized silicon dioxide layer with a capacitance of 14.9 nF/cm$^2$. Gold electrodes were deposited on the gate oxide layer to yield the bottom contact FETs.
Before deposition of the film, the FET was cleaned with acetone followed by isopropyl alcohol. It was then exposed to HMDS vapor for 1 hour followed by re-cleaning with isopropyl alcohol. After this, thin films (285 ± 4 nm) of the dendrons were deposited on the surface by spin coating a 1 wt% solution in chlorobenzene (1500 rpm for 45 seconds). The devices were then annealed for 1 hour at 80 °C. The channel width of all transistors was 10 mm while the four different channel lengths, 2.5 μ, 5 μ, 10 μ and 20 μ were used. All measurements were carried out under inert atmosphere using Agilent 4156C precision semiconductor parameter analyzer.

3.2.4 General synthetic procedures

3.2.4.1 General procedure for protection of alcohol (I)

In an oven-dried round-bottom flask equipped with a magnetic stir bar, the required alcohol was taken as a solution in dry DMF. The solution was cooled to 0°C and imidazole (1.5 eq) was added to the solution. This was allowed to stir under Ar for 15 min. tert-butyldimethylsilyl chloride (TBDMSCl), 1.1 eq, was then added to the solution. It was then allowed to warm to room temperature at which the reaction was carried out for 24 h. The reaction mixture poured into water and the product was extracted with ethyl acetate. The organic layer was dried over Na₂SO₄ and purified using flash chromatography using hexanes.

3.2.4.2 General procedure for C-N coupling (II)

In an oven-dried round-bottom flask equipped with a magnetic stir bar, the required amine, aryl bromide (1.5 equiv), NaOtBu (1.5 equiv) were taken and placed under high vacuum for 30 min. Pd₂(dba)₃ (0.015 equiv) and dppf (0.03 equiv) for secondary amine
or P(tBu)_3 (0.025 equiv) for tertiary amine were added. Freshly distilled toluene was added to this mixture which was then heated to 100 °C. The reaction was carried out under argon at this temperature for 24h in case of secondary amine synthesis while in case of tertiary amine synthesis, the reaction was complete in 2h. Continuing the reaction for longer durations led to cleavage of the silyl ether.

Upon completion of reaction, toluene was removed under reduced pressure. The reaction mixture was redispersed in ethyl acetate and washed with water. The organic layer was dried over Na_2SO_4 and purified using flash chromatography using ethyl acetate/hexanes.

### 3.2.4.3 General procedure for deprotection of silyl ether (III)

The required silyl ether was dissolved in minimum amount of dry THF. To this solution, tetrabutylammonium fluoride (1M solution in THF, 1.5 equiv) was added and the mixture was stirred under Ar for 24 h. After completion of reaction, the THF was removed in vacuo. The reaction mixture was dissolved in ethyl acetate and washed with plenty of water. The organic layer was dried over Na_2SO_4 and purified using flash chromatography using ethyl acetate/hexanes.

### 3.2.4.4 General procedure for conversion of benzyl alcohol to benzyl bromide (IV)

The appropriate benzyl alcohol (1 equiv) and dimethylaminopyridine, DMAP (0.05 equiv) were dissolved in THF and the solution was cooled to 0 °C under Ar. Triethylamine (2.5 equiv) was added and the reaction mixture was stirred for 15 min. Mesyl chloride (2 equiv) was added drop-wise, and the resultant solution was allowed to stir at room temperature for 3 h. Upon completion of reaction, water was added and the
compound was extracted with ethyl acetate. The organic layer was dried over Na$_2$SO$_4$ and concentrated under reduced pressure to afford crude mixture which was used as is for the next step.

To the above crude mixture in THF, LiBr (3-6 equiv) was added and the contents were allowed to reflux overnight. After completion of the reaction, the reaction mixture was partitioned between water and ethyl acetate. The aqueous layer was extracted twice with ethyl acetate and the organic layer was dried over Na$_2$SO$_4$ and evaporated under reduced pressure. The crude product was purified by column chromatography using ethyl acetate/hexane as the eluent.

3.2.4.5 General procedure for alkylation of phenols (V)

A mixture of phenol (1 equiv), appropriate bromomethyl compound (1-1.2 equiv per phenolic alcohol), dry K$_2$CO$_3$ (3-6 equiv), and 18-crown-6 (0.1 equiv) in THF was refluxed and stirred vigorously under argon for 18h. The reaction mixture was allowed to cool to room temperature and solvent was evaporated to dryness. The residue was partitioned between water and ethyl acetate. The organic layer was separated and aqueous layer was re-extracted with ethyl acetate. The combined organic layer was dried over Na$_2$SO$_4$ and evaporated to dryness. The crude product was purified by column chromatography.
3.3 Results and discussion

3.3.1 Materials

3.3.1.1 Synthesis of 3-11

Following general procedure I, 3-aminobenzy alcohol, imidazole and TBDMSCl were reacted in DMF. The product was purified using column chromatography using ethyl acetate/ hexanes (1:5) to afford the product in 85% yield. $^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 0.16 (s, 6H (f)), 1.00 (s, 9H (g)), 3.67 (bs, 2H (-NH$_2$)), 4.71 (s, 2H (a)), 6.57 (dd, 1H, $j = 8$Hz, 2Hz (e)), 6.71 (s, 1H (b)), 6.74-6.76 (m, 1H (c)), 7.13 (t, 1H, $J = 7.6$Hz (d)) $^{13}$C NMR (100 MHz, CDCl$_3$, $\delta$): -5.1, 18.6, 26.1, 65.0, 112.9, 113.8, 116.4, 129.2, 142.8, 146.5 m/z calculated for C$_{13}$H$_{23}$NOSi: 237.1549 found by FAB: 237.1552

3.3.1.2 Synthesis of 3-13

Following general procedure II, bromopyrene, 3-12 (1.5 equiv), NaOtBu (1.5 equiv), Pd$_2$(dba)$_3$ (0.015 equiv) and dppf (0.03 equiv) were reacted in freshly distilled toluene. The product was purified using column chromatography using ethyl acetate/
hexanes (1:50) to afford the product in 81% yield. \(^1\)H NMR (400 MHz, d\(_6\)-acetone, \(\delta\): 0.06 (s, 6H (b)), 0.85 (s, 9H (a)), 4.72 (s, 2H (c)), 6.87 (d, 1H, \(J = 7.2\)Hz (e)), 7.06 (d, 1H, \(J = 7.6\)Hz (g)), 7.21-7.24 (m, 2H (b,d)), 7.98-8.36 (m, 9H (h)) \(^13\)C NMR (100 MHz, d\(_6\)-acetone, \(\delta\): -5.2, 18.8, 26.2, 65.5, 115.4, 115.4, 116.6, 116.6, 118.8, 119.2, 119.3, 123.0, 123.6, 125.0, 125.3, 125.9, 126.0, 126.6, 126.9, 127.1, 127.2, 127.5, 128.4, 129.9, 132.5, 132.8, 138.9, 143.7, 146.2, 146.3 m/z calculated for C\(_{29}\)H\(_{31}\)NOSi: 437.2175 found by FAB: 437.2154

### 3.3.1.3 Synthesis of N-(3, 5-dimethoxyphenyl)-N-(3-tertbutyldimethylsiloxymethyl phenyl) aminopyrene

Following general procedure II, 3-8 (1 equiv), 3-5 (1.5 equiv), NaOtBu (1.5 equiv), Pd\(_2\)(dba)\(_3\) (0.015 equiv) and P(tBu)\(_3\) (0.025 equiv) were reacted in freshly distilled toluene. The product was purified using column chromatography using ethyl acetate/hexanes (1:50) to afford the product in 81% yield. \(^1\)H NMR (400 MHz, d\(_6\)-acetone, \(\delta\): -0.10 (s, 6H (a)), 0.66 (s, 9H (b)), 3.62 (s, 6H (l)), 4.63 (s, 2H (c)), 6.16 (t, 1H, \(J = 6\)Hz (j)), 6.19 (d, 2H, \(J = 2\)Hz (i, k)), 6.91 (d, 1H, \(J = 7.6\)Hz (e)), 7.02 (d, 1H, \(J = 8\)Hz (g)), 7.08 (s, 1H (d)), 7.22 (t, 1H, \(J = 8\)Hz (f)), 7.86-8.32 (m, 9H (h)) \(^13\)C NMR (100 MHz, d\(_6\)-acetone, \(\delta\): -5.3, 18.6, 26.0, 55.5, 65.0, 94.5, 101.5, 120.5, 121.1, 121.7, 124.1, 125.6,
126.1, 126.2, 127.0, 127.3, 128.1, 128.2, 128.6, 128.8, 129.2, 129.8, 130.7, 132.0, 132.3, 141.8, 143.9, 149.4, 151.4, 162.5 m/z calculated for C₃₇H₃₉NO₃Si: 573.2699 found by FAB: 573.2705

3.3.1.4 Synthesis of 3-5

Following general procedure III, 3-9 was reacted with TBAF in THF. The product was purified by column chromatography using ethyl acetate/ hexanes (1:5) to afford the product in 75% yield. ¹H NMR (400 MHz, d₆-acetone, δ): 3.61 (s, 6H (b)), 4.52 (d, 2H, J = 6Hz (a)), 6.14 (s, 3H (h-j)), 6.97-7.00 (m, 2H (d, f)), 7.19-7.24 (m, 2H (c, e)), 7.86-8.32 (m, 9H (g)) ¹³C NMR (100 MHz, d₆-acetone, δ): 55.5, 64.5, 94.3, 101.2, 121.5, 121.9, 122.4, 124.1, 125.5, 126.1, 126.3, 127.0, 128.1, 128.2, 128.6, 128.7, 129.2, 129.8, 130.6, 132.0, 132.3, 141.8, 144.9, 149.3, 151.6, 162.5 m/z calculated for C₃₁H₂₅NO₃: 459.1834 found by FAB: 459.1859
3.3.1.5 Synthesis of 3-9

Following general procedure IV, 3-10 was first reacted with NEt₃ (2.5 equiv), 4-DMAP (0.05 equiv) and mesyl chloride (2 equiv) in THF followed by LiBr (5 equiv) in THF. The product was purified by column chromatography using ethyl acetate/ hexanes (1:20) to afford the product in 80% yield. $^1\text{H NMR}$ (400 MHz, d₆-acetone, δ): 3.63 (s, 6H (b)), 4.55 (s, 2H (a)), 6.17-6.20 (m, 3H (h-j)), 6.94-6.96 (m, 1H (f)), 7.06 (d, 1H, $J = 8\text{Hz}$ (d)), 7.21-7.27 (m, 2H (c, e)), 7.88-8.34 (m, 9H (g)) $^{13}\text{C NMR}$ (100 MHz, d₆-acetone, δ): 34.4, 55.5, 95.0, 101.6, 123.0, 123.7, 123.9, 126.2, 126.4, 127.0, 127.1, 127.4, 128.2, 128.6, 128.9, 129.2, 130.5, 130.8, 122.0, 132.2, 140.3, 141.4, 149.6, 151.0, 162.6 m/z calculated for C$_{31}$H$_{24}$BrNO$_2$: 523.0970 found by FAB: (M+1) 524.0903

3.3.1.6 Synthesis of 3,5-dihydroxybromobenzene

In an oven dried 2 necked round bottom flask, a solution of 3,5-dimethoxybromo benzene in dichloromethane was cooled to -78°C under Ar. This temperature was maintained for 30 min after which BBr$_3$ (3 equiv) was added. The temperature was maintained for further 1h after which the reaction mixture was allowed to warm to room
temperature. The reaction was stirred overnight under Ar. The reaction was quenched using cold saturated ammonium chloride solution. Product was extracted into dichloromethane and purified by column chromatography using ethyl acetate/ hexanes (1:5) to afford the product in 81% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\)): 5.12 (bs, 2H (-OH)), 6.29 (t, 1H, \(J = 6\)Hz (c)), 6.59 (d, 2H, \(J = 2\)Hz (a, b)) \(^{13}\)C NMR (100 MHz, CDCl\(_3\), \(\delta\)) 102.2, 111.8, 123.0, 157.5 m/z calculated for C\(_6\)H\(_5\)BrO\(_2\): 187.9473 found by FAB: 187.9468

3.3.1.7 Synthesis of 3-15

Following general procedure I, 3,5-dihydroxybromobenzene, imidazole and TBDMSCl were reacted in DMF. The product was purified using column chromatography using hexanes to afford the product in 73% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\)): 0.20 (s, 12H (d)), 0.97 (s, 18H (e)), 6.26 (t, 1H, \(J = 6\)Hz (c)), 6.63 (d, 2H, \(J = 2\)Hz (a, b)) \(^{13}\)C NMR (100 MHz, CDCl\(_3\), \(\delta\)) -4.3, 18.3, 25.8, 111.3, 117.1, 122.3, 157.3 m/z calculated for C\(_{18}\)H\(_{33}\)BrO\(_2\)Si: 416.1202 found by FAB: 416.1221
3.3.1.8 Synthesis of 3-16

Following general procedure II, 3-13 (1 equiv), 3-15 (1.5 equiv), NaOtBu (1.5 equiv), Pd_2(dba)_3 (0.015 equiv) and P(tBu)_3 (0.025 equiv) were reacted in dry toluene. The product was purified using column chromatography using ethyl acetate/ hexanes (1:50) to afford the product in 90% yield. ^1H NMR (400 MHz, d_6-acetone, δ): -0.07 (s, 6H (b)), 0.02 (s, 12H (l)), 0.67 (s, 9H (a)), 0.84 (s, 18H (m)), 4.65 (s, 2H (c)), 6.01 (t, 1H, J = 2.4Hz (j)), 6.15 (d, 2H, J = 2Hz (i, k)), 6.95 (d, 1H, J = 7.6Hz (g)), 7.05 (d, 1H, J = 8Hz (e)), 7.10 (s, 1H (d)), 7.25 (t, 1H, J = 8Hz (f)), 7.85-8.33 (m, 9H (h)) ^13C NMR (100 MHz, d_6-acetone, δ): -5.3, -4.3, 18.7, 18.8, 26.0, 26.1, 65.1, 106.7, 108.0, 120.8, 121.3, 122.0, 124.0, 126.1, 126.3, 127.0, 127.1, 127.3, 128.1, 128.2, 128.5, 128.8, 129.8, 130.7, 132.0, 132.2, 141.7, 144.0, 149.2, 151.3, 158.1 m/z: calculated for C_{47}H_{63}NO_5Si_3: 773.4116 found by FAB: 773.4149
3.3.1.9 Synthesis of 3-10

Following general procedure III, 3-16 was reacted with TBAF in THF. The product was purified by column chromatography using ethyl acetate/ hexanes (1:2.5) to afford the product in 70% yield. $^1$H NMR (400 MHz, d$_6$-acetone, $\delta$): 4.15 (bs, 1H (-OH)), 4.51 (s, 2H (a)), 5.96-5.99 (m, 3H(f-h)), 6.98-7.24 (m, 4H (b-e)), 7.83-8.32 (m, 9H (i))

$^{13}$C NMR (100 MHz, d$_6$-acetone, $\delta$): 64.4, 97.5, 101.2, 121.4, 122.1, 122.6, 124.3, 125.6, 126.1, 126.2, 126.9, 127.3, 128.0, 128.2, 128.6, 128.7, 129.2, 129.8, 130.6, 132.3, 142.2, 144.7, 149.5, 151.7, 160.0 m/z calculated for C$_{29}$H$_{21}$NO$_3$: 431.1521 found by FAB: 431.1513
3.3.1.10 Synthesis of 3-6

Following general procedure V, **3-10** (1 equiv) was reacted with **3-9** (2.2 equiv), K$_2$CO$_3$ (5 equiv) and 18-crown-6 (0.01 equiv) in freshly distilled THF. The product was purified by column chromatography using dichloromethane/ethyl acetate/hexanes (1:3:6) to afford the product in 93% yield. $^1$H NMR (400 MHz, d$_6$-acetone, $\delta$): 3.54 (s, 12H (c)), 4.45 (d, 2H, $J$ = 6Hz (a)), 4.75 (s, 4H (b)), 6.04-6.11 (m, 9H (d)), 6.78-7.15 (m, 12H (e)), 7.72-8.26 (m, 27H (f)) $^{13}$C NMR (100 MHz, d$_6$-acetone, $\delta$): 55.5, 64.4, 70.1, 94.7, 96.1, 101.4, 102.1, 121.5, 121.9, 122.1, 122.3, 122.6, 124.0, 125.5, 126.1, 126.2, 126.3, 126.9, 127.0, 127.4, 127.6, 128.0, 128.1, 128.2, 128.3, 128.5, 128.6, 128.8, 128.9, 129.1, 129.8, 130.0, 130.7, 131.9, 132.2, 139.4, 141.5, 141.6, 144.8, 149.0, 149.3, 151.2, 151.3, 161.2, 162.5 m/z calculated for C$_{91}$H$_{67}$N$_3$O$_7$: 1313.50 found by MALDI-TOF: [M+2H]$^+$ 1316.45
3.3.1.11 Synthesis of 3-17

Following general procedure IV, 3-6 was first reacted with NEt$_3$ (2.5 equiv), 4-DMAP (0.05 equiv) and mesyl chloride (2 equiv) in THF followed by LiBr (5 equiv) in THF. The product was purified by column chromatography using ethyl acetate/ hexanes (1:4) to afford the product in 75% yield. $^1$H NMR (400 MHz, d$_6$-acetone, $\delta$): 3.54 (s, 12H (c)), 4.45 (s, 2H (a)), 4.77 (s, 4H (b)), 6.05-6.13 (m, 9H (d)), 6.79-7.14 (m, 12H (e)), 7.73-8.27 (m, 27H (f)) $^{13}$C NMR (100 MHz, d$_6$-acetone, $\delta$): 34.4, 55.5, 70.2, 94.7, 95.0, 101.4, 101.4, 121.8, 121.9, 122.0, 122.1, 122.6, 122.8, 122.9, 123.6, 123.8, 124.0, 125.4, 125.5, 126.0, 126.1, 126.2, 126.3, 126.9, 127.0, 127.1, 127.2, 127.3, 128.1, 128.1, 128.2, 128.5, 128.6, 128.8, 129.0, 129.1, 130.0, 130.7, 131.9, 132.2, 139.4, 139.5, 141.2, 141.5, 149.4, 151.1, 161.2, 162.5 m/z calculated for C$_{91}$H$_{66}$BrN$_3$O$_6$: 1377.41 found by FAB: [M+2H]$^+$ 1379.13
3.3.1.12 Synthesis of 3-7

Following general procedure V, 3-10 (1 equiv) was reacted with 3-17 (2.2 equiv), K$_2$CO$_3$ (5 equiv) and 18-crown-6 (0.01 equiv) in freshly distilled THF. The product was purified by column chromatography using dichloromethane to afford the product in 70% yield. $^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 3.51 (s, 24H (c)), 4.35 (d, 2H, $J = 6$Hz (a)), 4.47-4.56 (m, 12H (b)), 5.90-6.13 (m, 21H (d)), 6.73-7.04 (m, 28H (e)), 7.60-8.11 (m, 63H (f)) $^{13}$C NMR (100 MHz, CDCl$_3$, $\delta$): 55.3, 65.2, 69.9, 94.1, 95.5, 100.7, 101.7, 121.1, 121.35, 121.8, 121.9, 122.2, 123.3, 124.9, 125.2, 125.3, 126.1, 126.2, 126.3, 127.3, 127.7, 128.1, 128.4, 129.3, 129.5, 129.7, 129.8, 131.1, 131.3, 137.9, 138.0, 140.4, 140.5, 147.3, 148.5, 150.2, 150.4, 160.3, 161.4 m/z calculated for C$_{211}$H$_{151}$N$_{15}$O$_{15}$: 3024.49 found by MALDI-TOF: [M+4H]$^+$ 3028.74
3.3.1.13 Synthesis of 3-18

Following general procedure IV, 3-7 was first reacted with NEt₃ (2.5 equiv), 4-DMAP (0.05 equiv) and mesyl chloride (2 equiv) in THF followed by LiBr (5 equiv) in THF. The product was purified by column chromatography using dichloromethane to afford the product in 57% yield. $^1$H NMR (400 MHz, CDCl₃, δ): 3.52 (s, 24H (c)), 4.18 (d, 2H, $J = 44$Hz (a)), 4.49-4.56 (m, 12H (b)), 5.91-6.13 (m, 21H (d)), 6.74-7.01 (m, 28H (e)), 7.60-8.11 (m, 63H (f)) $^{13}$C NMR (100 MHz, CDCl₃, δ): 33.7, 55.3, 69.9, 94.1, 95.5, 100.7, 101.7, 101.9, 121.4, 121.8, 122.1, 122.2, 123.2, 123.3, 124.9, 125.2, 125.3, 126.1, 126.2, 126.3, 127.3, 127.7, 128.1, 128.4, 129.3, 129.6, 129.8, 131.1, 131.3, 137.8, 137.9, 140.4, 140.5, 148.4, 148.5, 150.2, 150.4, 160.3, 161.4 m/z calculated for $C_{211}H_{150}BrN_{7}O_{14}$: 3085.05 found by MALDI-TOF: 3086.59
3.3.1.14 Synthesis of 3-8

Following general procedure V, 3-10 (1 equiv) was reacted with 3-18 (2.2 equiv), K₂CO₃ (5 equiv) and 18-crown-6 (0.01 equiv) in freshly distilled THF. The product was purified by column chromatography using dichloromethane to afford the product in 70% yield. ¹H NMR (400 MHz, CDCl₃, δ): 3.48 (s, 48H (c)), 4.25 (d, 2H, J = 6Hz (a)), 4.37-4.56 (m, 28H (b)), 5.82-6.18 (m, 45H (d)), 6.67-7.00 (m, 60H (e)), 7.49-8.09 (m, 135H (f)) ¹³C NMR (100 MHz, CDCl₃, δ): 55.3, 65.2, 69.9, 94.1, 95.6, 100.7, 101.7, 121.4, 121.8, 122.2, 123.2, 123.3, 124.9, 125.2, 125.3, 126.1, 126.2, 126.3, 127.3, 127.6, 127.7, 128.1, 128.3, 128.4, 129.3, 129.7, 129.8, 131.1, 131.1, 131.3, 137.9, 140.4, 140.5, 148.3, 148.5, 150.3, 150.4, 160.3, 161.4 m/z calculated for C₄₅₁H₃₁₉N₁₅O₃₁: 6444.40 found by MALDI-TOF: 6450.80
3.3.2 Synthesis

Dendrons 3-1 – 3-4 were synthesized using the procedures previously described by us.\textsuperscript{21} To synthesize the benzyl ether dendrons 3-5 – 3-8, it is necessary that the peripheral units be synthesized as the corresponding benzyl bromides and the repeat units contain two phenolic functionalities and a hydroxymethyl moiety. Accordingly, our target precursors are represented by structures 3-9 and 3-10. The triarylamine building blocks themselves were assembled using the palladium catalyzed C-N coupling as the key step. To synthesize 3-9, tert-butyldimethysilyl (TBS)-protected \textit{m}-aminobenzyl alcohol 3-11 was treated with 1-bromopyrene (3-12) under the palladium-catalyzed amination conditions to obtain the secondary amine 3-13 in 81\% yield (Scheme 3.1). Compound 3-13 was further treated with 1-bromo-3,5-dimethoxybenzene (3-14) under the amination conditions to obtain the corresponding triarylamine in 89\% yield. This molecule was treated with tetrabutylammonium fluoride (TBAF) to liberate the TBS-ether as the corresponding hydroxymethyl compound, 3-5. The hydroxymethyl functionality was converted to bromomethyl group by a sequence of mesylation-bromination steps to afford the targeted peripheral triarylamine molecule 3-9 in 80\% yield over the two steps.
Scheme 3.1: Synthesis of peripheral triaryamine 3-9

The AB₂ repeat unit 10 was synthesized using a similar sequence of reactions. The key variation, however, is that the phenolic groups in the triaryamine should also be liberated after assembling the triaryamine using the palladium-catalyzed amination reactions. To accommodate this need, we first reacted 3-14 with borontribromide to obtain the corresponding diphenolic molecule in 81% yield. The phenolic functionalities were then protected with tert-butyldimethylsilyl functionality to obtain the TBS-ether 3-
in 75% yield. This molecule was treated with the amine 3-13 to obtain the triarylamine 3-16 in 90% yield. The TBS-ethers were converted to the corresponding hydroxy functionalities by treatment with TBAF to afford the targeted triarylamine repeat unit 3-10 in 70% yield (Scheme 3.2).

![Chemical structure diagram](image)

**Scheme 3.2: Synthesis of triarylamine 3-10**

The benzyl ether dendrons 3-6 – 3-8 were synthesized from 3-9 and 3-10 using the iterative convergent synthetic methodology. Two equivalents of the bromomethyl compound 3-9 was treated with the AB₂ monomer 3-10 in the presence of potassium carbonate and 18-crown-6 to obtain the G₁ dendron 3-6 in 92% yield. Conversion of the hydroxymethyl functionality in 3-6 to a bromomethyl moiety and reaction with the 3-10 afforded the G₂ dendron 3-7. Iteration of these two steps with 7 afforded the G₃ dendron 3-8, as shown in Scheme 3.3. All dendrons were characterized using ¹H NMR, ¹³C NMR and mass spectrometry.
Scheme 3.3: Synthesis of dendrimers 3-6 – 3-8
3.3.3 Measurement of mobility in dendrons

With all the targeted structures in hand, we investigated the charge transport characteristics of dendrons 3-1 – 3-4 in the field effect transistor (FET) mode. An example of the typical output and transfer characteristics is shown in Figure 3.1 using the data obtained for the G1 dendron 3-2. The hole mobility was calculated from the transfer characteristics using the slope of $I_{ds}^{1/2}$ vs. $V_g$. The hole mobility in the G0 dendron 3-1 and found to about $2.6 \times 10^{-6}$ cm$^2$/Vs.

![Figure 3.1: (a) Output and (b) transfer characteristics of 3-2 at W/L 500](image)

We find that the mobility systematically decreased with increasing generation in these dendrons, where the dendrons 3-2 – 3-4 (G1-G3) exhibit mobilities of $1.9 \times 10^{-6}$ cm$^2$/Vs, $1.5 \times 10^{-6}$ cm$^2$/Vs, and $7.3 \times 10^{-7}$ cm$^2$/Vs respectively (Table 3.1). The observed decrease can be attributed to the lower density of charge transport units within the dendrons with increase in generation. Note that these dendrons contain charge transporting functionalities only in their periphery and the internal units are non-conducting. These non-conducting units could inhibit charge hopping among the dendritic molecules and thus the entire device. On the other hand, dendrons are expected to become globular at higher generations and one could expect that in an ideal scenario, this globular shape could translate in to an encapsulation of the insulating units. The
observed decrease suggests that such an encapsulation does not occur at higher
generations, at least up to the third generation dendron studied here.

**Table 3.1: Hole mobility in dendrimers**

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>$\mu$ (cm$^2$/Vs)</th>
<th>Dendrimer</th>
<th>$\mu$ (cm$^2$/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-1</td>
<td>$2.58 \times 10^{-6}$</td>
<td>3-5</td>
<td>$9.87 \times 10^{-7}$</td>
</tr>
<tr>
<td>3-2</td>
<td>$1.92 \times 10^{-6}$</td>
<td>3-6</td>
<td>$4.05 \times 10^{-6}$</td>
</tr>
<tr>
<td>3-3</td>
<td>$1.50 \times 10^{-6}$</td>
<td>3-7</td>
<td>$2.82 \times 10^{-6}$</td>
</tr>
<tr>
<td>3-4</td>
<td>$7.30 \times 10^{-7}$</td>
<td>3-8</td>
<td>$2.83 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

To test the hypothesis that the decrease in charge mobility is due to the presence
of the insulating internal layers in dendrons, we designed the dendrons 3-5 – 3-8 and
tested their charge carrier mobilities. In these dendrons, the triarylamine units with
similar redox potentials are present in every repeat unit in the dendron. Thus, there are
no insulating repeat units in the dendron. The charge carrier mobility of the G0 dendron
3-5 in this case was found to be $9.8 \times 10^{-7}$ cm$^2$/Vs (Table 3.1). Interestingly, compared to
this G0 molecule, the hole mobility of the G1 dendron 3-6 was significantly higher
($4.1 \times 10^{-6}$ cm$^2$/Vs). Typical output and transfer characteristics of G1 dendron, 3-6, are
shown in Figure 3.2. The mobilities for the second and third generation dendrons were
found to be similar at $2.8 \times 10^{-6}$ cm$^2$/Vs.

**Figure 3.2:** (a) Output and (b) transfer characteristics of 3-6 at W/L 500
Thus, these mobilities were slightly lower than the first generation dendron, but still much higher than the corresponding dendrons where insulating units are present within the interior layers of the dendrons (Figure 3.3). We attribute the lowered mobilities at higher generation to the presence of lower density internal layer present in these dendrons. The fact that the first generation dendron exhibits high mobilities compared to the G0 small molecule shows that there are some advantages to using dendritic architecture for charge transport. However, higher generation dendrons are not necessary to attain the optimal charge carrier mobilities from these architectures.

![Figure 3.3: Comparison of hole mobility in dendrimers](image)

**3.3.3.1 Effect of annealing**

Mobility in dendrons was first measured in the as cast film. The mobility in these samples was found to improve marginally upon thermally annealing the samples at 80°C for 1h. This may be due to better arrangement of dendron molecules in the films after solvent evaporation at the elevated temperature. Figure 3.4 shows the effect of annealing on hole mobility observed in 3-5 – 3-8.
Figure 3.4: Effect of annealing on hole mobility in dendrimers 3-5 – 3-8

3.4 Conclusions

Understanding the charge transport properties of organic semiconductors is imperative to developing efficient organic electronic and optoelectronic devices. Dendrimers provide the advantage of bridging the gap between small molecules and polymers in systematically evaluating well-defined macromolecular charge transport materials. Previous reports on charge transfer dendrons suggest that the charge mobilities in dendrons decrease with increasing generation. We hypothesized that this observation could be attributed to the insulating internal layers within the dendrons, when only the periphery of these molecules is functionalized with charge transporting units. We tested this hypothesis by designing and synthesizing dendrons that contain electronically identical charge transporting functionalities in every repeat unit of the dendron. We find that the charge mobilities are indeed higher in these dendrons. Our findings here will be useful in designing the next generation of devices containing dendrons as one of the charge transporting components. For example, dendron-rod-coil based block copolymer architectures are interesting for achieving nanoscale solid state assemblies and these
molecules have shown promise for photoinduced charge separation in solution.\textsuperscript{20} To obtain the targeted solid state nanoassemblies, the dendritic component of the architecture should be preserved without compromising the charge carrier mobilities found in small molecules. Our results here suggest that dendritic structures can indeed be utilized to preserve or even enhance the charge mobilities observed with small molecules (\textit{i.e.} G0).
3.5 References


CHAPTER 4

CHARGE TRANSPORT PROPERTIES OF DONOR-ACCEPTOR-DONOR BASED OLIGOMERS

4.1 Introduction

Solution processable organic semiconductors have generated significant interest due to the need for efficient materials for organic electronics applications.\textsuperscript{1-3} Considering the recent surge in interest in these materials as possible active materials in photovoltaic devices, there has been an interest in combining the conducting properties with low band gap features. These are obvious requirements for active materials in photovoltaic devices, because: (\textit{i}) it is essential that the absorption spectrum of these molecules has significant overlap with that of the solar spectrum to efficiently generate excitons; (\textit{ii}) it is essential that the charges generated from the decomposition of the exciton are effectively transported to the electrodes. With these in mind, there have been several polymeric molecules that contain donor-acceptor components within their architectures.\textsuperscript{3-9} Low band gap in these systems is thought to result from the significant double bond character between the adjacent aromatic units that arises from the consecutive placement of electron rich and electron deficient moieties.\textsuperscript{9} In such reduced band gap systems, orbital partitioning is observed leading to the highest occupied molecular orbital (HOMO) resembling that of the donor component, while the acceptor component contributes most to the lowest unoccupied molecular orbital (LUMO).\textsuperscript{10,11} This feature allows for tuning the band gap of a material, while preferentially affecting only one of the frontier orbital energy levels.
Among the donor-acceptor polymeric systems, molecules where the acceptor is based on 2,1,3-benzothiadiazole (BZT) have attracted particular attention.\textsuperscript{12-17} In addition to the photophysical properties, the relative ease of synthetic manipulation of BZT moieties has contributed to the high attention received by this acceptor functionality.\textsuperscript{18, 19} While the donor-acceptor approach has been applied successfully to obtain polymers with low band gap, there are relatively few reports on the analogous small molecules and oligomers.\textsuperscript{16, 20, 21} Oligomers provide an excellent model system for understanding the structure-property relation in the molecules due to their monodisperse nature, ease of purification, and possible solution processability. As a result, we carried out a systematic study containing donor-acceptor-donor molecular triads, where the BZT acceptor moiety is attached to thiophenes with varying donor strengths (Chart 4.1).

\begin{center}
\textbf{Chart 4.1}: Structure of D-A-D molecules 4-1 – 4-4
\end{center}
4.2 Materials and Methods

4.2.1 Materials

2,1,3-benzothiadiazole, 2-tributylstannylthiophene, N-bromosuccinimide, 2,2’-bithiophene, potassium carbonate, hexamethyldisilazane (HMDS), tris(dibenzylideneacetone)dipalladium(0), dichlorobis(triphenylphosphine)palladium(II), tetrakis(triphenylphosphine)palladium(0) and other conventional reagents were purchased from Aldrich and used as received. N-bromosuccinimide was purchased from Aldrich and recrystallized from water before use. HPLC grade N,N-dimethylformamide (DMF), acetone and isopropyl alcohol were purchased from Fisher and were used as received. HPLC grade tetrahydrofuran (THF) was purchased from Fisher and dried over sodium and benzophenone.

4.2.2 Characterization Techniques

$^1$H-NMR spectra were recorded on a 400 MHz Bruker NMR spectrometer using the residual proton resonance of the solvent as the internal standard. Chemical shifts are reported in parts per million (ppm). When peak multiplicities are given, the following abbreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet; b, broad. $^{13}$C-NMR spectra were proton decoupled and recorded on a 100 MHz Bruker spectrometer using carbon signal of the deuterated solvent as the internal standard. Molecular weights were estimated by fast atom bombardment mass spectrometry. Cyclic voltammetry experiments were carried out at room temperature using a BASi C3 cell stand fitted with three electrodes: a platinum disk working electrode, platinum auxiliary electrode and Ag/Ag$^+$ reference electrode. The voltammograms were recorded in dry THF using
tetraethylammonium hexafluorophosphate as the supporting electrolyte and ferrocene as
the internal standard. UV-Visible spectra were obtained using a Cary 100
spectrophotometer and fluorescence data were collected using JASCO FP-6500
spectrofluorimeter. Atomic force microscopy was carried out using Dimension 3000
AFM in air at room temperature.

4.2.3 Synthetic Procedures

4.2.3.1 General procedure (I) for Stille coupling

In an oven dried flask, required dibromide (1.0 eq.) and tributylstannyl derivative
(2.5 eq.) were taken and dissolved in dry DMF. To this PdCl$_2$(PPh$_3$)$_2$ (0.05 eq) was added
and the solution was heated under argon at 70 °C for 24 h. The reaction was then allowed
to cool to room temperature and quenched by adding distilled water. The product was
extracted using ethyl acetate and purified using column chromatography.

4.2.3.2 General procedure (II) for Suzuki coupling

In an oven dried flask, the required monobromide and boronic acid pinacol ester
(0.4 eq) were taken and dissolved in degassed THF. To this Pd(PPh$_3$)$_4$ (0. 8 mol%) was
added and the solution was heated to 60 °C under argon. Degassed 2M aqueous K$_2$CO$_3$
solution (4 mL for 100 mg of monobromide) was added to this solution and it was
refluxed under argon for 12 h. The reaction was allowed to cool to room temperature. It
was then washed with distilled water and product was extracted in ethyl acetate and
purified using column chromatography.


### 4.2.3.3 Synthesis of 4-1

Following general procedure II, compound 4-6, phenyl boronic acid, Pd(PPh₃)₄
and 2M aq K₂CO₃ were reacted at 60 °C for 12 h. The crude product was purified using
column chromatography with hexanes as eluent to obtain product as a red solid in 80% yield. Product was recrystallized from chlorobenzene. ¹H NMR (400 MHz, CDCl₃, δ):
7.33 (d, 2H, J = 7.2 Hz (c)), 7.41-7.46 (m, 6H (e-g)), 7.71 (d, 4H, J = 7.2 Hz (d, h)), 7.90 (s, 2H (a)), 8.13 (d, 2H, J = 4Hz (b)) m/z calculated for C₂₆H₁₆N₂S₃: 452.0476, found by FAB: 452.0497. The structure of the molecule was confirmed by comparison of data with previous report²² and further confirmed by X-ray crystallography. Details of the crystal structure are discussed in the Appendix.

### 4.2.3.4 Synthesis of 4-2

Following general procedure I, compound 4-6, 2-tributylstannylthiophene and
PdCl₂(PPh₃)₂ were reacted under argon for 24 h at 70 °C. The crude product was purified using
column chromatography with 1:4 dichloromethane-hexanes as eluent. Product was obtained as dark red solid in 85% yield. Recrystallization was done using dichloromethane-hexanes. ¹H NMR (400 MHz, CDCl₃, δ): 7.06-7.08 (m, 2H(d)), 7.27-7.29 (m, 4H (c, f)), 7.30 (dd, 2H, J₁ = 3.6 Hz, J₂ = 0.8 Hz (e)), 7.87 (s, 2H (a)), 8.05 (d,
2H, $J = 4$ Hz (b)). $^{13}$C NMR (100 MHz, CDCl$_3$, $\delta$): 124.2, 124.8, 125.0, 125.4, 125.7, 128.2, 128.4, 137.4, 138.2, 139.0, 152.7 m/z calculated for C$_{22}$H$_{12}$N$_2$S$_5$: 463.9604, found by FAB: 463.9634. The structure of the molecule was further confirmed by X-ray crystallography. Details of the crystal structure are discussed in the Appendix.

4.2.3.5 Synthesis of 4-3

Following general procedure I, compound 4-7, monostannyl derivative of dithienothiophene 4-9 and PdCl$_2$(PPh$_3$)$_2$ were reacted under argon for 24 h at 70 °C. The crude product was purified using column chromatography with hexanes as eluent. Product was obtained as a dark red solid in 65% yield. Due to the limited solubility of this molecule in chloroform, low signal was obtained in NMR spectra. $^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 7.38-7.43 (m, 4H (c, d)), 7.90 (s, 2H (a)), 8.48 (s, 2H (b)) $^{13}$C NMR (100 MHz, CDCl$_3$, $\delta$): 117.4, 120.9, 121.0, 125.5, 126.5, 127.0, 129.5, 129.9, 139.9, 142.8, 155.7 m/z calculated for C$_{22}$H$_{8}$N$_2$S$_7$expected: 523.8732, found by FAB: 523.8721
4.2.3.6 Synthesis of 4-4

Following general procedure II, 4,7-diboronic acid pinacol ester of 2,1,3-benzothiadiazole, compound 4-10, Pd(PPh₃)₄ and 2M aq K₂CO₃ were reacted at 80 °C for 12 h. The crude product was purified using column chromatography with hexanes as eluent to obtain product as a purple solid in 80% yield. ¹H NMR (400 MHz, CDCl₃, δ): 0.91 (t, 6H, J = 7.2 Hz (l)), 1.25-1.74 (m, 16H (h-k)), 2.70-2.74 (t, 4H, J = 5.2 Hz (g)), 7.16 (d, 2H, J = 5.2 Hz (d)), 7.22 (d, 2H, J = 8.4 Hz (c)), 7.39 (d, 4H, J = 8.4 Hz (f)), 7.57 (d, 4H, J = 8.4 Hz (e)), 7.87 (s, 2H (a)), 8.39 (s, 2H (b)) ¹³C NMR (100 MHz, CDCl₃, δ): 14.3, 22.8, 29.2, 31.7, 31.9, 35.8, 112.4, 113.2, 117.0, 117.6, 123.0, 124.8, 124.9, 126.6, 129.9, 137.6, 141.4, 145.0 m/z calculated for C₄₆H₄₂N₄S₅: 810.2013, found by FAB: 810.2058

4.2.4 Organic Field-Effect Transistor (FET) Fabrication and Characterization

The field effect transistors were constructed using pre-patterned silicon substrates. The transistors were constituted by a heavily n-doped silicon substrate with a 230 nm thermally oxidized silicon dioxide layer with a capacitance of 14.9 nF/cm². Gold electrodes were deposited on the gate oxide layer to yield the bottom contact FETs.
Before deposition of the film, the FET substrates were cleaned with acetone followed by isopropyl alcohol. They were then exposed to HMDS vapor for 1h followed by re-cleaning with isopropyl alcohol. After this, thin films of the oligomers were deposited on the surface by spin coating a 0.5 wt% solution in chlorobenzene (1500 rpm for 45 seconds). The devices were then annealed for 1 hour at 80 °C. The channel width of all transistors was 10 mm and channel length was 5 μm or 2.5 μm. All measurements were carried out under inert atmosphere using Agilent 4156C precision semiconductor parameter analyzer.

4.3 Results and Discussion

4.3.1 Synthesis

The target molecules 4-1 – 4-4, containing the BZT acceptor, are shown in Chart 4.1. All these molecules were synthesized using Stille and Suzuki coupling reactions. Compounds 4-1 and 4-2 were synthesized by installing the terminal phenyl or thienyl units in the last step of the synthesis (Scheme 4.1).

Scheme 4.1: Synthesis of 4-1 and 4-2

Accordingly, the dibromo compound 4-6 was the intermediate synthetic target. 2,1,3-benzothiadiazole was brominated using bromine and hydrobromic acid to yield the 4,7-dibromo-2,1,3-benzothiadiazole (4-5). This was then reacted with 2-tributylstannylthiophene under Stille coupling conditions to yield the 4,7-dithienyl-2,1,3-
benzothiadiazole in 67% yield. This trimer was brominated using N-bromosuccinimide to yield the target intermediate 4-6.

**Scheme 4.2: Synthesis of 4-3 and 4-4**

This compound was reacted with phenyl boronic acid using Suzuki coupling conditions to obtain 4-1 in 70% yield and with 2-tributylstannylthiophene under Stille coupling conditions to achieve 4-2 in 85% yield. Single crystal X-ray diffraction was used to determine the structure of these two molecules (Figure 4.1).

**Figure 4.1: Crystal structure of molecules (a) 4-1 and (b) 4-2**

For synthesizing 4-3, the mono stannyl derivative of 4-7\textsuperscript{23,24} was reacted with 4-5 under Stille coupling conditions to obtain 4-3 in 65% yield (Scheme 4.2). For synthesizing 4-4, the Suzuki coupling of 4-5 and N-(4-hexylphenyl) dithienopyrrole-2-
boronic acid pinacol ester proved unsuccessful. We therefore attempted utilizing 4,7-diboronic acid pinacol ester of 2,1,3-benzothiadiazole for obtaining 4-4. For this, monobrominated dithienopyrrole 4-8\textsuperscript{25}, was reacted with 4,7-diboronic acid pinacol ester of 2,1,3-benzothiadiazole under Suzuki coupling conditions to successfully obtain 4-4 in 80% yield.

4.3.2 Optoelectronic Properties

The absorption and emission spectra of all oligomers were recorded in dichloromethane solution (Figure 4.2). The absorption spectra of all oligomers show two distinct peaks. The peak around 350 nm is associated with the thiophene backbone as observed in case of dihexylquaterthiophene.\textsuperscript{26} The lower energy peak, around 470-550 nm is associated with the intramolecular charge transfer (ICT) between the donor and BZT acceptor functionality.\textsuperscript{16} It is interesting to note that the extent of red shift of the charge transfer peak varies with the donor incorporated in the molecules. The largest shift is observed in case of 4-4, where dithienopyrrole is used as the donor, while 5-phenylthienyl group (in 4-1) behaves as the weakest donor providing the smallest red shift. The bithiophene and the dithienothiophene functionalities provide about the same extent of red shift ($\lambda_{\text{max}}$ = 504 nm and 506 nm, respectively) and thus can be considered to be donors with similar strengths.
Figure 4.2: Linear absorption (solid lines) and emission spectra (dashed lines) of 4-1 – 4-4

This observation shows that the tethering of bithiophene groups to lock their conformation using sulphur as the tether unit does not provide a significant advantage in terms of donor capacity. This is in agreement with previous reports, where effect of ring fusion was studied on the classical oligothiophene systems using sulphur and no significant change in the absorption spectra was observed even as the planarity of the molecule increased significantly. These observations suggest that it may suffice to utilize the simpler bithiophene functionality, instead of dithienothiophene structures, in generating D-A-D type organic semiconductors.

It is also interesting to note that the oscillator strength of the charge transfer transition in molecules 4-2 and 4-4 are much higher than those in 4-1 and 4-3. We do not have a direct structure-property explanation for this variation at this time. All D-A-D molecules 4-1 – 4-4 show a strong red emission with Stokes shifts of over 100 nm. This
indicates ICT in the molecule leading to an excited state with a significantly different structure as compared to the ground state.

Figure 4.3: Effect of solvent polarity on emission spectra of (a) 4-1; (b) 4-2; and (c) 4-4

When the emission spectra were recorded in dimethyl sulfoxide (DMSO) (Figure 4.3), a red shift of about 20 nm was observed in case of 4-2 and 4-4 while only 5 nm red shift was observed in case of 4-1 as compared to that in DCM. This further indicates greater ICT interaction and π-conjugation in 4-2 and 4-4 suggesting that donor functionalities in 4-2 and 4-4 are significantly stronger than that in 4-1.8 The dithienothiophene molecule 4-3 was not soluble in DMSO to obtain its emission spectrum in this solvent.
Table 4.1: Optoelectronic and charge transport properties of D-A-D oligomers. LUMO energy level calculated using optical bandgap $E_g$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Abs ($\lambda_{max}$, nm) ($\varepsilon$) ($\times 10^4$ mol$^{-1}$cm$^{-1}$)</th>
<th>PL ($\lambda_{max}$, nm)</th>
<th>$E_g$ (eV)</th>
<th>HOMO, LUMO (eV)</th>
<th>Hole Mobility ($\mu$, cm$^2$/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-1</td>
<td>474 (4.3) 339 (5.6)</td>
<td>599</td>
<td>2.19</td>
<td>-5.47, -3.28</td>
<td>$6.78 \times 10^{-4}$</td>
</tr>
<tr>
<td>4-2</td>
<td>504 (3.7) 354 (3.8)</td>
<td>607</td>
<td>2.00</td>
<td>-5.31, -3.31</td>
<td>$1.05 \times 10^{-3}$</td>
</tr>
<tr>
<td>4-3</td>
<td>506 (0.6) 390 (2.5)</td>
<td>607</td>
<td>1.88</td>
<td>-5.34, -3.46</td>
<td>$1.21 \times 10^{-4}$</td>
</tr>
<tr>
<td>4-4</td>
<td>551 (5.3) 365 (6.0)</td>
<td>654</td>
<td>1.77</td>
<td>-5.00, -3.23</td>
<td>$4.06 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

In order to estimate the frontier orbital energy levels of these molecules, we studied their redox properties using cyclic voltammetry. No reduction peak was observed in any of these oligomers; therefore optical band gap was used to calculate the LUMO energy level. Oxidation potential of 4-1 was found to be the highest at 670 mV, with respect to ferrocene. Surprisingly, oxidation potentials of 4-2 and 4-3 were similar, 4-3 being easier to oxidize by only 30 mV. Oxidation potential of 22 was found to be 200 mV. This further indicates that the donor strength in 4-1 < 4-2 ~ 4-3 < 4-4.

All oligomers exhibit an optical band gap in the range of 1.8 - 2.2 eV, estimated from the absorption spectra of these molecules. The spectral characteristics, redox potentials and frontier orbital energy level estimations of all oligomers are summarized in Table 4.1. As discussed before, in addition to the optical band gap characteristics, another important parameter for photovoltaics is the charge transport property of these materials. Thus, we examined the field effect mobility of these molecules.
4.3.3 Charge Transport Properties

Bottom contact field effect transistors were fabricated to determine the charge transport properties of the oligomers.

![Graphs showing output characteristics of 4-1, 4-2, 4-3, and 4-4 recorded at W/L = 2000](image)

**Figure 4.4**: Output characteristics of (a) 4-1; (b) 4-2; (c) 4-3 and (d) 4-4 recorded at W/L = 2000

All oligomers are soluble in common organic solvents, thus allowing for solution processing. Thin films were spin coated from 0.5 wt% solutions in chlorobenzene to obtain uniform films with thickness of about 150 nm. Hole mobility was measured under inert atmosphere. No measurable electron mobility was observed in any of the molecules. The output characteristics of 4-1 – 4-4 are shown in Figure 4.4. Hole mobility ($\mu$) was calculated in the saturation regime using the slope of plot of $I_d^{0.5}$ vs. $V_g$. The hole mobility in 4-2 at W/L of 2000 was found to be $1.1 \times 10^{-3}$ cm$^2$/V$s$. When the terminal thiophenes were replaced with phenyl groups in 4-1, the hole mobility dropped to $6.8 \times 10^{-4}$ cm$^2$/V$s$. Molecule 4-3, which has structural and spectral similarities to 4-2, also exhibited relatively lower hole mobility of $1.2 \times 10^{-4}$ cm$^2$/V$s$. This could be due to the limited film
forming capability of the molecule, which could be ascertained both by visual inspection of the devices as well as qualitative inspection of the films using AFM (Figure 4.5).

![Atomic force micrographs, height and phase, of (1) 4-1; (2) 4-2; (3) 4-3 and (4) 4-4](image)

**Figure 4.5:** Atomic force micrographs, height and phase, of (1) 4-1; (2) 4-2; (3) 4-3 and (4) 4-4

Finally, oligomer 4-4 provided four-fold increase in hole mobility, as compared to 4-2, as the hole mobility was $4.1 \times 10^{-3}$ cm$^2$/V s (Table 4.1). We also varied the W/L ratio of the transistor. At a W/L of 4000, molecules 4-1 – 4-3 did not show saturation regime and hence saturation mobility could not be calculated for those molecules. Molecule 4-4 did reach saturation (Figure 4.6) and hole mobility of 0.01 cm$^2$/V s was obtained in this molecule. This is comparable to some of the best hole mobilities observed in D-A-D based conjugated polymers.$^4, ^{14}$
The higher mobility in 4-4 as compared to the other oligomers may be due to the higher extent of double bond character between the BZT and the donor dithienopyrrole unit caused by the better donor capacity of the dithienopyrrole moiety. This may lead to better planarity and promote charge delocalization in the molecule as well as charge hopping between adjacent molecules. Thus, using strong donors for generating D-A-D molecules may be beneficial as this may provide better ability for charge delocalization over the molecule providing for a continuous path for charge transport. However, it is necessary that we add a cautionary note to this suggestion. Note that 4-2 and 4-3 are similar in donor capabilities; however, the charge transport characteristics are different. This is attributed to the film forming characteristics of the two molecules. Therefore, it should be noted that in addition to the electronic characteristics of 4-4, it is also necessary that these molecules exhibit the necessary film forming characteristics and organize themselves in the thin films for appropriate charge conduction.
4.4 Conclusions

In summary, we have designed and synthesized four oligomers based on the D-A-D molecular design containing the 2,1,3-benzothiadiazole unit as the acceptor unit and varied the donor unit to understand its effect on optoelectronic properties. We find that the donor functionality does indeed affect the photophysical properties, which in turn affect the charge transport characteristics. Bithiophene units substituted on either end of the BZT functionality provide low band gap as well as good charge mobility. Tethering the bithiophene to obtain the dithienothiophene functionality does not provide any significant advantage in the optoelectronic properties. On the other hand, N-(4-hexylphenyl) dithienopyrrole functionality provides a band gap of 1.77 eV and hole mobility of 0.01 cm²/Vs. This molecule not only shows excellent absorption in the visible spectrum, but also shows high charge mobility making it an interesting building block for organic electronics applications.
4.5 References


CHAPTER 5

CHARGE TRANSPORT IN CYCLOPENTADITHIOPHENE BASED SMALL MOLECULE ORGANIC SEMICONDUCTORS

5.1 Introduction

Solution processable organic semiconductors have generated tremendous interest due to their applicability in organic microelectronics.\(^1\)-\(^5\) Charge transporting capability is one of the basic requirements for active materials in devices such as organic light emitting diodes, organic photovoltaics and organic thin film transistors. These devices require p-type as well as n-type materials, with commensurate mobilities, for effective functioning. For effective utilization in organic electronic applications, organic semiconductors must allow efficient charge injection and charge transport. These materials must possess (i) the frontier orbital energy levels such that holes/electrons can be injected at accessible applied voltages; (ii) morphology that provides sufficient overlap of frontier orbitals to allow efficient charge migration between neighboring molecules; and (iii) high level of purity, as impurities act as charge traps.

Significant progress has been made in the development of materials possessing high charge mobilities. For instance, pentacene derivatives exhibit high hole mobilities\(^6\), while acene carboximide based materials have shown impressive electron mobilities\(^7\), \(^8\). Materials based on heteroaromatic molecules, such as thiophenes, have garnered specific interest. The first report of a polyheterocycle based FET utilized a polythiophene, with poly(3-hexylthiophene) and \(\alpha,\omega\)-dialkyloligothiophenes being the first high mobility polymeric and small molecule materials, respectively.\(^9\)-\(^11\) Significant advancement has been made on chemical modification of the thiophene core, ring-to-ring connectivity and
substitution pattern resulting in evaluation of a large number of thiophene based materials. Among these, fused ring bithiophene derivatives, such as dithienothiophene oligomers, have attracted considerable attention for their semiconducting properties.\textsuperscript{12, 13} Fused ring derivatives of aromatic or heteroaromatic molecules (e.g. fluorene vs. biphenyl, cyclopentadithiophene vs. bithiophene) lead to extended conjugation in the ground state, more planar molecular geometries and rigid structures. These tend to increase the degree of conjugation, lower the HOMO–LUMO separation and enable closer intermolecular interactions. The rigid fused ring structure also lowers the reorganization energy, a parameter that strongly affects the rate of intermolecular charge hopping and therefore the charge mobility in organic semiconductors.\textsuperscript{14}

The cyclopenta[2,1-\textit{b}:3,4-\textit{b’}]dithiophene, referred here as simply cyclopentadithiophene (CPD), unit can be said to be a combination of structural motifs found in fluorenes and oligothiophenes. The cyclopentadithiophene core can be functionalized at the bridgehead carbon to tune the HOMO–LUMO gap.\textsuperscript{15, 16} Installation of electron withdrawing functionalities at the bridgehead position has been commonly employed to achieve low bandgap oligomers and polymers. For instance, installation of a carbonyl group on the bridgehead position of simple cyclopentadithiophene ($\lambda_{\text{max}} = 474$ nm) leads to a red shift of 172 nm in the $\pi$-$\pi^*$ transition as compared to bithiophene ($\lambda_{\text{max}} = 302$ nm) and 162 nm as compared to cyclopentadithiophene ($\lambda_{\text{max}} = 312$ nm). The lowering of bandgap has been attributed to the presence of the electron-withdrawing carbonyl group, which strongly stabilizes the quinoid form. The oxidation potential of cyclopenta[2,1-\textit{b}:3,4-\textit{b’}]dithiophen-4-one (Chart 5.1) was found to be slightly higher (40-
60 mV) than that of bithiophene, indicating that the carbonyl group has only a moderate effect on the energy level of the HOMO.\(^\text{17}\)

![Diagram of molecules](image)

**Chart 5.1:** Structures of cyclopentadithiophene and its bridgehead functionalized derivatives

A stronger electron withdrawing functionality is the dicyanomethylene functionality which can be installed on the bridgehead position by reacting cyclopenta[2,1-\(b\):3,4-\(b\')]dithiophen-4-one in a Knoevenagel like coupling to obtain 4-dicyanomethylene-4\(H\)-cyclopenta[2,1-\(b\):3,4-\(b\')]dithiophene (Chart 5.1).\(^\text{15}\) This leads to further lowering of the bandgap, consistent with theoretical calculations comparing the effect of the dicyanomethylene and carbonyl groups on the electronic states of these molecules and their polymers.\(^\text{18}\) The calculations indicate that the dicyanomethylene group extends the conjugation outside of the conjugated bithiophene and that the presence of this group lowers the bandgap in both electron rich and electron deficient systems.

The \(\alpha\)-positions of the thiophenes in these monomers can be functionalized to obtain differentially substituted small molecules. Such functionalization has been utilized to convert an otherwise p-type core into n-type material by installation of strongly electron withdrawing functionalities such as fluoroalkyl substituents and ketones containing fluorinated alkyl chain substituents (Chart 5.2).\(^\text{19-23}\) Incorporation of fluorinated substituents has been shown to lower LUMO energy level, making electron injection easier, and hence impart n-type character to the molecule.\(^\text{19}\) However, the
factors underlying stabilization and transport of the injected electrons upon incorporation of these substituents are not fully understood.

Chart 5.2: Examples of thiophene based small molecules which convert from p-type to n-type semiconductors upon incorporation of electronegative fluorinated substituents

We have designed small molecules containing cyclopentadithiophene core which is functionalized at the bridgehead position with electron withdrawing carbonyl or dicyanomethylene functionality and the α-positions of which are either phenyl or pentafluorophenyl substituted. The structures of these molecules are shown in Chart 5.3. This molecular design allows us to systematically vary the functionality at the bridgehead position and α-positions to study their effect on opto-electronic and charge transport property independently.
5.2 Materials and Methods

5.2.1 Materials

The cyclopentadithiophene derivatives shown in Chart 5.3 were synthesized from common intermediates 2,6-dibromo-4,4-ethylenedioxy-4H-cyclopenta[2,1-b:3,4-b’]dithiophene and 2-bromo-4,4-ethylenedioxy-4H-cyclopenta[2,1-b:3,4-b’]dithiophene which were synthesized following literature reported procedures. All common reagents were purchased from Aldrich and used without further purification.

5.2.2 Characterization Techniques

All molecules were characterized using $^1$H NMR, $^{13}$C NMR and high resolution mass spectrometry to confirm the molecular structure. Cyclic voltammetry experiments were carried out at room temperature using a BASi C3 cell stand fitted with three electrodes: a platinum disk working electrode, platinum auxiliary electrode and Ag/Ag+
reference electrode. The voltammograms were recorded in dry dichloromethane (DCM) using tetrabutylammonium hexafluorophosphate as the supporting electrolyte and ferrocene as the internal standard under nitrogen atmosphere. The scan rate in all experiments was 0.1 V/s. UV-Visible spectra were obtained using a Cary 100 spectrophotometer and fluorescence data were collected using JASCO FP-6500 spectrofluorimeter.

5.2.3 Organic Thin Film Field-Effect Transistor (FET) Fabrication and Characterization

The field effect transistors were constructed using pre-patterned silicon substrates. The transistors were constituted by a heavily n-doped silicon substrate with a 230 nm thermally oxidized silicon dioxide layer with a capacitance of 14.9 nF/cm$^2$. Gold electrodes were deposited on the gate oxide layer to yield the bottom contact FETs. Before deposition of the film, the FET substrates were cleaned with acetone followed by isopropyl alcohol. They were then exposed to HMDS vapor for 1h followed by re-cleaning with isopropyl alcohol. After this, thin films of the oligomers were deposited on the surface by spin coating a 0.5 wt% solution in chlorobenzene (1500 rpm for 45 seconds). The devices were then annealed for 1 hour at 80 °C. The channel width of all transistors was 10 mm and channel length was 5 μm. All measurements were carried out under inert atmosphere using Agilent 4156C precision semiconductor parameter analyzer.
5.3 Results and Discussion

5.3.1 Synthesis

Suzuki coupling of 2,6-dibromo-4,4-ethylenedioxy-4H-cyclopenta[2,1-b:3,4-b′]dithiophene with phenyl boronic acid yielded 5-1 (Chart 5.3) which was hydrolyzed using hydrochloric acid and acetic acid to obtain 5-2 in 72% yield. Knoevenagel condensation of 5-2 with malononitrile yielded 5-3 in 69% yield. 4,4-ethylenedioxy-4H-cyclopenta[2,1-b:3,4-b′]dithiophene was reacted with n-butyl lithium followed by hexafluorobenzene to obtain 5-4 in 42% yield. This was then converted to ketone and dicyanomethylene derivatives 5-5 and 5-6 as described earlier. 2-bromo-4,4-ethylenedioxy-4H-cyclopenta[2,1-b:3,4-b′]dithiophene was reacted with phenyl boronic acid under Suzuki coupling conditions followed by n-butyl lithium and hexafluorobenzene to obtain the unsymmetrically substituted molecule 5-7. This was further hydrolyzed as discussed earlier to obtain 5-8 in 64% yield.

5.3.2 Optical Properties

The UV-vis absorption and emission spectra of phenyl derivatives 5-1 – 5-3, pentafluorophenyl derivatives 5-4 – 5-6 and unsymmetrically substituted monophenyl-monopentafluorophenyl derivatives 5-7 – 5-8 are shown in Figure 5.1. All spectra were recorded in dichloromethane to evaluate the effect of structural modifications on their opto-electronic properties. The optical band gap is determined from the onset of absorption in the UV-vis spectra. Table 5.1 summarizes the opto-electronic properties of all compounds in dichloromethane. A red shift in the π-π* transition band is observed upon conversion of bridgehead carbon from sp³ to sp² center. For instance, the π-π*
transition peak shifts by 144 nm from 409 nm in case of 5-1 to 553 nm in case of 5-2. Similarly, a red shift of 109 nm is observed in case of dipentafluorophenyl substituted molecules ($\lambda_{\text{max}}$: 398 nm in case of 5-4 as compared to 507 nm for 5-5).

Similarly, a red shift of 109 nm is observed in case of dipentafluorophenyl substituted molecules ($\lambda_{\text{max}}$: 398 nm in case of 5-4 as compared to 507 nm for 5-5).

$$\lambda_{\text{max}}: 398 \text{ nm in case of } 5-4 \text{ as compared to } 507 \text{ nm for } 5-5.$$}

**Figure 5.1:** UV-vis absorption and emission spectra of 5-1 – 5-3 (top left); 5-4 – 5-6 (top right) and 5-7 – 5-8 (bottom)

An intermediate red shift of 121 nm is observed in case of molecules containing one phenyl and one pentafluorophenyl substituent on $\alpha$-positions ($\lambda_{\text{max}}$: 405 nm for 5-7 as compared to 526 nm in case of 5-8). Interestingly, the absorption spectra of the dicyanomethylene functionalized molecules appear to be significantly blue shifted with the most prominent peak appearing at 333 nm in case of 5-3 and 330 nm in case of 5-6. This is attributed to the forbidden nature of the $\pi-\pi^*$ transition arising due to the apparent meta linkage of the dicyanomethylene group and the conjugated backbone of the
remainder molecule. A similar phenomenon is responsible for the low oscillator strength of the said transition in case of the carbonyl containing molecules 5-2 and 5-5.

Table 5.1: Optical properties of 5-1 – 5-8 recorded in dichloromethane

<table>
<thead>
<tr>
<th>Compound</th>
<th>λ_{max} (nm)</th>
<th>ε (M⁻¹cm⁻¹)</th>
<th>λ_{em} (nm)</th>
<th>E_g (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-1</td>
<td>409</td>
<td>5.0 \times 10^4</td>
<td>476</td>
<td>2.61</td>
</tr>
<tr>
<td>5-2</td>
<td>313, 353, 553</td>
<td>8.5 \times 10^4</td>
<td>-</td>
<td>1.77</td>
</tr>
<tr>
<td>5-3</td>
<td>333</td>
<td>7.2 \times 10^4</td>
<td>-</td>
<td>3.02</td>
</tr>
<tr>
<td>5-4</td>
<td>398</td>
<td>3.3 \times 10^4</td>
<td>454</td>
<td>2.69</td>
</tr>
<tr>
<td>5-5</td>
<td>309, 347, 507</td>
<td>7.5 \times 10^4</td>
<td>-</td>
<td>2.03</td>
</tr>
<tr>
<td>5-6</td>
<td>330</td>
<td>9.0 \times 10^4</td>
<td>-</td>
<td>3.10</td>
</tr>
<tr>
<td>5-7</td>
<td>405</td>
<td>6.7 \times 10^4</td>
<td>470</td>
<td>2.66</td>
</tr>
<tr>
<td>5-8</td>
<td>310, 353, 526</td>
<td>1.5 \times 10^4</td>
<td>-</td>
<td>1.90</td>
</tr>
</tbody>
</table>

Also interesting is the comparison of the absorption spectra of the diphenyl, dipentafluorophenyl and unsymmetrical monophenyl-monopentafluorophenyl substituted CPD molecules. In all the molecules, irrespective of the functional groups at the bridgehead position, the trends in absorption were found to be similar, viz. slight blue shift in absorption maxima upon replacement of phenyl groups with pentafluorophenyl groups (Figure 5.1). This can be attributed to the electron withdrawing nature of the pentafluorophenyl units which decreases the donor-acceptor character in the molecules by weakening the donor component.

Except the dioxolane derivatives, all other derivatives were found to be non-emissive. As in case of absorption spectra, a blue shift in emission maxima in the dioxolane derivatives is observed (5-1: 476 nm, 5-7: 470 nm, 5-4: 454 nm) upon successively replacing phenyl groups with electron withdrawing pentafluorophenyl.
groups. The absence of emission properties in ketone and dicyanomethylene containing molecules further indicates that the $S_0 \rightarrow S_1$ transition, i.e. the $\pi-\pi^*$ transition, is forbidden.\textsuperscript{25}

5.3.3 Electrochemical properties

The electrochemical properties of CPD derivatives 5-1 – 5-3 and 5-4 – 5-6 were investigated using cyclic voltammetry to determine the redox properties of these molecules. The cyclic voltammograms are shown in Figure 5.2. Dioxolane derivatives (5-1 & 5-4) showed one quasi-reversible oxidation peak. Upon introducing the carbonyl group, CPD derivatives (5-2 & 5-5) showed ambipolar redox behavior with one reversible oxidation and one reversible reduction peak. Further, upon introduction of dicyanomethylene functionality, the CPD derivatives (5-3 & 5-6) showed one reversible oxidation and two reversible reduction peaks. In the diphenyl functionalized molecules, upon conversion of dioxolane to carbonyl functionality and further to dicyanomethylene group, the first oxidation potential increases from 0.46 V (5-1) to 0.72 V (5-2) to 0.78 V (5-3) while the first reduction potential increases from -1.56 (5-2) to -1.07 V (5-3), consistent with the trend of the electron withdrawing nature of the bridgehead substituent. Similar trends were observed in the dipentafluorophenyl substituted molecules. The oxidation potentials vary from 0.92 V (5-4) to 1.10 V (5-5) to 1.16 V (5-6) and the first reduction potentials vary from -1.45 V (5-5) to -0.96 V (5-6). No reduction was observed for dioxolane derivatives (5-1 & 5-4) within the solvent window.
Figure 5.2: Cyclic voltammograms of 5-1 – 5-3 (left) and 5-4 – 5-6 (right)

The HOMO and LUMO energy levels and thus the electrochemical band gap, 
\[ E_g = (E_{\text{LUMO}} - E_{\text{HOMO}}) \], were calculated using the empirical relationship 
\[ E_{\text{HOMO/LUMO}} = - (4.8 + qE_{\text{ox/red}}) \text{ eV}. \]

The electrochemically derived HOMO and LUMO energy levels and bandgap are summarized in Table 5.2. The electrochemical band gaps in 5-2 and 5-5 were found to be slightly (0.3 eV) higher than their optical bandgap (Table 5.1). Due to forbidden \( \pi-\pi^* \) transition in 5-3 and 5-6, the electrochemical band gaps were found to be smaller than the optical band gaps. The lower LUMO levels and smaller band gaps in 5-3 & 5-6, compared to 5-2 & 5-5, indicate that the highly electron withdrawing dicyanomethylene functionality, as expected, has a greater effect on the LUMO energy level and leads to a greater \( \pi \)-electron delocalization due to the apparent donor-acceptor character of the molecules. It should be noted that replacing phenyl groups with the electron deficient pentafluorophenyl groups at the \( \alpha \)-position of the cyclopentadithiophene backbone leads to decrease in the HOMO energy level but interestingly, causes an increase in the LUMO energy level, leading to a higher band gap in the pentafluorophenyl CPD derivatives (5-5: 2.31 eV and 5-6: 1.91 eV) as compared to the phenyl CPD derivatives (5-2: 2.11 eV and 5-3: 1.66 eV). This may be due to greater
steric crowding of pentafluorophenyl groups leading to restricted conjugation as compared to phenyl derivatives as well as the reduced donor-acceptor nature of the molecule which is known to cause a decrease in the bandgap. In contrast, terminal perfluoro substituted oligothiophenes have been known to exhibit lowering of both the HOMO and LUMO frontier orbitals upon replacement of hydrocarbon substituent with fluorocarbon substituent.\textsuperscript{19, 23} At this time, we do not have a clear explanation for this variation in trend of change in energy levels upon incorporating fluorinated substituents. We were unable to record cyclic voltammograms for 5-8 due to solubility issues.

Table 5.2: Electrochemical properties of molecules 5-1 – 5-6. *Calculated using optical bandgap

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{\text{ox}}$ (eV)</th>
<th>$E_{\text{red}}$ (eV)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>$E_g$ (eV)</th>
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<tr>
<td>5-1</td>
<td>0.46</td>
<td>-</td>
<td>-5.49</td>
<td>-2.88*</td>
<td>2.61*</td>
</tr>
<tr>
<td>5-2</td>
<td>0.72</td>
<td>-1.56</td>
<td>-5.70</td>
<td>-3.59</td>
<td>2.11</td>
</tr>
<tr>
<td>5-3</td>
<td>0.78</td>
<td>-1.07, -1.64</td>
<td>-5.76</td>
<td>-4.10</td>
<td>1.66</td>
</tr>
<tr>
<td>5-4</td>
<td>0.92</td>
<td>-</td>
<td>-5.63</td>
<td>-2.94*</td>
<td>2.69*</td>
</tr>
<tr>
<td>5-5</td>
<td>1.10</td>
<td>-1.45</td>
<td>-5.77</td>
<td>-3.46</td>
<td>2.31</td>
</tr>
<tr>
<td>5-6</td>
<td>1.16</td>
<td>-0.96, -1.54</td>
<td>-5.84</td>
<td>-3.93</td>
<td>1.91</td>
</tr>
</tbody>
</table>

5.3.4 Charge transport properties

Charge transport properties were measured by fabricating bottom contact field effect transistors by spin coating thin films (~100 nm) on pre-fabricated transistor substrates. Charge mobility in the dioxolane derivatives could not be measured due to their limited film forming capability. Output characteristics of molecules 5-2 and 5-3 are shown in Figures 5.3 and those of 5-5 and 5-6 are shown in Figure 5.4. In case of 5-2 and 5-3, only hole mobility was observed. In molecule 5-2, hole mobility was found to be
8.8 \times 10^{-5} \text{ cm}^2/\text{Vs}. Upon changing the electron withdrawing functionality from carbonyl to dicyanomethylene functionality in molecule 5-3, hole mobility increased by over an order of magnitude and was found to be $1.9 \times 10^{-3} \text{ cm}^2/\text{Vs}$.

It is interesting to note that, upon increasing the acceptor strength of the electron withdrawing functionality in the molecule, while the LUMO energy level dropped by about 500 meV, no measurable electron mobility was observed. Instead, the hole mobility increased significantly. This indicates that the nature of charge that is transported through a molecule is not an exclusive function of the frontier orbital energy levels.

![Figure 5.3](image)

**Figure 5.3:** Output characteristics of (a) 5-2 and (b) 5-3

When pentafluorophenyl groups were incorporated in the molecules 5-5 and 5-6, a reversal in charge transport characteristics was observed. These molecules were found to be n-type materials with no measurable hole mobility being observed. The electron mobility in 5-5 was found to be $5.4 \times 10^{-5} \text{ cm}^2/\text{Vs}$ while that in 5-6 was $5.9 \times 10^{-5} \text{ cm}^2/\text{Vs}$. 

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Figure 5.4: Output characteristics of (a) 5-5 and (b) 5-6

No significant effect of varying strength of electron withdrawing functionality at the bridgehead position was observed in this case. From the electrochemical properties of these molecules, as discussed earlier, the LUMO energy levels of fluorinated molecules are higher as compared to the corresponding phenyl derivates. Yet the fluorinated molecules exhibit n-type behavior while the phenyl derivatives are p-type. Therefore, in this case, incorporation of fluorinated substituents imparts n-type character to the molecules without lowering their LUMO energy level. This further indicates that the determining the frontier orbital energy levels may not be a sufficient condition to understanding the charge transport properties of a molecule.

Figure 5.5: Output characteristics of unsymmetrically substituted ketone 5-8

We also studied the charge transport properties in 5-8 (Figure 5.5). This molecule contains a pentafluorophenyl group as one of the terminal substituents, and a phenyl group as the other. We hypothesized that the unsymmetrical substitution will impart
significantly different properties as compared to the symmetrically substituted molecules. The question that we were interested in answering was: is one terminal fluoro substituent sufficient to impart n-type character? We found that 5-8 was an exclusively p-type material, with significantly lower hole mobility as compared to 5-2. No measureable electron mobility was observed. The hole mobility was found to be $5.5 \times 10^{-7}$ cm$^2$/Vs. A comparison of charge mobility in all molecules studied here is shown in Figure 5.6.

![Figure 5.6: Comparison of charge mobility in 5-2 – 5-3, 5-5 – 5-6 and 5-8. Purple bars indicate hole mobility and orange bars indicate electron mobility](image)

**5.4 Conclusions**

We have designed and synthesized small molecule organic semiconductors containing a cyclopentadithiophene core which is differentially functionalized at the bridgehead position with electron withdrawing functionalities of varying strengths and at the α-positions with phenyl or pentafluorophenyl groups. The optoelectronic, electrochemical and charge transport properties of these molecules were measured. We find that the functionality at the bridgehead position affects the LUMO energy level more significantly than the HOMO energy level. The dicyanomethylene group lowers the LUMO energy level by about 500 meV in 5-3, yet the molecule remains a hole
conducting material. Also, in contrast to the literature reports of lowering of LUMO energy level upon incorporation of fluorinated substituents, we find that the LUMO energy level of pentafluorophenyl derivatives is slightly higher than that of the corresponding phenyl derivatives. Interestingly, even though their LUMO energy levels are higher than that of the phenyl derivatives, the dipentafluorophenyl derivatives show exclusively electron transport properties. This indicates that defining the frontier orbital energy levels in the molecule is not a sufficient condition to understanding its charge transport behavior. The unsymmetrically substituted monophenyl-monopentafluorophenyl derivative shows exclusive hole transport which is significantly lower in magnitude as compared to the phenyl derivative.
5.5 References


CHAPTER 6
SUMMARY AND FUTURE DIRECTIONS

6.1 Summary

Understanding structure-property relationship of molecules is imperative for designing efficient materials for organic semiconductors. Organic semiconductors are based on π-conjugated molecules, either small molecules or macromolecules such as dendrimers or polymers. While extensive research has been focused on understanding charge transport through small molecules and polymers, there is limited understanding of charge transport through dendritic semiconductors. Dendrimers provide an interesting macromolecular architecture as these bridge the gap between small molecules and polymers since dendrimers, like small molecules, are monodisperse and can be obtained in high purity, and like polymers, can be processed through simple solution processing techniques. Also, due to their globular-like shape, dendrimers are known to phase separate from flexible polymer chains.

We have utilized this property to design active materials for organic photovoltaics based on the dendron-rod-coil design. This molecular design provides high photo-induced charge separation efficiency and hence is an interesting system for active material for photovoltaic devices. We investigated the charge transport properties of these materials and the effect of varying generation of dendron on the charge mobility in the molecules using field-effect transistor measurements as well as time-of-flight measurements. We find that the charge mobility measured by both techniques decreases with increasing generation of dendron, possibly due to the increasing curvature of the
molecule which limits its packing abilities. While the dendron-rod-coil molecules show exclusively electron transport properties in field-effect transistor measurements, ambipolar charge transport is observed in time-of-flight mobility measurements. This indicates that photo-induced charges can be transported through the bulk film in diode configuration, but only field induced electrons can be transported in the x-y plane. Preliminary morphological analysis using small angle X-ray scattering indicates the lack of an organized dendron phase which may explain the lack of hole mobility in field-effect transistor measurements.

A decrease in charge mobility was observed upon increasing generation of dendron. In the dendrons studied here, the charge transporting functionalities were present as the peripheral functionalities. We investigated the effect of increasing the density of charge transporting functionalities in the dendron by incorporating these at every layer of the molecule. In this case, we find that at lower generations, the charge mobility increases with generation, possibly an effect of the compensation of large molecular size by higher density of charge transporting functionalities. At higher generations, the mobility falls slightly at stabilizes, albeit at a higher value as compared to comparable dendrons with charge transporting functionalities only at the periphery.

Low bandgap chromophores are required for efficient light absorption in organic photovoltaic devices. Often, the chromophore also functions as a charge transporting material in such a device. Therefore, understanding charge transporting properties of chromophores is of immense significance. Donor-acceptor molecules possess low bandgap attributed to the donor and acceptor conjugation. While it is well known that the optoelectronic properties of such molecules vary upon varying the donor and acceptor
functionalities, its effect on charge transporting properties in small molecules based on the donor-acceptor design is not well understood. Small molecules are ideal materials for structure-property relationship study as these can be obtained in high purity. We have studied donor-acceptor based small molecules containing 2,1,3-benzothiadiazole as the acceptor component and four different thiophene based donors. We find that varying composition of the molecules does indeed affect the charge transporting property.

Charge transport through organic materials is one of the most important processes that drive organic electronic devices. Yet, there is limited understanding of this phenomenon leading to lack of design principles which can be used to design new materials. For instance, whether a material is hole transporting or electron transporting is conventionally defined based on the frontier orbital energy levels, rather than the mobility of the said charge through the material. Substitution of hydrocarbon substituents with fluorocarbon substituents is known to reverse the charge transport properties from p-type to n-type. This is attributed to increased electron affinity which is reflected in the lowering of LUMO energy level of the molecule. In our study, we find that while incorporation of fluorocarbon substituents leads to reversal in charge transport properties and results in n-type behavior in cyclopentadithiophene based molecules, the change is not concurrent with lower LUMO energy level. In fact, the LUMO energy level was found to be slightly higher than the corresponding hydrocarbon derivative. This indicates that defining the frontier orbital energy levels in the molecule is not a sufficient condition to understanding its charge transport behavior.
6.2 Future Directions

Dendrimers provide significant advantages in photoinduced charge transfer in solution owing to their globular-like shape which provides the avenue for back-folding of peripheral functionalities at higher generations. This facilitates the charge transfer between the peripheral and the core functionalities. The back-folding effect can be said to compensate for larger distance between these functionalities as the size of the molecule increases. We have also shown that excited state energy transfer occurs between the donor functionality, triarylamine, and the core acceptor functionality. This process can further lead to charge transfer process as shown in Figure 6.1.

![Figure 6.1](image-url)

**Figure 6.1:** Schematic representation of excited state energy transfer and charge transfer in dendrimers with donor functionality at periphery and acceptor functionality at core
Like dendrimers, dendron-rod functionalities also exhibit excited state energy transfer and charge transfer processes. In fact, the charge transfer process in dendron-rod species (~70%) is significantly higher than that in dendrimers (~50%).\(^3\) This is attributed to the better solvent exposure of the rod functionality which helps in stabilization of the radical anion generated upon charge transfer. This high charge transfer efficiency combined with the globular-like shape of the dendron can be used to an advantage in dye-sensitized solar cells.

In dye-sensitized solar cells, a dye is adsorbed on a nanocrystalline TiO\(_2\) film deposited on ITO coated glass (Figure 6.2).\(^4\) This assembly is immersed in an electrolyte containing the redox couple I\(^{-}/\)I\(_{3}^-\) and platinum counter electrode. The efficiency of the cell depends on the short circuit current and open circuit voltage. The short circuit current is a function of light absorption and electron injection properties of the dye and its adsorption affinity on TiO\(_2\). The open circuit voltage depends on the driving force for charge separation provided by the frontier orbital energy levels. Therefore, it is restricted by the back electron transfer from the conduction band of TiO\(_2\) to the I\(_{3}^-\) in the electrolyte.

The interface between the electrolyte and the semiconductor (TiO\(_2\)) at which the photo-induced electron transfer occurs is therefore, important for cell performance. Modification of this interface to suppress the back electron transfer has been investigated by various groups using either alumina coated TiO\(_2\) particles or by alkylation of the dye to improve its adsorption on TiO\(_2\).\(^5\) In both cases, while the charge recombination rate decreases due to the barrier between TiO\(_2\) and the electrolyte, the charge separation rate...
was also found to be slower due to this barrier. Therefore, a barrier material which does not slow down the charge separation rate is of tremendous interest.

**Figure 6.2:** Schematic representation of dye sensitized solar cell

The dendron-rod molecules discussed earlier (Chapter 2) provide a molecular architecture which can shield the semiconductor electrode from the electrolyte (due to the globular-like shape of dendron). The dendron-rod molecules may be adsorbed by suitably functionalizing the rod functionality to adsorb on TiO$_2$. Upon excitation of the rod, intramolecular charge transfer from peripheral donor functionality to the acceptor functionality (rod) results in the radical anion being localized on the rod and the radical cation of the peripheral functionalities of the dendron. In such a case, for regeneration of the donor species for next intramolecular charge transfer event, the electron transfer must happen between the peripheral functionality and the redox electrolyte. Not only is this site spatially away from the TiO$_2$ surface but, at higher generations of dendrons, there are multiple functionalities at the periphery which can allow the shuttling of electrons into the rod functionality and further into the TiO$_2$ even if the charge transfer between the
radical cation on the peripheral functionality and the redox electrolyte were slow. Therefore, the probability of back electron transfer from the TiO$_2$ to the redox electrolyte is reduced significantly.

**Figure 6.3:** Schematic representation of charge transfer from dendron-rod to TiO$_2$ nanoparticle

The efficiency of this process can be studied by varying the generation and density of charge transport functionalities in the dendron and varying the redox properties of the rod functionality. Various designs for dendrons have been discussed in Chapters 2 and 3 while candidates for rod functionalities have been discussed in Chapter 4.
6.3 References


# APPENDIX

## CRYSTAL DATA

Crystallographic data for compounds 4-1 and 4-2

<table>
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<tr>
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<th>4-1</th>
<th>4-2</th>
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<td>C\textsubscript{22}H\textsubscript{12}N\textsubscript{2}S\textsubscript{5}</td>
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\[ aR = \frac{\sum | F_0 | - | F_c |}{\sum | F_0 |} \], \quad bR\textsubscript{w}(F_0^2) = \left\{ \frac{\sum w(F_0^2 - F_c^2)^2}{\sum wF_0^4} \right\}^{1/2}


Noda, T. and Shirota, Y. "5,5'-Bis(dimesitylboryl)-2,2'-bithiophene and 5.5''-Bis(dimesitylboryl)-2,2':5',2''-terthiophene As A Novel Family of Electron-Transporting Amorphous Molecular Materials." J. Am. Chem. Soc. **1998**, 120, 9714-9715.


