ACENES, HETEROACENES AND ANALOGOUS MOLECULES FOR ORGANIC PHOTOVOLTAIC AND FIELD EFFECT TRANSISTOR APPLICATIONS

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ACENES, HETEROACENES AND ANALOGOUS MOLECULES FOR ORGANIC PHOTOVOLTAIC AND FIELD EFFECT TRANSISTOR APPLICATIONS

DISSETRATION

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the College of Arts and Sciences at the University of Kentucky

By
Devin Benjamin Granger
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2017

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ABSTRACT OF DISSERTATION

ACENES, HETEROACENES AND ANALOGOUS MOLECULES FOR ORGANIC PHOTOVOLTAIC AND FIELD EFFECT TRANSISTOR APPLICATIONS

Polycyclic aromatic hydrocarbons composed of benzenoid rings fused in a linear fashion comprise the class of compounds known as acenes. The structures containing three to six ring fusions are brightly colored and possess band gaps and charge transport efficiencies sufficient for semiconductor applications. These molecules have been investigated throughout the past several decades to assess their optoelectronic properties. The absorption, emission and charge transport properties of this series of molecules has been studied extensively to elucidate structure-property relationships. A wide variety of analogous molecules, incorporating heterocycles in place of benzenoid rings, demonstrate similar properties to the parent compounds and have likewise been investigated.

Functionalization of acene compounds by placement of groups around the molecule affects the way in which molecules interact in the solid state, in addition to the energetics of the molecule. The use of electron donating or electron withdrawing groups affects the frontier molecular orbitals and thus affects the optical and electronic gaps of the molecules. The use of bulky side groups such as alkylsilylthynyl groups allows for crystal engineering of molecular aggregates, and changing the volume and dimensions of the alkylsilyl groups affects the intermolecular interactions and thus changes the packing motif.

In chapter 2, a series of tetracene and pentacene molecules with strongly electron withdrawing groups is described. The investigation focuses on the change in energetics of the frontier molecular orbitals between the base acene and the nitrile and dicyanovinyl derivatives as well as the differences between the pentacene and tetracene molecules. The differences in close packing motifs through use of bulky alkylsilylthynyl groups is also discussed in relation to electron acceptor material design and bulk heterojunction organic photovoltaic characteristics.

Chapter 3 focuses on molecular acceptor and donor molecules for bulk heterojunction organic photovoltaics based on anthrathiophene and benzo[1,2-b:4,5-
b’)dithiophene central units like literature molecules containing fluorene and dithieno[2,3-b:2’,3’-d]silole cores. The synthetic strategies of developing reduced symmetry benzo[1,2-b:4,5-b’]dithiophene to study the effect of substitution around the central unit is also described. The optical and electronic properties of the donors and acceptors are described along with the performance and characteristics of devices employing these molecules.

The final two data chapters focus on new nitrogen containing polycyclic hydrocarbons containing indolizine and (2.2.2) cyclazine units. The optical, electronic and other physical properties of these molecules are explored, in addition to the synthetic strategies for incorporating the indolizine and cyclazine units. By use of alkylsilylethynyl groups, crystal engineering was investigated for the benzo[2,3-b:5,6-b’]diindolizine chromophore described in chapter 4 to target the 2-D “brick-work” packing motif for application in field effect transistor devices. Optical and electronic properties of the cyclazine end-capped acene molecules described in chapter 5 were investigated and described in relation to the base acene molecules. In both cases, density functional theory calculations were conducted to better understand unexpected optical properties of these molecules, which are like the linear acene series despite the non-linear attachment.

KEYWORDS: Organic Photovoltaic, Organic Field Effect Transistor, Acene, Organic Semiconductor, Indolizine, Cyclazine
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1 Introduction

1.1 Organic Semiconductors vs. Inorganic Semiconductors

Much of modern technology is built on the properties of inorganic semiconductors. Silicon is a champion material in the field of such semiconductors, providing the basis of modern computing. Inorganic semiconductors possess well defined band structures with narrow energy gaps, and charges generated in the material have low effective mass and are highly mobile, demonstrating mobility (μ) exceeding several thousand cm²/Vs. Organic molecules do not benefit from strong covalent networks and mobilities of 10²-10³, however. The fact that they are molecular materials implies reliance on electrostatic models of charge transport,¹ though band-like transport can be observed in highly ordered systems and mobility values of <10 cm²/Vs are observed for champion organic materials.²

This difference begs the question; if inorganic materials exhibit such superior performance to organic materials, why would we investigate organics for semiconductor applications? If we were only concerned with high mobility values, there would be no interest in organic semiconducting materials. However, there are a myriad of issues that lead to organics as viable materials for a variety of applications.

While silicon is the second most abundant element in the earth’s crust, it is not readily available in pure form. Instead it is primarily present as its oxide, in the form of sand, and must be processed to liberate and purify the silicon. Silicon is produced from quartz by reduction with elemental carbon in an arc electric furnace at a temperature of 2000 °C.³

¹ This process produces silicon of 96% purity or greater, but also produces large amounts
of carbon monoxide as the main byproduct. The silicon produced from this process is drawn into rods, which must then be further processed for semiconductor applications.

Organic materials, on the other hand, can be synthesized from petrochemical precursors that are readily available and less energy intensive to produce and process. With increased costs of petroleum, there has been interest in developing renewable chemical feedstocks (a quick Scifinder search reveals more than 400 references to the topic in the past 5 years with a year to year increase). Though these sources seem on their face to be expensive, the cost involved in securing organic precursors is vastly cheaper than the production of pure silicon or other metals from their ores. The reduced cost of chemical precursors leads to lower costs for materials and, ultimately, devices.

Organic semiconductors can be synthesized with the inclusion of solubilizing groups to allow low temperature solvent processing, leading to lower production costs. One of the most promising advantages of low temperature processing is the ability to apply devices to a wider range of substrates, such as plastic laminates and films leading to flexible, lightweight and portable devices, and several examples of efforts to realize flexible substrates as well as electrodes and other technologies can be found in the recent literature,\textsuperscript{5-7} which may lead to a wider range of applications for organic semiconductors. Though the development of flexible substrates for organic electronics is an exciting step forward in the field, this report is focused on advancement of materials and will discuss devices on standard substrates.
1.1.1 Acene Semiconductors

Much work over the past several decades has focused on aryl polymers for optoelectronic applications, which have inherent challenges associated with them, e.g. molecular weight and polydispersity, that can be inconsistent between batches. Small molecule organic semiconductors, on the other hand, do not suffer from polydispersity or degree of polymerization issues, due to the size and shape of organic small molecules being inherently consistent throughout a given batch and across batches. There are a variety of small molecule organic semiconductors that have been investigated for use in organic optoelectronic devices, but rather than give a survey of the various molecules from the available literature, it is more prudent to focus on acenes, as much of the work presented here focuses on acenes and their analogues.

![Acenes of two (naphthalene) to seven (heptacene) linear fused rings](image)

**Figure 1-1:** Acenes of two (naphthalene) to seven (heptacene) linear fused rings

Acenes are defined as linearly fused aromatic systems composed of benzenoid rings with one Clar sextet [Figure 1-1], and have been studied extensively as optoelectronic organic materials for the past several decades, either on their own, as moieties in small molecules or as part of polymer frameworks. As the number of linearly fused rings increases, the optical gap of the acene is drastically lowered as the HOMO energy
increases with additional conjugation.\textsuperscript{9} This coarse tuning afforded by acene length is offset by significant decreases in stability and solubility as acene length increases.\textsuperscript{10}

Pentacene has excellent charge carrier mobilities relative to other organic semiconductors (1 cm\textsuperscript{2}/Vs).\textsuperscript{11} Additionally, pentacene has a blue color due to light absorption in the visible region with a maximum at 670 nm.\textsuperscript{12} Absorption in the visible spectrum, increased stability relative to larger acenes and excellent charge carrier mobility suggest that pentacene should be a good material for organic electronics. Unfortunately, unsubstituted pentacene is highly insoluble and requires vapor deposition or depositing pentacene precursors to make films.\textsuperscript{13-14}

The advent of solution processable pentacene derivatives greatly increased the possible applications for pentacene. One method employed by the Anthony group at the University of Kentucky involves the use of trialkysilylethynyl groups to the pentacene core to afford solubility to the molecule, and early inspection of this method demonstrated its usefulness beyond simply improving solubility, but also affording control over solid state arrangement and improving electrical properties such as resistivity.\textsuperscript{15} The prototypical ethynyl substituted pentacene, 6,13-bis(triisopropyl-silylethynyl)pentacene (TIPS-pentacene), has been demonstrated to be potentially useful as field effect transistor material.\textsuperscript{16} Additionally, TIPS-pentacene was investigated for use as a donor material for OPV devices and showed a power conversion efficiency of 0.5% after initial optimization.\textsuperscript{17} While the results are not astounding, this work does demonstrate a proof of concept and that similar molecules may be applicable in organic photovoltaic research.
In order to modify the pentacene chromophore for use as an electron acceptor molecule for OPV devices, it is necessary to lower the LUMO energy to increase the reduction potential, thus making the reduction more facile.\textsuperscript{18} This has been accomplished by the use of electron withdrawing groups attached to the pentacene core.\textsuperscript{18-19} Furthermore, altering the size of alkyl groups on the silylentynyl group was shown to have a strong effect on packing arrangement, including relative placement of molecules and π-π close packing distances.\textsuperscript{18-19} The best performance, up to 1.3% PCE, for this type of material was found with 2-cyano-6,13-bistri(cyclo-pentyl)silylethynyl pentacene.\textsuperscript{19-20} This has been ascribed to the favorable LUMO energy, close π-stacking contacts and molecular arrangement in the crystal, e.g. the “sandwich herringbone” crystal packing.\textsuperscript{20}

The substitution of carbon atoms in the acene structure with heteroatoms has a significant effect on the physical and chemical properties of the chromophore. The substitution of carbon with more electronegative atoms in aromatic hydrocarbons tends to raise the reduction potential.\textsuperscript{21} Various heteroacenes have been synthesized by either substitution of carbons with heteroatoms or substitution of benzene moieties with pyridine, pyrrole, or its analogs.\textsuperscript{22-23}

Exchange of benzenoid rings in the chromophore for thiophene or its analogues is another common motif that has been studied extensively.\textsuperscript{24} Due to the lower electronegativity of sulfur and the weaker orbital overlap between sulfur and carbon, different electronic effects are observed for thiophene containing acenes than are observed for N-substituted acenes, for example anthradithiophene derivatives tend to show larger band gaps than pentacene analogs, leading to lower absorption wavelength
These molecules also possess good charge transport properties and the solid state arrangement, close contacts and electronic properties of ADT can be tuned in a similar manner to pentacene. Substitution around these molecules can be realized at the carbon adjacent to the sulfur atoms of thienoacenes, resulting in linear molecules with increased π-conjugation.

1.2 Photovoltaics

As world energy demand rises, it is necessary for civilization to continuously find new energy sources. To appreciate the potential impact of photovoltaic devices, we need to consider the volume of solar energy that reaches the Earth’s surface. On a clear, sunny day in North America, approximately 1000 W/m² reaches the surface of the Earth. This standard radiation reference is linked to a 37° tilt of the earth’s surface in relation to the sun, which is the average tilt angle in the continuous 48 United States, on a cloudless day and designated the air mass 1.5 (AM1.5) solar spectrum. Based on this measure for the sun’s energy output at the earth’s surface, 4380 kWh would reach the earth’s surface in North America per m² per year considering that the average daylight time is 12 hours. This does not account for cloud cover and the wax and wane of the days throughout the year, but it does give us an idea of how much energy reaches the earth from the sun in a year as a function of surface area.

In addition to the total energy reaching the earth from the sun, we can consider the average energy consumption for a US household. As of 2009, the average US household consumed 26,300 kWh in a year’s energy usage. If all the energy reaching the earth’s surface could be collected in any given area, 6 m² of the sun’s illumination would be
needed to provide an entire year’s energy consumption for the average household. However, we cannot collect all the sun’s energy reaching a given area of the earth’s surface. There are several limitations to light harvesting efficiency of photovoltaic devices, many of which will be discussed here. Suffice it to say, a much larger area than 6 m\(^2\) would be necessary to provide a year of electric power to a typical home.

The top performing photovoltaic devices to date use silicon as the light harvesting semiconductor material. Investigation into commercial devices has found power conversion efficiencies between 6% and 16% for a range of silicon devices employing a variety of silicon morphologies and device architectures.\(^{31}\) Power conversion efficiency (PCE) for photovoltaic devices refers to the percentage of incident photons that are converted into electric current. Twenty large scale commercial photovoltaic modules were investigated in this examination by Ito et al at a site in Hokuto, Japan.\(^{31}\) The data examination accounts for the tilt angle and solar incident power of the sun at this location.

Seeing that silicon photovoltaic devices can achieve high power conversion efficiencies begs the question of why we would investigate organic semiconductors for use in photovoltaic devices. Here we must consider the costs of fabrication of these devices and environmental impact. This is also investigated in the publication by Ito et al.\(^{31}\) which compares the energy investment versus the energy recovered through operation, time frame of investment recovery (1 to 4 yrs.) and CO\(_2\) cost of production of the modules. These investment and recovery figures are calculated based on standard production processes. Crystalline silicon has the largest energy investment and CO\(_2\) cost,
while amorphous silicon has the lowest costs of the materials used in the production of these modules.

1.2.1 **Organic Photovoltaic Devices**

Organic photovoltaic (OPV) devices share many similarities with silicon and other inorganic photovoltaic (PV) devices. The general architecture of the device is essentially the same, where an active layer composed of one or more components is sandwiched between two electrodes, at least one of which must be transparent to let light into the active material. The major differences between inorganic and organic PV devices arise from the active layer rather than device architecture.32-33

A great deal of research in the field of OPV’s is aimed at materials that generate higher power conversion efficiency (PCE) as the primary method of increasing device performance. There is, however, research interest in developing new device architectures, which includes tandem and cascade devices of which there are several examples in recent years.34 The focus of this report will be on the former with an examination of standard photovoltaic devices such as bilayer heterojunction and bulk heterojunction (BHJ) OPV’s [Figure 1-3], rather than an investigation of new device architectures.

Inorganic semiconductors used in PV’s, such as silicon, can be used as a majority component of the active material in the device, arising from the fact that atoms in these materials form covalent networks, resulting in the appearance of continuous valence and conduction bands.35 This is a consequence of the proximity of the metal atoms and the regular, repeating spacing of atoms characteristic of crystal lattices, where this repeating
structure leads to wave forms that are solutions of the Bloch theorem and thus energy bands. The material has both a valence band stemming from the highest occupied molecular orbitals and conduction band formed by the lowest unoccupied molecular orbitals. When incoming photons of appropriate energy interact with the semiconductor, an electron from the valence band is excited to the conduction band. This excitation generates a bound electron/hole pair, termed an exciton. Inorganic semiconductors often produce large, diffuse Wannier excitons because of the coherent bands in the material.\textsuperscript{36-38} The energy required to dissociate these excitons into free charges is on the order of thermal energy (kT) in the inorganic semiconductor.

In contrast to the inorganic system, organic semiconductors rarely have coherent band structures throughout the material (although there are examples of organic molecular metals, and several reviews of this topic can be found in the scientific literature). Organic molecules are discrete entities with weak orbital overlap between adjacent molecules.\textsuperscript{38} Therefore, excitons generated in organic semiconductors tend to be Frenkel type excitons, which are tightly bound and localized to one molecule or a small number of molecules and require higher energy to dissociate into free charges. The dissociation energy of these Frenkel excitons is on the order of a few tenths to one electron volt.\textsuperscript{38-39}

It has become apparent that the use of two or more organic semiconductors is needed to efficiently produce electric energy from OPV devices. Generally, an electron donor molecule (D) is used in conjunction with an electron acceptor molecule (A) to facilitate dissociation of an exciton into free mobile charges. This process requires appropriate
energy offsets of donor and acceptor energy levels as well as good orbital overlap between adjacent molecules in the solid state. These topics are expanded upon in the more detailed discussion of bilayer heterojunction OPV devices below.

1.2.2 OPV Device Characteristics

When discussing photovoltaic devices, it is necessary to keep in mind some key characteristics of the devices beyond just power conversion efficiency. These characteristics include open circuit voltage (V\text{OC}), short circuit current density (J\text{SC}), fill factor (FF), series resistance (R\text{S}) and shunt resistance (R\text{P}). These characteristics of the device and associated circuitry directly contribute to the PCE. As such, each of these characteristics needs to be carefully considered and optimized to optimize the device performance and the corresponding PCE.

Open circuit voltage is a measure of the voltage generated by the device when no external load is applied to the device and therefore no current. The V\text{OC} is illustrated in Figure 1-2 as the intercept of the I-V curve at the voltage axis. Maximum V\text{OC} can be estimated for an OPV device by comparison of the donor HOMO and the acceptor LUMO.\textsuperscript{33, 40} A simple calculation that utilizes these energy values and the minimum exciton dissociation energy allows us to estimate the V\text{OC}. The calculation for V\text{OC} is as follows:\textsuperscript{40}

\[
V_{\text{OC}} = \frac{1}{e} (|E_{\text{DONOR HOMO}}| - |E_{\text{ACCEPTOR LUMO}}|) - 0.3 \text{ V} \tag{1-1}
\]

Short circuit current (I\text{SC}) is a measure of the current of the PV device when the voltage of the system is zero, and is shown in Figure 1-2 as the intercept of the I-V curve at the
current axis. The $I_{SC}$ can be enhanced by the incorporation of lower band gap donor materials to increase the number of photons that can be harvested during device operation.\textsuperscript{41} Lowering the band gap of the donor material increases the number of potential excitation events in the active layer which could produce free charge carriers.

![Figure 1-2: Representative I-V curve for an OPV device](image)

The fill factor (FF) is calculated from experimental data using the $V_{OC}$, $I_{SC}$ and voltage and current at maximum power output of the device. The quotient of the product of the voltage and current density at maximum power and theoretical maximum power output derived from the product of the $V_{OC}$ and $I_{SC}$ gives us a calculation for the fill factor:\textsuperscript{42}

$$\text{FF} = \frac{(V_{MP} \times I_{MP})}{(V_{OC} \times I_{SC})} \quad (1-2)$$

Higher fill factor is indicative of a higher performing device. Fill factor is strongly influenced by both the series and shunt resistances. Values for both resistances can be calculated from experimental data collected from an OPV device.\textsuperscript{43} The slope of the I-V curve at the $V_{OC}$ and $I_{SC}$ intercepts are the inverse of the series resistance ($R_S$) and shunt resistance ($R_P$) respectively. To maximize the FF of the device, it necessary to achieve low $R_S$ and high $R_P$. 

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The series resistance, \( R_s \), is a measure of the internal resistance of a device. This is a cumulative effect of the resistance within the material, between the interfaces of all of the components and the contact with the electrodes. It is necessary to keep \( R_s \) as low as possible to reduce voltage loss during device operation and promote a high FF. Strategies for realizing low \( R_s \) can involve improving interfacial contacts between components in the device, maintaining high purity of components to reduce the prevalence defects and deposition methods for active materials that result in fewer occurrences of defects.

Contrary to series resistance, shunt resistance (\( R_p \)) should be as high as possible. The shunt is a parallel pathway to the cell that allows current leakage and power loss. The shunt resistance can be used as a measure of the unproductive exciton recombination and charge trapping within the active material. It is desirable to have a high shunt resistance as this indicates that the cell is the predominant pathway for generated current and losses are subsequently low. It is possible to calculate \( R_p \) as the inverse of the slope of the I-V curve at the short circuit current intercept. A larger slope indicates decreased \( R_p \) and leads to a lower fill factor.

Achieving good control over the \( V_{OC} \), \( I_{SC} \) and resistances of a photovoltaic cell and producing favorable values for each of these values should allow for improved performance in OPV devices. Nevertheless, the performance of OPV devices is intimately tied to the materials employed. Devices with low \( V_{OC} \) and low \( I_{SC} \) but good fill factor are unlikely to provide high power conversion efficiency, since for this value we also need to
consider the incident power of the light source and spectral width of the source. Consider the equation for PCE (η) below:\textsuperscript{40-43}

\[ \eta = \frac{V_{OC} \times I_{SC} \times FF}{P_{in}} \]  \hspace{1cm} (1-3)

The value generated from the numerator of \textit{Equation 1-2} is the product of the voltage and current density at maximum device power output of the device. The values of \( V_{MP} \) and \( I_{MP} \) are largely controlled by the \( V_{OC} \) and \( I_{SC} \) as these are the maximum possible values for device operation. Lower \( V_{MP} \) and \( I_{MP} \) give a lower numerator for \textit{Equation 1-3}. Given that \( P_{in} \) is intended to be the light power produced by the sun and the Earth’s surface and should be unchanged, if \( V_{MP} \times I_{MP} \) decreases, the PCE (η) will also decrease.

\textbf{1.2.3 Bilayer Heterojunction OPV Devices}

Early device architectures for organic photovoltaic devices used two organic semiconductors layered one on top of the other to form a consistent bilayer interface [\textit{Figure 1-3}].\textsuperscript{45} This active layer interface showed some initial promise over single component Schottky type OPV devices modeled directly on inorganic photovoltaic cells where conduction properties of the organic material is directly affected by the electrode materials employed.\textsuperscript{45-46} The advent of this device architecture allowed for improved device performance as well as elucidating the optical and physical processes of organic photovoltaic devices.

The conversion of incident photons into electric current in a bilayer heterojunction follows five basic steps [\textit{Figure 1-4}]:\textsuperscript{33, 43, 47}

1. Photon absorption by molecules in the active layer to form excitons
2. Exciton diffusion to donor-acceptor interface

3. Exciton dissociate and generation of free charge carriers

4. Charge transport to the electrodes

5. Charge collection at the electrodes

**Figure 1-3:** Combined schematics of standard organic photovoltaic architectures, left: bulk heterojunction, right: bilayer heterojunction

This is certainly a simplified description of the processes involved in photovoltaic energy production. The production of free charge carriers from excitons and the transport of excitons and carriers through the bulk of the materials has been scrutinized in the past several years, suggesting charge-transfer states at the D-A interface play a significant and pivotal role in the conversion of light into electrical current. There are several other investigations into these processes, and, though interesting, will only receive cursory attention.
Materials will only absorb photons that are of energy equal to or greater than the band gap of the material. It is not possible to absorb photons of lower energy due to the absence of allowed quantum states in the band gap of the material. In an ultraviolet-visible spectrum for a material, the long wavelength cutoff observed corresponds to the energy of the band gap in the material. The absorption of photons by the active materials in the device leads to production of excitons.

Considering that the Frenkel type exciton produced in organic materials is tightly bound and localized to one molecule or a small number of molecules, the driving force for the dissociation of the exciton in organic semiconductors is dependent on the energy offset of the donor and acceptor lowest unoccupied molecular orbitals (LUMO’s) or highest occupied molecular orbitals (HOMO’s). Because the exciton dissociation energy is far above the scale of thermal energy, the energy differences between the LUMO’s or HOMO’s of the donors and acceptors must be sufficient to make the formation of an intermolecular charge transfer complex favorable. This process is feasible for electron transfer from the donor to acceptor LUMO’s or the donor to acceptor HOMO’s depending on which molecule is photoexcited and maintains the same requirements regardless of the orbitals involved in formation of the charge transfer complex. This charge transfer complex is then separated by the internal voltage gradient produced by the electrodes.

The excitons generated by photoexcitation are not all produced at a D/A interface and therefore must diffuse through the active materials after formation to reach the heterojunction. These processes rely on energy transfer between adjacent molecules
(Dexter energy transfer) or long range Forster energy transfers, allowing the exciton to diffuse to the interface between the active layers. The consequence of this diffusion is that the exciton does not need to be generated at the donor/acceptor interface. The limitation derives from the average diffusion distance of excitons in organic semiconductors which is on the order of 10’s of nanometers. Excitons generated outside the bounds of this diffusion length will not reach the interface, but will undergo geminate recombination. Control over this process can potentially be achieved by limiting the thickness of the active layer to the order of exciton diffusion length, though practical limitations have to be considered. Decreased thickness of the active material limits the number of photons that can be absorbed, thus decreasing the current density that can be produced by the device, and very thin layers can also develop pin holes which may cause device short-circuits.

**Figure 1-4**: Schematic representation of photogeneration of current in OPV heterojunction devices. 

\[ \text{Figure 1-4: Schematic representation of photogeneration of current in OPV heterojunction devices}^{33, 43, 47, 51} \]
Charge transport in organic semiconductors is subject to the same limitations as exciton diffusion. Due to the weak orbital overlap between molecules, direct electron and hole transport over the lattice points is not possible.\textsuperscript{43,47} Thus, the electrons and holes that develop in the materials must move via a hopping mechanism, where electrons transfer sequentially between molecules as they move toward the electrodes.\textsuperscript{37}

The electrodes employed in the device create a built-in potential gradient that directs the charges to opposite electrodes after exciton dissociation into an electron/hole pair.\textsuperscript{54-55} This potential gradient arises in part from the difference in work functions of the metals used for each electrode. The low work function metal is used for the cathode, allowing photo-generated electrons to migrate to and collect on the cathode surface. The high work function metal is used for the anode which allows for the holes to migrate to and collect on the anode. The potential difference results in a voltage drift which directs the charges to the respective electrodes.\textsuperscript{55}

1.2.4 Bulk Heterojunction Solar Cells

To improve device performance, many device architecture modifications have been developed. Most applicable of these improvements to this report is the bulk heterojunction active layer [Figure 1-3: left]. This involves co-depositing the donor and acceptor organic semiconductors to decrease the size of the domains of the donor and acceptor to the scale of the exciton diffusion length.\textsuperscript{52} This is intended to avoid having to reduce the thickness of the active layer to the order of the exciton diffusion length which has physical, efficiency, and processing limitations.
There are inherent benefits and drawbacks to the bulk heterojunction approach. The use of the bulk heterojunction increases the likelihood that photo-generated excitons will reach an interface between the two materials. With the increase in the number of excitons reaching the heterojunction, an increased in the number of dissociation events leading to charge carriers is also expected. This increase in charge carriers should lead to improved device performance and PCE with a major drawback to this device type involving the pathways of charge carriers. If these carriers do not have a continuous path to the electrodes through their respective donor or acceptor materials, the charges can become trapped and lead to higher charge carrier recombination leading to lower shunt resistance rather than increased charge extraction.

1.2.5 Organic Semiconductors for OPV Devices

The two main categories of organic materials for OPV are polymeric semiconductors and small molecule semiconductors. Despite their differences, these two categories of materials have several fundamental similarities. These similarities stem from the common characteristics of aromatic hydrocarbons and the various synthetic and design strategies employed in the synthesis of organic semiconductors.

In general, organic semiconductors have conjugated aromatic backbones with various substituents intended to impart solubility or tune electronic properties of the materials. Polymers are very large molecules that have repeating subunits or mixtures of subunits arranged in long chains with or without branching. Small molecule organic semiconductors, on the other hand, tend to have one or a few subunits and do not have the long repeating structures observed in polymers.
Design strategies for polymer and small molecule organic semiconductors are very similar, and substituents are employed to target specific material properties. To tune electrochemical properties, the use of electron donating or electron withdrawing groups are widely applicable. These groups are often incorporated by connecting aromatic units bearing these units, leading to conjugation of the units and hybridization of the orbital of each unit. An increase in π-conjugation tends to decrease the band gap of a material by simultaneous elevation of the HOMO and reduction of the LUMO of the semiconductor. An increase in π-conjugation tends to decrease the band gap of a material by simultaneous elevation of the HOMO and reduction of the LUMO of the semiconductor. Addition of electron donating functional groups can serve to further increase the energy of the HOMO, leading to lower oxidation potential of the molecule. The use of electron withdrawing groups tends to act on the LUMO of the semiconductor by decreasing the reduction potential of the molecule, thus lowering the LUMO energy. A combination of electron donating and electron withdrawing groups as substituents of organic semiconductors has great potential for the design of targeted HOMO/LUMO energies for substrate and function specific molecules.

Both polymer and small molecule organic semiconductors are the subjects of intense study for use in electronic and optoelectronic devices. There are some difficult issues to overcome with polymeric materials however. Control of polydispersity (PDI) during polymer synthesis is important to reliable and consistent polymeric materials. The PDI describes the relative distribution of polymer chain length in the bulk of the material. Larger polydispersity for the polymer describes a wider range of molecular weights in the bulk of the material, and may be difficult to control between batches of polymers. Degree
of polymerization describes the relative length of the polymer chains on average in the bulk of the material, and varies between batches. Variations in degree of polymerization, as with polydispersity, can have major effects on physical properties of the material which may affect processing as well as how the material performs in devices by altering semiconductor morphology, which is very important to device operation and performance.\textsuperscript{62}

\textbf{Figure 1-5}: Structures of P3HT (left) and PC\textsubscript{60}BM (right)

A classic model for organic photovoltaic devices uses a combination of poly(3-hexylthiophene) (P3HT) and phenyl-C61-butyric acid methyl ester (PC60BM) [Figure 1-5].\textsuperscript{64-66} This is largely due to P3HT and PC60BM being cheap relative to other organic materials, leading to higher likelihood of commercial device production. Much work has been invested in optimizing the P3HT/PCBM system and has elucidated methods for optimization in other systems. Power conversion efficiency for these devices have been improved to between 3-5% by changing active layer morphology, material blend ratios and various other parameters.\textsuperscript{64, 66} These methods of optimization have potential application with other D-A systems. There are a variety of materials and device
architectures that have been studied over the past couple decades, and relevant studies will be discussed as necessary in relation to the work presented here.

1.2.6  Singlet Fission

A potential method of boosting PCE from OPV devices is through singlet fission, where a molecule is excited to the first excited singlet state ($S_1$), then transfers its excitation energy to two first excited triplet states ($T_1$) [Figure 1-6]. The singlet fission process is a spin allowed transition because the total spin of the excited singlet and paired triplets are the same, resulting in a fast process (10-100 ps) that can take place on the time scale of internal conversion pathways which is much faster than fluorescence (ns).

Since the objective is to convert one excited state to two excited states, the energy balance of the process needs to be isoergic or exoergic, $\Delta E_1 \leq \Delta E_2$ [Figure 1-6, b]. If the total energy of the two resultant triplets is endoergic, the process would require the input of the excess energy to proceed, making the process nonspontaneous and less efficient. If this energy increase were very small, on the order of thermal energy, then we could imagine phonon coupling could provide the excess energy, and if this energy difference were otherwise very large, we should expect the fission process to be significantly inhibited. In the isoergic and exoergic cases, no excess energy is required for fission to occur and we should then expect the process to proceed rapidly.
Figure 1-6: The energetic process of singlet fission, (a) general scheme of excitation (blue line) and singlet fission (red line), (b) Jablonski diagram of the excitation (blue line), fluorescence (green line), phosphorescence (orange line), internal conversion and intersystem crossing (red wavy lines) and singlet fission (red dotted line). Singlet fission processes have been identified as a potential method for increasing the external quantum efficiency and thus greatly improve the power conversion efficiency of OPV devices.\textsuperscript{69-70} Presumably, if a highly efficient singlet fission material were used as an active material in photovoltaic devices, each excitation event could produce two triplet excitons and subsequently two electrons per photon, and for this process to be useful for boosting power generation, it must be highly efficient. A limiting factor for power conversion in devices is the significant reduction in $V_{OC}$ which must accompany the use of SF in OPV devices due to the decrease in offset between the HOMO and LUMO of the donor and acceptor materials respectively, limiting the theoretical maximum efficiency to around 40\%.\textsuperscript{71}

Few molecules are known to have appropriate $S_1$ and $T_1$ energies for singlet fission, primary of these is the acene series. It is important to note that the higher acenes,
pentacene and longer, demonstrate exoergic energies necessary for singlet fission.\textsuperscript{72} Identifying new singlet fission chromophores is difficult due to the difficulty in identifying the physical mechanism of the SF process.\textsuperscript{69} Though it is known that some molecular interaction is necessary for singlet fission to proceed, the relation between molecules participating in this process are not well understood.\textsuperscript{69,72}

1,3-Diphenylisobenzofuran has been studied extensively in order to elucidate the singlet fission mechanism.\textsuperscript{73} These studies show that there are competing processes in crystalline films that reduce SF efficiency, such as fluorescence, excimer formation and exciton trapping.\textsuperscript{73} The orientation of molecules in the film were shown to have a dramatic impact on singlet fission, with increased tendency for excimer formation in the β polymorph having a negative impact on singlet fission efficiency.\textsuperscript{73b} This competition between a variety of energetic pathways and reliance on crystal packing motifs and intermolecular interactions has been observed for other chromophores, such as alkylsilylethylene anthracene.\textsuperscript{74}

1.3 Field Effect Transistors

Transistors are fundamentally a current modulation device with an on and off state which are used in integrated circuits, power amplifiers and logic devices. Organic field effect transistors (OFET) are a class of transistor devices that operate by aligning charges in an organic semiconductor layer by applying a bias between the source and gate electrodes ($V_G$), where this alignment of charge modulates current flow between the source and drain electrodes ($I_D$) [Figure 1-7].\textsuperscript{75-77} When the $V_G < 0$ V, negative charge accumulates at the surface of the gate electrode, inducing polarization in the dielectric
layer. This results in the filling of traps and accumulation of positive charge carriers at the surface of the semiconducting material. Increasing gate bias aligns more charge carriers at the semiconductor-dielectric interface and allows for increased drain current flow ($I_D$) when a bias is applied between the source and drain ($V_D$).

![Diagram of transistor architecture and operation](image)

**Figure 1-7:** Top gate, bottom contact transistor device architecture and operation, (a) device architecture, (b) schematic of the active channel of the transistor, showing the length ($L$) and width ($W$), (c) gate electrode biasing and charge accumulation, (d) drain current flow through semiconductor

There are three varieties of transistor materials, i.e. p-type (hole transport, **Figure 1-7**), n-type (electron transport) and ambipolar capable of both p- and n-type behavior. Ideal devices should be in the off state when the gate bias is 0 V, where the device would be in the off state with flat bands at 0 V and switch to the on state by charge accumulation at increasing bias. In non-ideal cases, the device may be on until reverse bias is
established at the gate electrode, requiring constant energy to keep the device in the off state.

### 1.3.1 Devices Characteristics of Field Effect Transistors

OFET devices display several key characteristics during operation, related to voltages applied to the device electrodes and current produced in the device. The gate voltage at which the device begins to produce current between the source and drain, is referred to as the threshold voltage ($V_{TH}$) and can be estimated by extrapolating the linear region of the current-voltage (I-V) curve to the $V_G$ axis, shown as the black dashed line overlaid on the red curve in **Figure 1-8, a**. The ratio of the on and off current is also important to devices, as this describes the current amplification observed when the device is on. This is further demonstrated by $V_G$ series curves like **Figure 1-8, b**, where increasing current with increased $V_G$ is observed as the drain voltage is increased to higher bias.

From these curves, the mobility ($\mu$) of the semiconductor material can be extracted. We can use either the slope of the linear region of the I-V curve or the $I^{1/2}$-V curve in the saturation regime, though the second option is often used. We can use the following equations to extract the mobility from the data:

\[
I_{D}^{sat} = \mu \frac{W}{2L} C_i (V_G - V_{TH})^2
\]  \hspace{1cm} (1-4)

\[
\mu = \frac{2L}{W C_i} \left( \frac{\delta \sqrt{I_D}}{\delta V_G} \right)^2
\]  \hspace{1cm} (1-5)

Where $W$ and $L$ are the width and length of the conducting channel, respectively (**Figure 1-7, b**), and $C_i$ is the capacitance of the dielectric layer.
Figure 1-8: Characteristic current-voltage curves generated from OFET devices, (a) representative trans conductance plot showing both drain current-gate voltage plot (red) and drain current$^{1/2}$-gate voltage plot (blue), dashed line is the linear fit for extrapolation to find the threshold voltage ($V_{TH}$), (b) representative trans conductance plot of drain current-drain voltage curve for various gate voltages.

It is important to carefully examine the current-voltage characteristics of devices and the conclusions drawn from the data. Non-ideal transistor behavior can result in multiple slopes being observed for the $I^{1/2}$-$V$ curve in the saturation regime. Fitting a line to these slopes results in discrepancies in both the mobility and threshold voltage for each measurement. The discrepancy is derived from gate-bias dependence of contact resistance in the device and can lead to overestimating the mobility by an order of magnitude.

1.3.2 Acene Materials for Field Effect Transistor Applications

A large variety of organic molecules have been investigated for field effect transistor applications, though the most illustrative examples for this report are acenes and their derivatives. An archetypal example of a p-type acene semiconductor is pentacene along with its derivatives. 

Examining the crystal packing motifs and charge transfer in these
materials can give us insight that we can apply to the development of new organic semiconductors.

Charges pass between chromophores in aggregates via $\pi$-surface interactions, and appropriate contact between the molecules is necessary for efficient charge transfer. This mode of charge transfer requires packing motifs that align the molecules properly and maximize orbital overlap between adjacent molecules, in addition to active layers containing a minimal number of defects. Single crystal devices tend to display much higher charge carrier mobility in transistor devices since large crystals tend to be highly pure and exhibit fewer defects than solution deposited films which may contain polymorphs or dislocation, omission and other lattice defects.\textsuperscript{84-85} Defects act as scattering points for mobile charges in the material, leading to decreased charge mobility.

Molecule orientation in OFET devices is paramount to device operation, both in how the molecules are aligned with the substrate and the alignment between the source and drain electrodes.\textsuperscript{81,83} Pentacene, and other acenes, adopt an edge to surface orientation on oxide surfaces with the $\pi$-surface oriented parallel to the substrate surface.\textsuperscript{82,85} The charges do not move equally well in all direction of pentacene, where mobility measurements in single crystals show significant changes in charge mobility depending on placement of the electrodes.\textsuperscript{83} We can envision this effect holding true for alkylsilylethynyl acene materials, also. The alkylsilyl groups tend to align with the surface for these molecules, leading to $\pi$-surface, and charge transport, alignment parallel to the surface as seen for bare acenes [Figure 1-9].\textsuperscript{83}
Figure 1-9: Molecular contact of various pentacene derivatives with polar surfaces, (a) pentacene surface contact is edge to surface, (b) TIPS-pentacene surface contact is with the alkylsilyl groups, red arrows show the two distinct charge transport pathways, (c) TES-pentacene surface contact is with the alkylsilyl groups, red arrow shows the charge transport pathway between the adjacent π-surfaces

Materials that have reduced charge transfer anisotropy, i.e. multiple charge-transfer pathways, have the potential to maximize device performance.\textsuperscript{86,87} It has been observed that the 2-D packing motif shows improved charge transport characteristics compared to 1-D motifs.\textsuperscript{86,87} In 2-D materials, there are an increased number of possible orientations of molecules that lead to coherent charge transport pathways between two electrodes [Figure 1-9]. Not only are there two conduction path directions for each molecule in the film, but the 2-D packing motif tends to develop into 2-demensional domains, potentially covering more electrode surface. Materials with 1-demensional motifs tend to grow needles, long thin domains, which have more of a chance of not fully bridging the electrode gap. By many crystalline domains forming in the electrode channel, these 1-D materials can still form working devices by intersection of crystal grains, which happens even in devices employing 2-D materials, such as TIPS-pentacene. These grain boundaries do, however, lead to decreased charge mobility in devices by misalignment of molecules, resulting in barriers to charge transfer between grains, thus resistance to charge flow.\textsuperscript{88}
1.4 References


2 Nitrile Derivatives of Acenes for Photovoltaic Devices

We investigated several electron-deficient acenes for potential use as acceptors in bulk heterojunction organic photovoltaic (BHJ OPV) devices. These new molecules are composed of an acene chromophore, e.g. tetracene or pentacene, substituted with electron withdrawing substituents of varying strength in addition to solubilizing substituents employed for processing and targeting of crystal packing motifs. These molecules will be introduced and examined here independently, though some common design rationale and concerns will be outlined first.

A suitable band gap is one major target in designing organic semiconductors suitable for use in photovoltaic devices. The material needs to absorb a large portion of the solar spectrum to increase the potential number of photoexcitation events and maximize the short circuit current ($I_{sc}$).\textsuperscript{1} In addition, an acceptor molecule needs to have appropriate HOMO and LUMO energy to facilitate electron transfer from the donor, regardless of whether photoexcitation occurs at the donor or acceptor, and maximize open circuit voltage ($V_{oc}$) simultaneously.\textsuperscript{1c}

Those molecules that demonstrate favorable electronic properties must also exhibit suitable crystal packing motifs. The crystal packing of the molecule needs to have short contacts between π-faces, generally on the order of 3.2 – 3.4 Å, to facilitate electron transport after charge carrier generation.\textsuperscript{2} Furthermore, the semiconductor needs to have continuous stacks in one or more dimensions to transfer electrons through the material via percolation pathways.\textsuperscript{3}
With the moderate success of 2-cyano-6,13-tri(cyclo-pentyl)silylethynyl pentacene (CN-TCPS-Pn)\(^4\) as an acceptor with poly(3-hexyl thiophene) (P3HT) donor in BHJ solar cells, various nitrile derivatives of acenes were investigated as possible acceptors for these devices. The success of CN-TCPS-Pn can be attributed to both the electronic structure and the crystal packing motif of the molecule. Appropriately placed LUMO (-3.50 eV) and HOMO (-5.31 eV) potentials,\(^4\) relative to vacuum, facilitate electron transfer from P3HT to the acceptor, while the packing motif facilitates electron transport in the bulk of the acceptor domains.

**Figure 2-1**: Crystal structure diagrams of CN-TCPS-Pn\(^4\) (a) structure, protons omitted for clarity, (b) crystal packing viewed along b axis, (c) space filling models of crystal bulk showing availability of \(\pi\)-surface from two crystal surfaces.
Figure 2-2: General structures, common names and abbreviations of acene nitrile derivatives.

The crystal packing of the CN-TCPS-Pn leads to favorable charge transport by a variant of 1-D π-stack arrangement [Figure 2-1, b]. This “sandwich-herringbone” stacking allows dissociated electrons to hop along a row of molecules after exciton dissociation and the alternating orientation of 1-D stacks allows for interfacial contact between P3HT and CN-TCPS-Pn from nearly any domain arrangement in the bulk heterojunction [Figure 2-1, c]. We can consider this in the terms laid out by Anthony et al.\textsuperscript{5} where it is illustrated that the aliphatic, or greasy, groups provide a barrier to charge injection and raise the resistivity of the material. By utilizing packing arrangements that provide π-surfaces in a maximum number of orientations, we have a better opportunity to maximize device performance by decreasing charge injection anisotropy. With these basic properties as
targets for substituted acenes as acceptors in organic BHJ solar cells, several targets were selected for investigation [Figure 2-2].

Figure 2-3: Comparison of HOMO and LUMO levels of P3HT,\textsuperscript{10} cyano pentacene\textsuperscript{4} and other acene nitrile derivatives

We can demonstrate that electron withdrawing groups (EWGs) employed as substituents on acenes can significantly affect molecular orbital energies [Figure 2-3]. EWGs tend to have a larger effect on the LUMO of the molecule,\textsuperscript{6} though the HOMO of these molecules appears to be largely controlled by the core chromophore, as estimated from electrochemical reduction and oxidation potentials shown for each molecule below. The decision to include tetracene derivatives and not hexacene, or larger, derivatives was two-fold. Increasing the number of linearly fused benzenoid rings reduces optical and
thermal stability of acenes by large degrees. In addition, the HOMO energy should be higher as the number of linear benzenoid rings increases, which would put dicyanovinyl-hexacene HOMO energies too close to that of P3HT HOMO energy, decreasing the driving force for exciton dissociation in photovoltaic devices.

2.1 2-Dicyanovinyl-6,13-bistrialkysilylethynyl pentacenes

The use of the stronger dicyanovinyl electron withdrawing group, as compared to the nitrile group, on the pentacene chromophore is expected to have an increased effect on the energy level of the LUMO of the chromophore. Because of a deeper LUMO energy and relatively equal HOMO energy, the optical gap of the molecule is lower than that observed for cyano-pentacenes (CN-Pn). From ultraviolet-visible (UV-vis) spectra we can observe a decrease in the optical energy gap and cyclic voltammetry allows us to estimate the orbital energies for the HOMO and LUMO of dicyanovinyl-pentacene (DCV-Pn).

![Synthetic route to dicyanovinyl-pentacenes](image)

**Figure 2-4:** Synthetic route to dicyanovinyl-pentacenes; (i.) DIBAL-H (ii.) Malononitrile, triethylamine

Dicyanovinyl-pentacene derivatives were synthesized from cyano-pentacene precursors [Figure 2-4], which were prepared via literature methods. These pentacene nitriles were then reduced with di(iso-butyl)aluminum hydride (DIBAL-H) in solution at -78 °C until the reaction was observed to be complete by thin layer chromatography (TLC),
at which point they were quenched by the addition of 10% hydrochloric acid solution while maintaining -78 °C conditions to obtain pentacene aldehydes in good yields. These aldehydes were then subjected to Knoevenagel conditions with malononitrile and triethylamine to form the DCV products.

A comparison of estimated HOMO and LUMO energies from cyclic voltammetry for CN-TCPS-Pn and DCV-TCPS-Pn illustrates the effect of using the stronger electron withdrawing DCV functional group [Figure 2-3]. The data shows a 0.1 eV decrease in LUMO energy from nitrile to dicyanovinyl functional groups and very little effect on the HOMO energies of the two compounds. Frontier orbital energy levels were estimated from cyclic voltammetry [Figure 2-5] of 2-dicyanovinyl-6,13-bis(tri-iso-propylsilylethynyl) pentacene in methylene chloride with ferrocene reference. Values were calculated by averaging the anodic and cathodic reduction and oxidation potentials by use of Equation 2-1, making it possible to estimate the HOMO and LUMO energies [Figure 2-3].

\[ E = -4.8 - (\text{Reduction/Oxidation Potential} - \text{Ferrocene Oxidation Potential}) \] (2-1)

The effect of the electron withdrawing strength on frontier orbitals is also illustrated by a comparison of the UV-vis spectra for cyano-pentacene versus dicyanovinyl-pentacene [Figure 2-5, a]. A decreased optical gap for a chromophore is expected to translate into longer wavelength absorbance of light, as these properties are inversely related. The use of the DCV group induces an observed bathochromic shift in light
absorption of \( \sim 60 \) nm, thus pushing the absorption maximum closer to the near infrared (NIR).

**Figure 2-5**: UV-vis and electrochemical characteristics of DCV-TCPS-Pn, (a) UV-visible spectra comparison of methylene chloride solutions of 2-cyano-TCPS-pentacene (blue trace) and 2-dicyanovinyl-TCPS-pentacene (green trace), (b) Cyclic voltammetry of 2-dicyanovinyl-TIPS-pentacene in methylene chloride with 0.1 M \( \text{Bu}_4\text{NPF}_6 \) electrolyte support

Lowering the LUMO energy of a chromophore is expected to have competing effects on device performance. On one hand, a lower optical gap allows for the absorption of a wider range of the solar spectrum which has the potential to increase short-circuit current density \( (J_{SC}) \) and power conversion efficiency \( (PCE) \). However, the decrease in LUMO energy is expected to decrease open-circuit voltage \( (V_{OC}) \) in devices if acceptor molecules being compared are used in conjunction with the same donor molecule, though morphology of the junction and strength of intermolecular interactions contribute to the \( V_{OC} \) value. In this case, with a 0.1 eV decrease in LUMO energy and static HOMO energy, we expect a 0.1 V decrease in \( V_{OC} \) to 1.24 V. It is interesting to note that the estimated \( V_{OC} \) using the HOMO for P3HT from [4] does not compare well with experiment, and HOMO and LUMO energies for P3HT of -4.7 eV and -2.8 eV,\(^{13-14} \) respectively, seem to be
in better agreement with measured $V_{OC}$ for acene devices, leading to a calculated $V_{OC}$ of 0.78 V for DCV-Pn/P3HT devices in much better agreement with experiment.

Devices were fabricated using DCV-TCPS-Pn and DCV-TIPS-Pn by researchers at KAUST (King Abdullah University of Science and Technology) in Saudi Arabia, with P3HT as the donor in bulk heterojunction architecture, as described previously. Maximum power conversion efficiencies were found to be around 0.03% for DCV-TCPS-Pn as compared to about 0.5% for concurrent devices fabricated with CN-TCPS-Pn as the acceptor material. Fluorescence quenching experiments were conducted at KAUST and showed efficient quenching of P3HT photoluminescence by DCV-TCPS-Pn. In effect, generated excitons are dissociated leading to decreased fluorescence of P3HT and generation of charge carriers. It was determined based on this finding that efficiency losses in BHJ devices are due to “recombination and weak extraction of carriers.” This conclusion seems reasonable considering that $I_{SC}$ (0.23 mA/cm²) and fill factor (0.23%) are both quite low for the devices and the $V_{OC}$ (0.65 V) is moderately close to the calculated $V_{OC}$ maximum (0.78 V). This suggests high series resistance and low shunt resistance where these resistances are related to recombination events, e.g. low shunt resistance, and inability to transfer charges between interfaces, e.g. high series resistance.

We also need to consider the solid state packing of the molecule. Considering that the “sandwich-herringbone” packing arrangement demonstrates the best device performance for solar cells and by changing the size and steric volume of the trialkylsilyl substituents we can attempt to target this packing motif. The effect of changes in solubilizing groups can be seen by the examples illustrated below (Figure 2-6 and Figure
and though it is possible to drastically alter the solid state arrangement of acene molecules, it is not possible to predict the packing arrangement without trial and error.

Figure 2-6: Crystal structure diagrams of DCV-TIPS-Pn (a) structure, protons omitted for clarity, (b) crystal packing diagram, trialkysilyl groups and protons omitted for clarity, (c) and (d) molecular surface diagrams from two orientations with rotation of 90° around the z-axis, alkylsilyl groups in black and aromatic backbone in red

The tri(3-iso-propyl)silylethynyl derivative [Figure 2-6] shows a clear 2-D π-stack arrangement in part b of the figure. This packing motif has been demonstrated to be ineffective for OPV devices, yet quite useful for field effect transitors. This is due to the interaction of the alkylsilyl groups with the substrates in transistor devices which orient the π-stacking of the molecules perpendicular to the substrate and directs charge
carriers between the electrodes.\textsuperscript{16} Parts c and d of Figure 2-6 and Figure 2-7 show why this packing motif is ineffective for OPV devices, where isotropic charge injection is preferable. From the diagram we can see that \(\pi\)-surfaces available for charge injection are only available in two of the three orientations of the material.

\textbf{Figure 2-7:} Crystal structure diagrams of DCV-TCPS-Pn (a) structure, protons omitted for clarity, (b) crystal packing diagram, trialkylsilyl groups and protons omitted for clarity, (c) and (d) molecular surface diagrams from two orientations with rotation of 90° around the z-axis, alkylysilyl groups in black and aromatic backbone in red

By changing the silyl group to the tri(cyclo-pentyl)silyl ethynyl derivative [Figure 2-7], the crystal packing becomes a 1-D slip-stack arrangement of molecule pairs with strong
π-π interactions between molecules in one direction. Part b of the diagram shows the packing motif, where molecular pairs are arranged end to end with offset of the DCV groups and other interactions in the solid state are limited to edge to edge interactions and interactions of aliphatic substituents. Based on the 1-D π-stacking motif, due to the limited π-surface orientation in the crystal shown in parts c and d of the figure, it should be expected that this material will demonstrate far worse OPV performance than CN-TCPS-Pn.

2.2 2-Cyano-6,11-trialkylsilylethynyl-tetracenes

Tetracene chromophores have a larger HOMO-LUMO energy gap than pentacene chromophores and therefore absorption of light in these materials has a shorter wavelength threshold than their pentacene counterparts. The main practical limitation from this lower wavelength absorption cutoff is a decrease in the range of absorption of the solar spectrum. This can in practice lead to poor device performance by contributing to lower short circuit current and intrinsically lower PCE in BHJ devices. Since both donor and acceptor molecules can absorb light in the device, decreasing the absorption profile of either material reduces the number of potential excitation events, thus reducing the number of potential charge carrier generation events.

The absorption spectrum of PC60BM has very strong absorption up to a wavelength of 450 nm13, 17 while 6,11-triethylsilylethynyl tetracene absorbs visible light to about 550 nm.18 The use of strong electron withdrawing groups pushes the absorption cutoff for tetracene materials to longer wavelengths, yet still leaves the absorption threshold significantly lower than analogous pentacenes. Consider the absorption spectra for an
6,11-triethylsilylethynyl tetracene core and 2-cyano-6,11-tri(cyclo-pentyl)silylethynyl tetracene (CN-TCPS-Tt) [Figure 2-8]; from the two spectra, we can observe a 20-30 nm red shift in the absorption for nitrile substitutedtrialklysilylethynyl tetracene over trialklysilylethynyl tetracene.

**Figure 2-8:** UV-vis of TES-Tetracene\(^{18}\) (—) and CN-TCPS-Tt (----)

**Figure 2-9:** Electrochemical characteristics of CN-TCPS-Tt in methylene chloride with 0.1 M Bu\(_3\)NPF\(_6\) electrolyte, Left: cyclic voltammetry with ferrocene reference, Right: differential pulse voltammetry of reduction potentials

The energy level alignment of the electron deficient tetracenes relative to P3HT is appropriate for electron transfer, however. The energies of the HOMO and LUMO for cyano-tetracenes were calculated from cyclic voltammetry of CN-TCPS-Tt [Figure 2-9]. A
quasi reversible reduction at -1.00 V and a reversible oxidation at 0.47 V correspond to LUMO energy of -3.33 eV and HOMO energy of -5.54 eV, respectively. Using Equation 2-1, a maximum $V_{oc}$ of 1.07 V is calculated and while this does to some extent offset the lower visible light absorption, device parameters cannot be estimated without device testing because of further considerations such as film morphology and molecular interfaces.

Figure 2-10: Crystal structure diagrams of CN-TCPS-Tt (a) structure, protons removed for clarity (b) crystal packing diagram, protons removed for clarity, (c) and (d) molecular surface diagrams from two orientations with rotation of 90° around the z-axis, alkysilyl groups in black and aromatic backbone in red
The crystal structure of CN-TCPS-Tt [Figure 2-10] demonstrates a 1-D π-stack arrangement somewhat akin to the “sandwich-herringbone” motif. The major difference in this case is the lack of alternating orientation of adjacent stacks, where instead all the stacks are oriented in the same direction. From the expanded crystal packing diagrams shown in Figure 2-10 c & d, the effect of the lack of alternation in stack orientation is apparent, where one face of the crystal lacks available π-surface.

![Crystal Structure Diagram](image)

**Figure 2-11**: Synthetic route to CN-TCPS-Tt; (i.) NBS, AIBN (ii.) KOAc (iii.) K$_2$CO$_3$, EtOH (iv.) Swern oxidation (v.) EtOH, NaOH (vi.) 1. tri(cyclo-pentyl)silyl acetylide 2. SnCl$_2$, HCl (vii.) KCN, Pd(PPh$_3$)$_4$, Cul

Synthesis of cyano-TCPS-tetracene was like that of cyano-pentacenes [Figure 2-11], where the synthesis was realized through 2-iodo-tetracene quinone. The quinone was prepared through aldol condensation between 4-iodo phthalaldehyde$^{10}$ and 1,4-dihydroxynaphthalene. The iodo-tetracene quinone was ethynylated using lithium tri(cyclo-pentyl)silyl acetylide, followed by reductive dihydroxylation using tin(II) chloride.
The nitrile group was then incorporated by catalytic cyanation using potassium cyanide, copper(I) iodide and a palladium(0) source.

![Crystal structure diagrams of CN-TIBS-Tt](image)

**Figure 2-12**: Crystal structure diagrams of CN-TIBS-Tt (a) structure, protons omitted for clarity, (b) crystal packing diagram, protons omitted for clarity, (c) and (d) molecular surface diagrams from two orientations with rotation of 90° around the z-axis, alkylsilyl groups in black and aromatic backbone in red

The tri(iso-butyl)silylethynyl derivative of 2-cyano-tetracene [Figure 2-12] was also synthesized and, in this case, the preferred “sandwich-herringbone” crystal packing is observed. The close contacts between π-faces of adjacent molecules are 3.4 Å which is at Van der Walls distance between carbons in the π-system, potentially leading to strong π-overlap between molecules. We can again observe the alternating orientation between
\(\pi\)-stacks, and in Figure 2-12, c & d we can see the available \(\pi\)-surface on all the faces of the crystal.

Even though we observe the targeted crystal packing, it is unlikely that cyano-tetracenes will perform well in OPV devices. This is due to the high LUMO energy relative to P3HT which would introduce a barrier to charge transfer processes. For tetracene derivatives to be appropriate for OPV devices, the LUMO energy needs to be lowered which can be achieved by further derivatization using the dicyanovinyl group.

![Synthetic route to CN-TIBS-Tt](image)

**Figure 2-13:** Synthetic route to CN-TIBS-Tt; (i.) MeOH, \(\text{H}_2\text{SO}_4\) (ii.) DIBAL-H (iii.) Swern oxidation (iv.) EtOH, KOH (v.) 1. Tri(iso-butyl)silyl acetylide, 2. \(\text{SnCl}_2\), HCl (vi.) \(\text{Zn(CN)}_2\), DMF, Pd(\(\text{PPh}_3\)_4

Synthesis of the CN-TIBS-Tt derivative was like that of the CN-TCPS-Tt derivative with the principle difference being the use of brominated starting materials [Figure 2-13]. Bromo-phthalaldehyde was prepared from 4-bromo phthalic anhydride in good yields via a three-step reaction sequence. This 4-bromo phthalaldehyde was then used in conjunction with 1,4-dihydroxynapthalene in an aldol condensation to yield 2-bromo tetracene quinone. This quinone was then ethynylated in the same manner as TCPS.
derivative above with lithium tri(iso-butyl)silyl acetylide. The nitrile group was incorporated zinc cyanide with a palladium(0) source in dimethyl formamide.

2.3 2-Dicyanovinyl-6,11-trialkylsilylethynyl tetracenes

In same manner that previously investigated cyano-pentacenes were converted to dicyanovinyl-pentacenes to lower the band gap of the material by lowering the LUMO, 2-cyano-6,11-bistri(cyclo-pentyl)silylethynyl tetracene was converted to the corresponding dicyanovinyl-tetracene (DCV-Tt). Shifting of the LUMO energy was much higher in magnitude for the tetracene chromophore (0.29 eV decrease) compared to the pentacene chromophore (0.12 eV decrease). The LUMO energies for the DCV-Tt and DCV-Pn are both -3.62 eV, demonstrating that the very strong electron withdrawing DCV substituent exerts significant influence over LUMO energy levels. The HOMO of the tetracene chromophore was not significantly affected by moving from the CN to DCV groups as observed with pentacene derivatives.

![Figure 2-14](image)

**Figure 2-14:** Electrochemical characteristics of DCV-TCPS-Tt in DCM with 0.1 M Bu₄NPF₆ as electrolyte support, (a) cyclic voltammetry, (b) differential pulse voltammetry

Frontier orbital energy levels were again calculated from cyclic voltammetry measurements [Figure 2-14, a] as previously measured for DCV-Pn and CN-Tt. In this case,
a clear reversible oxidation is seen at 1.05 V corresponding to HOMO energy of -5.55 eV versus vacuum.\textsuperscript{11} On the other hand, the reduction corresponding to the LUMO appears to be obscured by a subsequent, stronger LUMO +1 reduction.

In addition, this reduction does not appear to be reversible on initial inspection by CV. To further inspect the LUMO of DCV-TCPS-Tt, differential pulse voltammetry was conducted [Figure 2-14, b]. From the DPV, it is observed the first reduction of DCV-TCPS-Tt is quasi-reversible and rather close in energy to a second reversible reduction. Using this data, the LUMO energy of DCV-TCPS-Tt was calculated\textsuperscript{11} to be -3.62 eV from the average first reduction potential of -0.892 V.

\textbf{Figure 2-15}: UV-vis spectra comparison of CN-TCPS-Tt (red trace) and DCV-TCPS-Tt (purple trace)

From the HOMO and LUMO energies of DCV-TCPS-Tt, it was concluded that the dicyanovinyl substituent resulted in a large reduction in the band gap of the tetracene chromophore. This conclusion is further supported by the bathochromic shift in visible light absorption of DCV-Tt versus CN-Tt [Figure 2-15], where a substantial red shift in the absorption cutoff wavelength, \textasciitilde70 nm, for DCV-TCPS-Tt is evident.
Single crystal x-ray analysis of DCV-TCPS-Tt crystals shows a triclinic unit cell with c/a ratio of 1.25. Molecules in this structure are arranged in 1-D π-stacks with similar orientation relative to each other [Figure 2-16]. The packing motif is relatively unchanged from parent CN-TCPS-Tt and concerns for material interfacial charge transfer are still in the forefront.

**Figure 2-16:** Crystal structure diagrams of DCV-TCPS-Tt (a) structure, protons omitted for clarity, (b) crystal packing diagram, protons omitted for clarity, (c) and (d) molecular surface diagrams from two orientations with rotation of 90° around the z-axis, alkylsilyl groups in black and aromatic backbone in red
The same synthetic methods for converting cyano-pentacenes to dicyanovinyl-pentacenes were employed for the synthesis of DCV-TCPS-Tt [Figure 2-17]. The CN-TCPS-Tt was reduced and hydrolyzed to the aldehyde by use of di(iso-butyl)aluminum hydride at -78 °C. This aldehyde intermediate was then used in a Knoevenagel reaction with malononitrile and Hunig’s base to produce the dicyanovinyl group.

![Figure 2-17: Synthetic route to DCV-TCPS-Tt; i.) DIBAL-H ii.) Malononitrile, Hunig’s base](image)

**2.4 Conclusions**

Although pentacene nitriles showed some early promise as acceptors for organic photovoltaics, further derivatization to dicyanovinyl groups to improve frontier orbital energy alignments has demonstrated a few pitfalls. The DCV group does reduce the LUMO energy of the acene chromophore relative to vacuum and as such should improve charge transfer from P3HT, but molecular arrangement in the solid state is also of high importance. The DCV acene derivatives explored here, show may other crystal packing motifs, and none are in the same vein as “sandwich herringbone.” In the bulk heterojunction, material domains are arranged randomly and a crystal packing motif that offers π-surface in three dimensions is ideal. Thus, devices that have been fabricated performed poorly and other DCV acene materials are expected to perform poorly as well.
2.5 Experimental

Bulk solvents were purchased from VWR, Fisher Scientific or Pharmco-Aaper. Reagents and starting materials were purchased from one of the major chemical suppliers, i.e. Sigma Aldrich, Oakwood Chemical, Fisher Scientific etc. Tri(iso-propyl)silyl acetylene and triethylsilyl acetylene were purchased from GFS chemicals.

Proton and carbon NMR spectra were collected using a 400 MHz Varian Unity spectrometer. Chemical shifts of each spectrum are reported in ppm and referenced to their corresponding deuterated solvents as listed. GC-MS was measured using a Bruker Scion-SQ GC-MS with an EI source. MALDI-TOF was measured at the UK mass spectroscopy center using a Bruker Daltonics MALDI-TOFMS ultraflex TOF/TOF in negative ion mode or by the UIUC mass spectroscopy center using a Bruker Daltonics MALDI-TOFMS flex with DHB matrix in positive ion mode. UV-visible spectra were measured using a StellarNet Inc Black-Comet UV-vis or Hewlett Packard 8453 UV-vis spectrophotometer. Fluorescence spectra were collected using a StellarNet Inc Silver-Nova spectrophotometer with a SL1-LED excitation source. Cyclic voltammetry and differential pulse voltammetry were measured using a BAS CV-50W potentiostat at a scan rate of 20 mV/s with a button glassy carbon working electrode, a platinum wire counter electrode and an Ag/AgCl reference electrode. A solution of 0.1 M Bu₄NPF₆ in methylene chloride was used as a supporting electrolyte solution under a blanket of N₂ with Fc/Fc⁺ as an internal reference. Differential scanning calorimetry (DSC) was measured using a TA Instruments DSC Q100 with a ramp rate of 10 °C/minute.
**Tri(cyclo-pentyl)silyl acetylene**

In a flame-dried, nitrogen purged 1 L round bottom flask, 18.9 mL of trichlorosilane (188 mmol) was dissolved in 250 mL of dry THF and cooled to -78 °C. A dry addition funnel was connected to the flask and charged with 300 mL of 2.0 M cyclo-pentyl magnesium chloride (600 mmol) in ether. The grignard solution was added to the trichlorosilane solution drop-wise under nitrogen. After addition, the ether was boiled out of the flask at 60 ºC and kept at 60 ºC for 96 hours. The reaction was then cooled to room temperature and 10% HCl was added to the flask until all solids were dissolved. The layers were separated and the aqueous layer extracted with diethyl ether. The combined organic layers were combined and then dried using MgSO₄, filtered and concentrated. The resulting oil was run through a thick pad of silica using hexanes as eluent. The crude oil product was purified by vacuum distillation where the product was collected at an internal temperature of 73-75 ºC. GC-MS (m/z): (C₁₀H₁₉Si) 167 Da, (C₁₅H₂₈Si) 236 Da.

In a flame-dried, nitrogen purged 250 mL round bottom flask, 11.72 g of trimethylsilyl acetylene (119 mmol) was dissolved in 50 mL of dry THF and cooled to 0 ºC. 67.2 mL 1.6 M n-BuLi (107 mmol) was added drop-wise to the solution. The reaction mixture was then brought to room temperature and stirred for 1 hour while preparing tri(cyclo-pentyl)silyl bromide.

In a separate 250 mL round bottom flask, 14.11 g of tri-cyclo-pentylsilane (59.7 mmol) was dissolved in 100 mL of 1,2-dichloroethane. 9.54 g of Br₂ (58.7 mmol) was added drop-wise to the solution. After addition, the solution was refluxed for 20 minutes to remove
excess bromine and HBr. The solvent was then removed in vacuo. GC-MS (m/z): (C\textsubscript{10}H\textsubscript{18}SiBr) 245 Da, (C\textsubscript{15}H\textsubscript{27}SiBr\textsuperscript{+}) 314 Da.

The tri(cyclo-pentyl)silyl bromide was added drop-wise to the trimethylsilyl acetylene solution at 0 °C. The reaction mixture was brought to room temperature and stirred for 16 hours. The reaction was quenched with 20 mL of saturated ammonium chloride and the solution was extracted with hexanes. The combined organic solution was dried with MgSO\textsubscript{4}, filtered and concentrated. The resultant oil was purified by filtration through a thick pad of silica using hexanes as eluent. 18.93 g (95%) of 1-tri(cyclo-pentyl)silyl-2-trimethylsilyl acetylene was collected as colorless oil. GS-MS (m/z): (C\textsubscript{15}H\textsubscript{27}Si\textsubscript{2}+\textsuperscript{+}) 263 Da, (C\textsubscript{20}H\textsubscript{36}Si\textsubscript{2}+) 332 Da.

18.93 g 1-tri(cyclo-pentyl)silyl-2-trimethylsilyl acetylene (56.9 mmol) was mixed with 100 mL of methanol in a round bottom flask. Minimal THF (~10 mL) was added to the mixture until the solution became homogeneous. 3.93 g of potassium carbonate (28.5 mmol) was added to the flask and stirred 1 hour. 50 mL of water was added to the flask to dissolve excess potassium carbonate and the solution was extracted with hexanes. The combined hexanes extracts were washed with brine and then dried with MgSO\textsubscript{4}, filtered and concentrated. The resulting oil was purified by vacuum distillation to yield 13.76 g (92%) of clear, colorless oil. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, ppm): 1.01-1.06 (m, 3 H), 1.41-1.51 (m, 18 H), 1.60-1.82 (m, 6 H), 2.27 (s, 1 H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}, ppm): 23.6, 26.9, 29.0, 86.8, 93.8; GC-MS (m/z): (C\textsubscript{12}H\textsubscript{19}Si) 191 Da, (C\textsubscript{17}H\textsubscript{28}Si\textsuperscript{+}) 260 Da.
**Tri(iso-butyl)silyl acetylene**

100 mL of 0.5 M ethynyl magnesium bromide (50.0 mmol) in THF was added to a flame dried 250 mL round bottom flask. 10.0 g of tri(iso-butyl)silyl chloride (42.6 mmol) was added to the flask drop-wise and stirred for 48 hours. The reaction was quenched with saturated ammonium chloride and extracted with hexanes. The combined hexanes solution was washed with brine and then dried with MgSO₄, filtered and the solvent removed *in vacuo*. The crude product was filtered through a thick pad of silica using hexanes as eluent and the resulting oil was purified by vacuum distillation to yield 7.82 g (81%) of clear, colorless oil. ¹H NMR (400 MHz, CDCl₃, ppm): 0.67 (d, 2 H, J = 6.8 Hz), 1.01 (d, 6 H, J = 6.4 Hz), 1.91 (m, 1 H, J = 6.4 Hz), 2.42 (s, 1 H); ¹³C NMR (100 MHz, CDCl₃, ppm): 25.1, 25.2, 26.4, 89.7, 94.8; GC-MS (m/z): (C₁₀H₁₉Si⁻) 167 Da, (C₁₄H₂₈Si) 224 Da.

**6,11-bistriethylsilylethynyl tetracene**

A nitrogen purged, flame dried 250 mL round bottom flask was charged with 80 mL of hexanes and 1.7 mL of triethylsilyl acetylene (9.49 mmol) at 0 °C. To this solution was added 3.1 mL of 2.5 M n-butyl lithium in hexanes (7.75 mmol) and the reaction was stirred for 30 minutes at 0 °C. 0.50 g of naphthacene quinone (1.94 mmol) was added to the flask in one portion, followed by 8 mL of dry tetrahydrofuran. The reaction was brought to room temperature and stirring continued for 20 hours. The reaction was quenched by the addition of 15 mL of water and the solvent removed *in vacuo*. The crude ethynylated acene diol was purified by filtration through a thick pad of silica using hexanes as eluent.
to remove residual triethylsilyl acetylene, followed by methylene chloride to collect the diol. The solvent was removed \textit{in vacuo} to and the diol was collected as a pale-yellow oil.

The ethynylated acene diol was dissolved in 50 mL of tetrahydrofuran and 10 mL of 10% sulfuric acid. This solution was stirred vigorously at room temperature and 1.97 g of tin(II) chloride dehydrate (8.73 mmol) was added in one portion. The reaction was stirred at room temperature for 1 hour, then diluted with 50 mL water and extracted with hexanes (3x 50 mL). The combined organics were washed with brine, dried with magnesium sulfate, filtered and the solvent removed \textit{in vacuo}. The crude product was purified by filtration through a thick pad of silica using hexanes as eluent. The red solid was further purified by recrystallization from hexanes to yield 0.67 g (68%) of dark-red, interlocking plates. $^1$H NMR (400 MHz, CDCl$_3$, ppm): 0.91 (q, 12 H, J = 8.2 Hz), 1.26 (t, 18 H, J = 8.2 Hz), 7.45-7.48 (m, 2 H), 7.54-7.56 (m, 2 H), 8.03-8.06 (m, 2 H), 8.60-8.63 (m, 2 H), 9.27 (s, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): 5.8, 8.7, 107.8, 114.8, 119.5, 126.9, 127.2, 127.6, 128.4, 129.5, 131.2, 133.2, 133.6; MALDI-TOF (m/z): 504.3 Da.

2-formyl-6,13-bistri(iso-propyl)silylethynyl pentacene (2.1a)

In a flame dried 50 mL round bottom flask, 77.4 mg of 2-cyano-6,13-bistri(iso-propyl)silylethynyl pentacene (0.117 mmol) was dissolved in 10 mL of methylene chloride and cooled to -78 °C. 0.23 mL of 1.0 M DIBAL-H (0.23 mmol) was added to the reaction solution. The reaction mixture was stirred for 1 hour at -78 °C. 2 mL of 10% HCl was added to the reaction flask and stirred for 1 hour at -78 °C. The reaction mixture was then brought to room temperature and washed with water. The methylene chloride solution
was dried with MgSO₄, filtered and the solvent removed in vacuo. The resultant blue solid was run through a thick pad of silica using methylene chloride as eluent. 44 mg (56%) of dark blue powder were collected. ¹H NMR (400 MHz, CDCl₃, ppm): 1.33-1.55 (m, 42 H), 7.45-7.48 (m, 2 H), 7.85 (dd, 1 H, J₁ = 16 Hz, J₂ = 1.2 Hz), 7.99-8.01 (m, 3 H), 8.44 (s, 1 H), 9.32-9.34 (m, 3 H), 9.49 (s, 1 H), 10.19 (s, 1 H); ¹³C NMR (100 MHz, CDCl₃, ppm): 11.7, 19.0, 104.2, 108.0, 108.2, 118.8, 121.1, 126.37, 126.43, 126.47, 126.52, 126.58, 126.9, 128.7, 129.9, 130.1, 130.70, 130.74, 130.9, 131.0, 131.7, 132.5, 132.7, 133.1, 134.5, 138.4, 191.8; MALDI-TOF (m/z): 667.5 Da.

2-formyl-6,13-bistri(cyclo-pentyl)silylethynyl pentacene (2.1b)

In a flame dried, nitrogen purged 500 mL round bottom flask, 0.65 g of 2-cyano-6,13-bis(tri-cyclo-pentylsilylethynyl)pentacene (0.79 mmol) was dissolved in 250 mL of toluene and cooled to -78 °C. 3.17 mL of 1.0 M DIBAL-H (3.17 mmol) was added to solution dropwise to the solution and stirred for 3 hours. The reaction was quenched by slow addition of 7 mL of 10% HCl at -78 °C. The reaction mixture was then brought to room temperature and extracted with hexanes and washed with water. The combined organic solution was dried with MgSO₄, filtered and the solvent removed in vacuo. The resultant blue solid was run through a thick pad of silica using methylene chloride as eluent. 577 mg (88%) of dark blue powder were collected. ¹H NMR (400 MHz, CDCl₃, ppm): 1.30-1.40 (m, 6 H), 1.57-1.84 (m, 36 H), 2.05-2.07 (m, 12 H), 7.44-7.46 (m, 2 H), 7.83 (d, 1 H, J = 9 Hz), 7.96-8.0 (m, 3 H), 8.41 (s, 1 H), 9.26-9.28 (m, 3 H), 9.45 (s, 1 H), 10.18 (s, 1 H); ¹³C NMR (100 MHz, CDCl₃, ppm): 23.9, 27.1, 29.4, 103.21, 108.6, 108.9, 118.8, 119.4, 121.1, 126.37, 126.45,
126.47, 126.6, 126.9, 128.6, 129.9, 130.0, 130.7, 130.9, 131.0, 131.6, 132.5, 132.7, 133.1, 134.5, 138.5, 191.8; MALDI-TOF (m/z): 823.5 Da.

2-dicyanovinyl-6,13-bistri(iso-propyl)silylethynyl pentacene (2.2a)

In a 100 mL round bottom flask, 0.75 g of 2-formyl-6,13-bistri(iso-propyl)silylethynyl pentacene (1.12 mmol) and 0.15 g of malononitrile (2.25 mmol) were dissolved in 50 mL of 1,2-dichloroethane. To this solution was added 10 drops of triethylamine and the reaction was stirred for 2 hours. 20 mL of 15% KOH was added to the reaction and the solution was extracted with methylene chloride. The combined organic solution was washed with water and dried with MgSO₄, filtered and the solvent removed in vacuo. The crude product was subjected to silica gel chromatography using 1:1 hexanes:methylene chloride as eluent. 0.65 g of product was collected as a dark green solid. The product was recrystallized from 1,2-dichloroethane to yield 0.50 g (61%) of dark green crystals. ¹H NMR (400 MHz, CDCl₃, ppm): 1.31-1.40 (m, 42 H), 7.44-7.47 (m, 2 H), 7.82 (s, 1 H), 7.97-7.99 (m, 4 H), 8.28 (s, 1 H), 9.26 (s, 1 H), 9.30 (s, 2 H), 9.37 (s, 1H); ¹³C NMR (100 MHz, CDCl₃, ppm): 11.6, 19.0, 77.17, 81.7, 103.9, 108.3, 108.9, 112.9, 114.2, 119.0, 119.8, 121.9, 126.52, 126.58, 126.7, 127.1, 128.64, 128.67, 129.4, 130.5, 130.74, 130.77, 130.78, 130.80, 131.2, 131.7, 131.8, 132.7, 132.9, 138.4, 158.5; MALDI-TOF (m/z): 715.5 Da; MP range: 312-326 °C.

2-dicyanovinyl-6,13-bistri(cyclo-pentyl)silylethynyl pentacene (2.2b)

The 577 mg of 2-formyl-6,13-bistri(cyclo-propyl)silylethynyl pentacene intermediate (0.72 mmol) was dissolved in 100 mL of 1,2-dichloroethane in a 250 mL round bottom
flask. 105 mg of malononitrile (1.58 mmol) and twelve drops of triethylamine were added to the solution and stirred for 4 hours. The reaction was extracted with methylene chloride and the combined organic solution was washed with water, dried with MgSO₄ and the solvent removed in vacuo. The dark green solid was purified by silica gel chromatography with 1:1 hexanes:methylene chloride as eluent. 0.58 g (84%) of dark green solid was recovered and recrystallized from 1,2-dichloroethane. \(^1\)H NMR (400 MHz, CDCl₃, ppm): 1.32-1.37 (m, 6 H), 1.62-1.83 (m, 46 H), 2.03-2.09 (m, 12 H), 7.45-7.47 (m, 2 H), 7.86 (s, 1 H), 7.96-7.99 (m, 3 H), 8.06 (d, 1H, J = 9.2 Hz), 8.28 (s, 1 H), 9.24-9.27 (m, 3 H), 9.37 (s, 1 H); \(^{13}\)C NMR (100 MHz, CDCl₃, ppm): 23.8, 27.1, 29.4, 77.2, 81.6, 103.0, 108.9, 109.5, 113.0, 114.3, 119.1, 119.8, 121.8, 126.52, 126.57, 126.7, 127.1, 128.6, 129.4, 130.5, 130.8, 130.9, 131.2, 131.70, 131.78, 132.7, 132.9, 138.6, 158.6; MALDI-TOF (m/z): 871.6 Da; MP range: 287-300 °C.

\(\alpha,\alpha’\)-dibromo-4-iodo-o-xylene (2.3)\(^{10}\)

To a 500 mL round bottom flask, 33.20 g of 4-iodo-o-xylene (143 mmol) and 250 mL of 1,2-dichloroethane were combined. To this solution was added 101.86 g of NBS (572 mmol) and a catalytic amount of AIBN. The reaction mixture was heated to 98 °C with stirring under nitrogen for 40 hours. The reaction was then cooled to room temperature and succinimide was filtered out. The 1,2-dichloroethane was evaporated from the resulting solution. The recovered oil was run through a thick pad of silica using 2:1 hexanes:methylene chloride as eluent. The yellow oil collected (33.13 g) was a mixture of mono- and di-bromo products and used in the next step without further purification. GC-MS (m/z): (C\(_8\)H\(_8\)BrI) 310 Da + 312 Da, (C\(_8\)H\(_7\)Br\(_2\)I) 388 Da + 390 Da + 392 Da.
\( \alpha,\alpha'\text{-diacetoxy} \)\( \alpha' \)-methyl-4-iodo-o-xylene (2.4)\(^{10} \)

To a 250 mL round bottom flask, the bromination product mixture (33.13 g) from the previous step, 100 mL of DMF and 33.36 g of potassium acetate (340 mmol) were combined. The reaction mixture was heated to 60 °C for 40 hours. The reaction mixture was cooled to room temperature and 50 mL of water was added to dissolve water soluble salts. This mixture was then extracted with methylene chloride (3x 100 mL) and washed with brine. The organic phases were combined then dried with MgSO\(_4\), filtered and the solvent removed \textit{in vacuo}. The resulting oil was subjected to silica gel chromatography using 4:1 hexanes:ethyl acetate as eluent. 29.53 g (59% over 2 steps) of light yellow oil was collected from the column. \(^1\)H NMR (400 MHz, CDCl\(_3\), ppm): 2.05 (s, 3H), 2.07 (s, 3H), 5.09 (s, 4H), 7.08 (d, 1 H, J = 8 Hz), 7.62 (d, 1 H, J = 8 Hz), 7.71 (s, 1 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), ppm): 20.7, 62.6, 63.0, 94.1, 131.3, 134.1, 136.7, 137.6, 138.2, 170.16, 170.19; GC-MS (m/z): (C\(_{10}\)H\(_9\)O\(_2\)) 288 Da.

4-iodobenzene-1,2-dicarbinol (2.5)\(^{10} \)

In a 250 mL round bottom flask, 29.53 g of \( \alpha,\alpha'\text{-diacetoxy} \)\( \alpha' \)-methyl-4-iodo-o-xylene (84.8 mmol), 100 mL of THF, 50 mL of ethanol and 46.89 g of potassium carbonate (339 mmol) were combined. The reaction mixture was heated to 87 °C for 16 hours. The reaction was cooled to room temperature extracted with methylene chloride and washed with brine. The organic layers were combined, dried with MgSO\(_4\), filtered and concentrated \textit{in vacuo}. The resulting solid was purified by column chromatography using methylene chloride as eluent to remove by-products, followed by 9:1 methylene
chloride:acetone to collect the product. 15.47 g (78%) of product was collected as a waxy orange solid. $^1$H NMR (400 MHz, CDCl$_3$, ppm): 4.48 (d, 2 H, J = 5.5 Hz), 4.51 (d, 2 H, J = 5.5 Hz), 5.20 (t, 1 H, J = 5.5 Hz), 5.26 (t, 1 H, J = 5.5 Hz), 7.19 (d, 1 H, J = 8.2 Hz), 7.59 (d, 1 H, J = 8.2 Hz), 7.75 (s, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): 59.6, 59.9, 92.2, 129.0, 134.9, 135.0, 138.9, 142.0; GC-MS (m/z): (C$_8$H$_9$IO$_2$) 264 Da.

4-iodo-phthalaldehyde (2.6)$^{10}$

To a flame dried, nitrogen purged 500 mL round bottom flask, 80 mL of methylene chloride and 9.75 mL of oxalyl chloride (114 mmol) were combined and cooled to -78 °C. 16.13 mL of dimethyl sulfoxide (DMSO) (227 mmol) was mixed with 10 mL of methylene chloride and added drop-wise to the reaction solution. After addition of the DMSO solution, the reaction was stirred for 5 minutes. While the reaction was stirring, 7.5 g of 4-iodo-benzene-1,2-dicarbinol (28.4 mmol) was dissolved in minimal DMSO and diluted with 10 mL of DCM. This solution was added drop-wise to the reaction mixture. The reaction was stirred for an additional 30 minutes after addition of the starting material. An additional 20 mL of DCM was added to dilute the reaction mixture. The reaction was stirred for an additional 30 minutes and 67.34 mL of triethylamine was added dropwise to the reaction. After addition of the amine, the reaction was brought to room temperature and stir for 16 hours. 200 mL of ice water was added to the reaction and the reaction was extracted with DCM while the solution was still cold. The combined organic solutions were washed with brine and dried with MgSO$_4$. The product was filtered through a thick pad of silica with DCM as eluent. After recrystallization, 4.29 g (58%) of the product was collected as yellow needles. $^1$H NMR (400 MHz, DMSO-d$_6$, ppm): 7.66 (d,
1H, J = 8 Hz), 8.19 (dd, 1 H, J₁ = 8 Hz, J₂ = 1.6 Hz), 8.24 (d, 1 H, J = 1.6 Hz), 10.36 (s, 1 H), 10.39 (s, 1 H); ¹³C NMR (100 MHz, DMSO-d₆, ppm): 102.7, 131.8, 135.7, 137.6, 138.8, 142.8, 192.3, 192.9; GC-MS (m/z): (C₈H₅O₂I⁻) 260 Da.

2-iodotetracene-6,11-quinone (2.7)

Naphthalene-1,4-hydroquinone was prepared by adding a solution of 4.40 g of sodium dithionite (25.3 mmol) in 50 mL of water to a suspension of 1.0 g of 1,4-naphthoquinone (6.32 mmol) in 100 mL of diethyl ether and 30 mL of methylene chloride. This biphasic solution was then stirred for 16 hours, after which the layers were separated and the organic layer was dried with magnesium sulfate, filtered and the solvent removed in vacuo. The crude hydroquinone was used without purification.

1.47 g of 4-iodo-phthalaldehyde (5.65 mmol) and 1,4-dihydroxynaphthalene were dissolved in 3 mL of hot ethanol. Three drops of 15% of KOH were added to the reaction solution with vigorous stirring. A yellow precipitate evolved from the solution which was filtered and washed successively with methanol, acetone and ether. The resultant yellow powder was dried under atmospheric conditions overnight. 2.12 g (97%) of yellow, insoluble powder was collected and used in subsequent reactions without further purification. MALDI-TOF (m/z): 384.0 Da.

2-ido-6,11-bistricyclo(pentyl)silylethylnyl tetracene (2.8)

In a flame dried, nitrogen purged 100 mL round bottom flask, 1.01 g of tri-cyclo-pentylsilyl acetylene (3.87 mmol) was dissolved in 10 mL of n-heptane and cooled to 0 °C. 1.51 mL of n-BuLi (3.78 mmol) was added drop-wise to the reaction solution and stirred
for 1 hour. The reaction solution was diluted with 40 mL of n-heptane. 0.37 g of 2-iodo-6,11-tetracene quinone (0.97 mmol) was added to the reaction solution, followed by 5 mL of dry THF. The reaction mixture was brought to room temperature and stir for 16 hours. The reaction was quenched with 10 mL of water, extracted with DCM and the combined organic solution washed with water. The organic solution was dried with MgSO₄, filtered and the solvent evaporated *in vacuo*. The resultant yellow oil was run through a thick pad of silica using hexanes as eluent to remove excess acetylene, followed by DCM to collect the ethynylated tetracene diol as yellow-red oil.

The ethynylated tetracene diol was dissolved in 30 mL of THF and 10 mL of 10% HCl. 0.98 g of SnCl₂·2H₂O (4.34 mmol) was added to the reaction solution and stirred for 1 h. The solution was extracted with hexanes and the combined organic solution was washed with brine. The organic solution was dried with MgSO₄, filtered and the solvent removed *in vacuo*. The resultant red solid was run through a thick pad of silica using hexanes as eluent. 0.55 g (65%) of red solid was collected after removal of the solvent. ¹H NMR (400 MHz, CDCl₃, ppm): 1.26-1.33 (m, 6 H), 1.54-1.77 (m, 46 H), 2.01-2.06 (m, 12 H), 7.54-7.56 (m, 2 H), 7.57 (dd, 1 H, J₁ = 9.2 Hz, J₂ = 1.6 Hz), 7.72 (d, 1 H, 8.8 Hz), 8.42 (s, 1 H), 8.58-8.61 (m, 2 H), 9.14 (s, 1 H), 9.22 (s, 1 H); ¹³C NMR (100 MHz, CDCl₃, ppm): 23.9, 27.1, 29.4, 92.1, 102.7, 106.8, 107.0, 118.8, 118.9, 124.9, 125.3, 126.7, 126.9, 127.4, 129.9, 130.3, 130.4, 132.8, 132.9, 133.2, 134.2, 137.3; MALDI-TOF (m/z): 869.7 Da.
2-cyano-6,11-bistri(cyclo-pentyl)silylethynyl tetracene (2.9)

In a flame dried, nitrogen purged 250 mL round bottom flask, 0.6 g of 2-iodo-6,11-bistri(cyclo-pentyl)silylethynyl tetracene (0.6 mmol) was dissolved in 50 mL of THF. Oxygen was removed from the solution by a steady stream of nitrogen gas over a period of 1 hour. 0.18 g of KCN (2.8 mmol), 0.03 g of CuI (0.1 mmol) and 0.12 g of Pd(PPh3)4 (0.10 mmol) were added to the reaction solution and the solution was degassed of oxygen for an additional 15 minutes. The reaction was heated to 80 °C for 3 hours. The reaction was cooled to room temperature and the resultant solid was run through a thick pad of silica using 1:1 hexanes:methylene chloride as eluent. 0.34 g (64%) of red solid was collected. The product was recrystallized from dichloroethane to give red blocks. 1H NMR (400 MHz, CDCl3, ppm): 1.28-1.34 (m, 6 H), 1.57-1.78 (m, 46 H), 2.00-2.05 (m, 12 H), 7.48 (d, 1 H, J = 9.2 Hz), 7.58-7.60 (m, 2 H), 8.03 (d, 1 H, J = 9.2 Hz), 8.41 (s, 1 H), 8.59-8.61 (m, 2 H), 9.29 (s, 1 H), 9.33 (s, 1 H); 13C NMR (100 MHz, CDCl3, ppm): 24.0, 27.1, 29.5, 102.5, 102.6, 107.7, 108.1, 109.6, 119.1, 119.6, 124.7, 127.2, 127.3, 127.5, 127.6, 128.5, 130.1, 130.8, 131.5, 131.6, 133.3, 133.6, 136.4; MALDI-TOF (m/z): 769.5 Da.

Dimethyl 4-bromobenzene-1,2-dicarboxylate (2.10)

In a 250 mL round bottom flask, 12.67 g of 4-bromophthalic anhydride (55.8 mmol) was combined with 100 mL of methanol, to which 10 mL of concentrated sulfuric acid was added. The reaction mixture was then heated to reflux for 16 hours. The resultant solution was then cooled to room temperature, neutralized with 30.24 g of sodium bicarbonate and extracted with diethyl ether. The combined organic layers were washed with 50 mL
of brine (3x), dried with MgSO₄, filtered and the solvent removed in vacuo. The crude product was purified by filtration through a thick pad of silica gel using 4:1 hexanes:ethyl acetate as eluent, yielding 14.67 g (95%) of clear, colorless oil that slowly solidifies into a colorless, waxy solid. ¹H NMR (400 MHz, CDCl₃, ppm): 3.88 (s, 3 H), 3.90 (s, 3 H), 7.60 (d, 1 H, j = 8.2 Hz), 7.65 (dd, 1 H, j₁ = 8.2 Hz, j₂ = 2.0 Hz), 7.82 (d, 1 H, j = 2.0 Hz); ¹³C NMR (100 MHz, CDCl₃, ppm): 52.8, 52.9, 124.9, 125.8, 130.3, 130.5, 131.8, 134.0, 166.8, 167.0; GC-MS (m/z): (C₉H₆BrO₃⁻) 241 Da + 243 Da, (C₁₀H₉BrO₄⁻) 272 Da + 274 Da.

4-bromobenzene-1,2-dicarbinol (2.11)

In a nitrogen purged, flame dried 1 L round bottom flask, 14.01 g of dimethyl 4-bromobenzene-1,2-dicarboxylate was dissolved in 100 mL of DCM and cooled to 0 °C. With constant stirring, 257 mL 1.0 M of diisobutyl aluminum hydride in hexanes (257 mmol) was added dropwise to the reaction. The reaction was then allowed to warm to room temperature and stirred for 16 hours. The reaction solution was then cooled to 0 °C and carefully quenched with 10.28 mL of water, followed by 10.28 mL of 15% KOH and finally 25.7 mL of water. The suspension was filtered and the salts trichterated with 250 mL of ethyl acetate and filtered (2x). The combined organic solution was dried with MgSO₄, filtered and the solvent removed in vacuo. The crude product was purified by filtration through a thick pad of silica using 9:1 methylene chloride:acetone as eluent to yield 10.49 g (94%) of a colorless, waxy solid. ¹H NMR (400 MHz, DMSO-d₆, ppm): 4.49 (s, 2 H), 4.54 (s, 2 H), 7.34 (d, 1 H, j = 8.2 Hz), 7.41 (dd, 1 H, j₁ = 8.2 Hz, j₂ = 2.3 Hz), 7.57 (d, 1 H, j = 2.3 Hz); ¹³C NMR (100 MHz, DMSO-d₆, ppm): 59.6, 59.8, 119.9, 124.5, 128.8, 129.1, 138.5, 142.2; GC-MS (m/z): (C₈H₇BrO⁻) 198 Da + 200 Da, (C₈H₉BrO₂⁻) 216 Da + 218 Da.
4-bromophthalaldehyde (2.12)

A flame dried, nitrogen purged 500 mL round bottom flask was charged with 9.3 mL of oxalyl chloride (109 mmol) and 100 mL of DCM and cooled to -78 °C. A solution of 15.4 mL of DMSO (217 mmol) and 10 mL of DCM was added dropwise to the reaction solution. After stirring for 15 minutes at -78 °C, a solution of 5.90 g of 4-bromobenzene-1,2-dicarbinol (27.2 mmol) in minimal DMSO and 10 mL of DCM was added dropwise to the solution. After 30 minutes of stirring at -78 °C, 64.5 mL of trimethylamine (462 mmol) was added dropwise to the reaction. After 30 minutes, the reaction was warmed to room temperature and stir for 16 hours. 200 mL of ice water was added to the flask and the biphasic mixture was mixed vigorously and separated. The organic layer was then washed with 100 mL of ice water (3x), dried with MgSO₄, filtered and the solvent removed in vacuo. The crude product was purified by filtration through a thick pad of silica using methylene chloride as eluent. The product was further purified by recrystallization in hexanes and ethyl acetate to yield 3.0 g (51%) of tan needles. ¹H NMR (400 MHz, DMSO-d₆, ppm): 7.90 (d, 1 H, j = 8.2 Hz), 8.06 (dd, 1 H, j₁ = 8.2 Hz, j₂ = 2.0 Hz), 8.11 (d, 1 H, j = 2.0 Hz), 10.42 (s, 1 H), 10.44 (s, 1 H); ¹³C NMR (100 MHz, DMSO-d₆, ppm): 128.2, 132.4, 132.9, 135.5, 136.9, 138.2, 192.3, 192.6; GC-MS (m/z): (C₉H₅BrO₂⁻) 212 Da + 214 Da.

2-bromotetracene-6,11-quinone (2.13)

1,4-dihydroxy-naphthalene was prepared by adding a solution of 4.40 g of sodium dithionite (25.3 mmol) in 50 mL of water to a suspension of 1.0 g of 1,4-naphthoquinone (6.32 mmol) in 100 mL of diethyl ether and 30 mL of methylene chloride. This biphasic
solution was then stirred for 16 hours, after which the layers were separated and the organic layer was dried with magnesium sulfate, filtered and the solvent removed in vacuo. The crude hydroquinone was used without purification.

1.20 g of 4-bromo-phthalaldehyde (5.65 mmol) and 1,4-dihydroxynaphthalene were dissolved in 3 mL of hot ethanol. Three drops of 15% KOH were added to the reaction solution with vigorous stirring. A yellow precipitate evolved from the solution which was filtered and washed successively with methanol, acetone and ether. The resultant yellow powder was dried under atmospheric conditions overnight. 1.82 g (95%) of yellow powder was collected and used in subsequent reactions without further purification. MALDI-TOF (m/z): 336.0 Da + 338.0 Da.

2-bromo-6,11-bistri(iso-butyl)silylethynyl tetracene (2.14)

In a flame-dried, nitrogen purged 250 mL round bottom flask, 2.66 g of tri(iso-butyl)silyl acetylene (11.9 mmol) was dissolved in 20 mL of n-heptane and cooled to 0 °C. 4.45 mL of 2.5 M n-BuLi (11.1 mmol) was added drop-wise to the solution and the solution stirred for 1 hour. The solution was diluted to 100 mL with n-heptane and 1.00 g of 2-bromo-6,11-tertacene quinone (2.97 mmol) along with 5 mL of dry THF were added to the flask and stirred for 16 hours. The reaction was quenched with water and washed with brine. The organic solution was dried with MgSO₄, filtered and the solvent removed in vacuo. The resulting oil was run through a thick pad of silica using hexanes as eluent to remove unreacted acetylene, followed by DCM to collect the ethynylated tetracene diol.
The ethynylated tetracene diol was dissolved in 50 mL of THF and 15 mL of 10% HCl. 3.02 g of SnCl$_2$·2H$_2$O (13.4 mmol) was added to the solution and the reaction stirred for 2 hours at room temperature. The solution was extracted with hexanes. The combined hexanes extract was dried with MgSO$_4$, filtered and the solvent removed *in vacuo*. The red solid was run through a thick pad of silica using hexanes as eluent. 1.55 g (69%) of product was collected as a red solid. $^1$H NMR (400 MHz, CDCl$_3$, ppm): 0.92 (dd, 12 H, $J_1 = 6.8$ Hz, $J_2 = 2.5$ Hz), 1.14 (ddd, 36 H, $J_1 = 6.8$ Hz, $J_2 = 2.5$ Hz, $J_3 = 1$ Hz), 2.13 (spt, 6 H, $J = 6.8$ Hz), 7.48-7.55 (m, 3 H), 7.87 (d, 1 H, $J = 9.0$ Hz), 8.17 (s, 1 H), 8.57-8.60 (m, 2 H), 9.15 (s, 1 H), 9.22 (s, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): 26.3, 26.4, 27.4, 104.6, 110.0, 110.1, 119.7, 119.8, 121.2, 126.3, 127.6, 127.7, 127.8, 128.36, 128.38, 130.5, 131.0, 131.1, 131.2, 131.3, 131.6, 133.6, 133.8, 134.0; MALDI-TOF ($m/z$): 750.5 Da + 752.5 Da.

2-cyano-6,11-bistri(iso-butyl)sily lethynyl tetracene (2.15)

In a flame dried, nitrogen purged 250 mL round bottom flask, 1.03 g of 2-bromo-6,11-bistri(iso-butyl)sily lethynyl tetracene (1.37 mmol) was dissolved in 40 mL of dry DMF. Oxygen was removed from solution by a steady stream of nitrogen over a period of 1 hour. 0.64 g of Zn(CN)$_2$ (5.48 mmol) and 0.16 g of Pd(PPh$_3$)$_4$ (0.14 mmol) were added to the flask and the solution bubbled with nitrogen an additional 15 minutes. The solution was heated to 90 °C for 40 hours. The reaction was then cooled to room temperature and 160 mL of water was added to the flask. The red precipitate was separated by filtration and then dissolved with DCM. The DCM solution was dried with MgSO$_4$, filtered and the solvent removed *in vacuo*. The red solid was purified by silica gel column chromatography using 1:1 hexanes:methylene chloride as eluent. The product was recrystallized by slow
evaporation of dichloroethane to yield 0.45 g (47%) of large red plates. $^1$H NMR (400 MHz, CDCl$_3$, ppm): 0.94 (t, 12 H, $J = 2.8$ Hz), 1.12-1.18 (m, 36 H), 2.11-2.17 (m, 6 H), 7.50 (d, 1 H, $J = 7.6$ Hz), 7.52-7.62 (m, 2 H), 8.07 (d, 1 H, $J = 8.4$ Hz), 8.44 (s, 1 H), 8.61-8.64 (m, 2 H), 9.30 (s, 1 H), 9.34 (s, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): 25.3, 25.4, 26.5, 103.15, 103.24, 109.4, 109.7, 110.0, 118.9, 119.38, 119.42, 124.6, 124.9, 127.0, 127.3, 127.4, 127.5, 128.3, 130.0, 130.1, 130.7, 131.4, 131.5, 133.2, 133.5, 136.4; MALDI-TOF (m/z): 697.5 Da; MP range: 150-165 °C.

2-formyl-6,11-bistri(cyclo-pentyl)silylethynyl tetracene (2.16)

In a flame dried, nitrogen purged 100 mL round bottom flask, 0.64 g of 2-cyano-6,11-bistri(cyclo-pentyl)silylethynyl tetracene (0.83 mmol) was dissolved in 50 mL of toluene and cooled to -78 °C. 1.7 mL of 1.0 M DIBAL-H in hexanes (1.7 mmol) was added drop-wise to the reaction solution and stirred at -78 °C for 2 hours. 5 mL of 10% HCl was added drop-wise to the solution at -78 °C and the solution was brought to room temperature. The solution was extracted with DCM (3x 25 mL) and the combined organic solution was washed with brine, dried with MgSO$_4$, filtered and the solvent removed in vacuo. The resultant red solid was purified by silica gel column chromatography using 1:1 hexanes:methylene chloride as eluent to yield 0.49 g (76%) as red powder. $^1$H NMR (400 MHz, CDCl$_3$, ppm): 1.27-1.35 (m, 6 H), 1.61-1.74 (m, 36 H), 2.01-2.03 (m, 12 H), 7.58-7.60 (m, 2 H), 7.90 (d, 1 H, $J = 9$ Hz), 8.05 (d, 1 H, $J = 8.6$ Hz), 8.47 (s, 1 H), 8.60-8.63 (m, 2 H), 9.29 (s, 1 H), 9.46 (s, 1 H), 10.20 (s, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): 23.8, 27.0, 29.4, 102.4, 107.3, 107.5, 118.9, 119.4, 121.3, 126.8, 127.1, 127.42, 127.45, 127.5, 129.6, 129.9, 130.6, 130.8, 131.7, 132.9, 133.2, 133.4, 134.4, 138.0, 191.8; MALDI-TOF (m/z): 773.5 Da.
2-dicyanovinyl-6,11-bistri(cyclo-pentyl)silylethynyl tetracene (2.17)

The 2-formyl-6,11-bistri(cyclo-pentyl)silylethynyl tetracene intermediate (0.49 g, 0.63 mmol) was dissolved in 150 mL of 1,2-dichloroethane and 150 mg of malononitrile (2.27 mmol) was added to the solution. Twenty drops of Hunig’s base was added to the solution and stirred for 2 hours. The solution was washed with brine (3x 50 mL), then dried with MgSO$_4$, filtered and the solvent removed in vacuo. The purple solid was purified by silica gel column chromatography using 1:1 hexanes:methylene chloride as eluent. The semi-crystalline purple solid (0.43 g, 83%) was recrystallized from 1,2-dichloroethane to yield 0.36 g (69%) as purple blocks. $^1$H NMR (400 MHz, CDCl$_3$, ppm): 1.28-1.32 (m, 6 H), 1.55-1.72 (m, 36 H), 1.99-2.01 (m, 12 H), 7.59-7.61 (m, 2 H), 7.88 (s, 1 H), 8.05 (d, 1 H, J = 9 Hz), 8.12 (d, 1 H, J = 9.4 Hz), 8.32 (s, 1 H), 8.58-8.61 (m, 2 H), 9.25 (s, 1 H), 9.37 (s, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): 23.8, 27.0, 29.3, 77.2, 81.9, 102.2, 108.1, 113.0, 119.1, 119.7, 122.0, 127.0, 127.40, 127.47, 127.56, 127.8, 129.2, 130.41, 130.46, 130.6, 130.7, 131.9, 133.1, 133.6, 138.2, 158.8; MALDI-TOF (m/z): 821.5 Da; MP range: 260-270 °C.

2.6 References

3 Molecular Organic Acceptors/Donors for Photovoltaic Devices

Over the past decade, numerous molecular donors for organic photovoltaics has been developed around a central fluorene or dithienosilole (DTS) unit [Figure 3-1]. These molecular units have intrinsic curvature which carries through to the larger donor molecule. Directionality in the solubilizing properties is built into these units and can lead to columnar or 1-D slip-stack packing motifs as seen in some small molecule examples. We sought to replace these central fluorine/DTS units with a similarly sized linear counterpart to study the effect of linearized molecular donors on OPV performance.

![Figure 3-1: Molecular structure and columnar packing arrangement, (a) general structures and substitution patterns of fluorine (left) and dithieno[2,3-b:2’,3’-d]silole (right), (b) cartoon of columnar stacking, looking down the stack and from the side, (c) curved molecule that exhibits columnar stacking.](image)

A variety of acene based linear units are described in the literature, though we restricted our focus to aromatic chromophores with terminal thiophene units. The attachment of additional moieties at the thiophene C2 position will be roughly in the
center of the short axis of the acene unit. Anthrathiophene and benzo[1,2-b:4,5-b']dithiophene were chosen as the basis for the molecular donors described here, where additional molecular units are attached at the carbon adjacent to the thiophene sulfur [Figure 3-2].

The extension of the aromatic framework by placement of aromatic groups around the central unit allows for extended π-conjugation. In effect, the substitution decreases the optical gap in the materials and extends the available π-surface available for networking in aggregates. The curvature of the central unit has been attributed to the ability of aggregated molecules to pack closely and for adjacent stacks of molecules to interdigitate, facilitating charge transport and increasing defect tolerance. An example of a molecule with this central curvature is shown in Figure 3-1, c.

![Figure 3-2: General structures and substitution patterns of anthra[2,3-b]thiophene (left) and benzo[1,2-b:4,5-b']dithiophene (right)](image)

Described below are several molecules incorporating the linear central units anthrathiophene (TA) and benzodithiophene (BDT). If increased curvature leads to closer plane to plane distances between molecules and therefore increased photovoltaic response, it should be expected that these linearized molecules should demonstrate decreased photovoltaic response compared to their bent analogues. It is interesting to
note that despite the linear geometry of BDT, a large series of high performance semiconductors have been synthesized\(^8\) with photovoltaic performance up to 10.2% power conversion efficiency in combination with fullerene acceptors.\(^9\) In regards to the small molecule benzodithiophene based donor molecules discussed here, we were able to study the difference between molecules with one and two central solubilizing units, shown as R in Figure 3-2.

### 3.1 2-(6'-Dicyanovinylbenzothiadiazole)-5,10-bistri(iso-butyl)silylethynyl anthra[2,3-b]thiophene

Work by the Burn group at the University of Queensland\(^{10-13}\) has shown that simple small organic molecules containing dicyanovinylene substituted benzothiadiazole (BT-DCV) units are potentially high performance n-type semiconductors. The BT-DCV group is likely the driving force for the n-type behavior due to the electron deficient nature of the group. These materials have strong intermolecular interactions in the solid state, form beneficial film morphology and provide efficient charge carrier transport,\(^{11}\) with power conversion efficiencies of 0.73% and above with P3HT as the donor material.\(^{10}\)

Synthesis of the acene derivative was straightforward, and proceeded through five synthetic steps [Figure 3-3]. The quinone was synthesized by an aldol condensation between 1,4-dihydroxynaphthalene and 2-iodo-thiophene-4,5-dialdehyde which was synthesized by reaction between thiophene-2,3-dialdehyde, molecular iodine and bis(trifluoroacetoxy) iodobenzene as an oxidant. The quinone was subsequently functionalized by ethynylation and deoxygenation to yield the iodo-anthrathiophene (3.3). The stannane was synthesized by reaction with n-butyl lithium, followed by
tributyltin chloride and used directly in a Stille coupling with 3-bromo-6-formyl benzothiadiazole. A Knoevenagel reaction between the resultant aldehyde and malononitrile resulted in the final compound (3.4). It was not possible to grow x-ray quality crystals of 3.4 and, as such, comparison of crystal structures of the literature molecule and 3.4 was not possible.

**Figure 3-3:** Synthetic route to TIBS-TA-BT-DCV, (i.) I₂, BTI (ii.) EtOH/THF, NaOH (iii.) 1. lithium tri(iso-butyl)silyl acetylide, 2. SnCl₂, HCl (iv.) 1. n-BuLi, 2. Bu₃SnCl, 3. Pd(PPh₃)₄, Br-BTD-CHO, 4. malononitrile, Hunig’s base

Measurements of UV-vis absorption were taken from solid films and solution in dichloromethane. Solution measurements were obtained in the Anthony lab and show a long wavelength cutoff around 720 nm [**Figure 3-4, a**]. Solid film analysis was conducted at Princeton University using the Loo group’s instrumentation. The long wavelength cutoff for thin film measurements was extended to 760 nm, showing a small bathochromic shift of UV-vis absorption by around 0.09 eV for thin films of 3.4 [**Figure 3-4, c**]. This extension
of the absorption profile in the solid state is indicative of aggregate formation, leading to orbital mixing between adjacent molecules in the thin film.

Figure 3-4: UV-vis and electrochemical properties of TIBS-TA-BT-DCV, (a) UV-visible spectrum of TIBS-TA-BT-DCV (3.4) in methylene chloride, (b) cyclic voltammetry of 3.4 with 0.1 M Bu₄NPF₆ electrolyte support in methylene chloride, (c) thin film UV-visible spectra of 3.4 (−) and 3.4 + P3HT mixture (−) (courtesy of Anna Hiszpinski from the Loo group at Princeton University)

It was possible to estimate the HOMO and LUMO energies of 3.4 by cyclic voltammetry [Figure 3-4, b].\(^\text{14}\) A reversible reduction at an average potential of -0.83 V corresponds to LUMO energy of -3.76 eV. A reversible oxidation at average potential of 0.90 V corresponds to HOMO energy of -5.49 eV which was close to the value, -5.59 eV, measured and calculated by photoelectron spectroscopy in air (PESA) on an AC-2E instrument by the Loo group at Princeton University. From these values, a maximum $V_{OC}$
of 0.64 V is calculated which compares well with experimental results collected at Princeton University showing a device $V_{OC}$ average of 0.54 V.

I travelled to Princeton University to learn about device fabrication methods from the Loo group, where Anna Hiszpantski demonstrated the fabrication method and allowed me to practice with compound 3.4. First, an indium tin oxide (ITO) coated glass slide was cleaned and a photoresist was applied. On exposure of UV radiation with a mask covering a strip of ITO down the middle of the slide. The plate was dipped in a developer and exposed photoresist and the ITO beneath it was removed with hydrochloric acid. The remaining patterned photoresist was dissolved and the plate was cleaned, dried and treated with ozone. Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) was next spin coated onto the slide and annealed, followed by a mixture of 3.4 and P3HT (1:1 w/w) with annealing. The annealing is intended to improve molecular ordering and film crystallinity. Aluminum top electrodes were evaporated onto the surface of the plate using a mask that gives six identical 0.18 cm$^2$ devices per slide.

Using a probe station with a computer controlled potentiostat and a AM 1.5G solar simulator, J-V curves were measured for 12 devices on 2 plates. Calculations done by the computer on each individual curve yielded the short-circuit current density ($J_{SC}$), open-circuit voltage ($V_{OC}$), fill factor (FF), series resistance ($R_S$), shunt resistance ($R_P$) and power conversion efficiency (PCE). Short circuit current density (0.12 mA/cm$^2$) and fill factor (0.15) were both quite low, suggesting significant barriers to charge formation and charge transport in addition to high $R_S$ and low $R_P$. It was observed from the data that the series resistance was quite high (~7000 $\Omega$), where ideally it would be minimal, and the shunt
resistance was lower than it should be ideally. Due to low $J_{SC}$ and FF, the power conversion efficiency was likewise very low at a maximum of 0.03%.

3.2 Electrophilic aromatic substitution of benzo[1,2-b:4,5-b’]dithiophene

Benzo[1,2-b:4,5-b’]dithiophene (BDT) is used extensively as a subunit in high performance organic semiconductor molecules, both small molecules and polymers, for OPV applications.\textsuperscript{8,15} BDT moieties are commonly functionalized at the 4 and 8 positions for solubility or control of packing effects. Conventional methods for incorporating these substituents proceed through BDT quinone,\textsuperscript{16} though this route imposes some limitations to the groups that can be incorporated into the BDT unit and prohibits the possibility of incorporating a single substituent at position 4 [Figure 3-5].

![Figure 3-5: Structure and numbering scheme of benzo[1,2-b:4,5-b’]dithiophene](image)

**Figure 3-5:** Structure and numbering scheme of benzo[1,2-b:4,5-b’]dithiophene

**Figure 3-6:** Synthesis of 4-nitro benzo[1,2-b:4,5-b’]dithiophene, i.) TMSA, PdCl$_2$(PPh$_3$)$_2$, Cul, Et$_3$N, ii.) 1. t-BuLi, 2. sulfur, 3. EtOH, iii.) Cu(NO$_3$)$_2$ 3H$_2$O, Ac$_2$O, 80°C, iv.) TBAF
We have devised a simple method to introduce substituents at the 4 and 8 position of BDT via direct electrophilic aromatic substitution, involving a range of different substituents. To achieve regiospecificity, it was necessary to protect the 2 and 6 positions of the BDT molecule with trialkysilyl groups. The alkylsilyl groups were incorporated by design during the synthesis of the BDT molecule by chemoselective Sonogashira coupling between 1,4-dibromo-2,5-diiodobenzene (3.5)\textsuperscript{17} and a trialkysilyl acetylene, followed by nucleophilic sulfur annulation to yield 2,6-bis(trimethylsilyl) benzo[1,2-b:4,5-b']dithiophene (TMS-BDT, 3.7) [Figure 3-6 and Figure 3-7, a].\textsuperscript{18}

**Figure 3-7:** TMS-BDT and NO\textsubscript{2}-BDT crystal structure diagrams, (a) Crystal structure of TMS-BDT, (b) crystal structure of NO\textsubscript{2}-BDT, (c) crystal packing diagram of NO\textsubscript{2}-BDT showing the network of close contacts (red dashed lines), d.) image of NO\textsubscript{2}-BDT and P3HT film
The first attempted electrophilic aromatic substitution of BDT was through nitration, with the intention of making further synthetic changes to introduce new functionalities. Nitration of TMS-BDT was achieved under Menke conditions by use of cupric nitrate in acetic anhydride at 80 °C. The nitrated BDT was isolated in good yields and the silyl groups could then be removed by reaction with tetrabutylammonium fluoride in methylene chloride to yield 4-nitro benzo[1,2-b:4,5-b']dithiophene (NO$_2$-BDT, 3.9) [Figure 3-6]. NO$_2$-BDT was recrystallized from ethanol and benzene to yield yellow needles that were analyzed by x-ray crystallography [Figure 3-7 b].

![Cyclic voltammetry of NO$_2$-BDT with 0.1 M Bu$_4$NPF$_6$ electrolyte support in methylene chloride](image)

**Figure 3-8**: Cyclic voltammetry of NO$_2$-BDT with 0.1 M Bu$_4$NPF$_6$ electrolyte support in methylene chloride

The crystal packing of this molecule is quite interesting and displays some of the characteristics desired for subsequent target molecules [Figure 3-7, c]. Inspection of the crystal structure of NO$_2$-BDT shows 1-D columnar π-stacking with adjacent stacks having numerous close contacts by a variety of atoms between the molecules. In addition to carbon-carbon close contacts within π-stacks, a cluster of close contacts is observed
between a sulfur atom and another sulfur atom, one of the nitro oxygens and a carbon
atom.

Cyclic voltammetry was measured for nitro-benzodithiophene leading to an estimated
LUMO of -3.37 eV [Figure 3-8]. The HOMO of the molecule could not be measured by
CV however, because it lies outside the window of the instrument. The measured LUMO
energy of the material aligns well for use as an acceptor versus P3HT and was used to
fabricate bulk heterojunction devices. Despite having the desirable close contact network
and a favorable LUMO energy, devices suffered from poor device characteristics, likely
stemming from phase separation between NO$_2$-BDT and P3HT [Figure 3-7, d].

**Figure 3-9:** Synthesis of bistri(iso-propyl)silyl benzo[1,2-b:4,5-b’]dithiophene and subsequent
electrophilic aromatic substitution reactions, i.) TMSA, PdCl$_2$(PPh$_3$)$_2$, Cul, Et$_3$N, ii.) 1. s-BuLi, 2.
sulfur, 3. EtOH, iii.) CHCl$_3$, NBS (1.1 eq), iv.) CHCl$_3$, NBS (2.2 eq), v.) CHCl$_3$, ACN, NIS, TFA, vi.)
CHCl$_3$, ACN, NIS, TFA, vii.) AcCl, AlCl$_3$
To introduce more readily exchanged halogen atoms, electrophilic aromatic substitution with benzodithiophene and electrophilic sources of halogens was examined. Trimethylsilyl (TMS) groups were suitable for the nitration conditions used, but it was necessary to use tri(iso-propyl)silyl (TIPS) groups for all other substitution conditions. This is due to desilylation of the TMS groups during halogenation. TIPS-BDT (3.11) was synthesized by an analogous method to TMS-BDT via Sonogashira between 1,4-dibromo-2,5-diiodo benzene (3.5) and TIPS acetylene followed by nucleophilic sulfur annulation [Figure 3-9].

In addition to the concerns of desilylation reactions under halogenation conditions, the steric bulk of the TIPS group helps contribute to regioselectivity of the electrophilic aromatic substitution reactions, as observed between bromination and iodination reactions [Figure 3-9]. The mono-bromination with N-bromosuccinimide was largely selective for the 4 position of BDT (3.12), though there was a significant fraction of the product that was brominated at the 3 position of BDT (marked by asterisks), ~15% as observed by GC-MS. The percentage of product that was brominated at position 3 could be influenced by solvent and temperature, but could not be reduced below 12-15%. In the case of di-bromination, a complex mixture of brominated isomers was collected with 4,8-dibromo-BDT (3.13) as the major product, ~80% as observed by GC-MS, as well as 3,8-dibromo-BDT (15%) and 3,7-dibromo-BDT (5%).

In contrast, the iodination reaction with N-iodosuccinimide (NIS) and catalytic trifluoroacetic acid (TFA)^20 was much more selective for the 4 position with nearly 100% selectivity in 1:1 chloroform:acetonitrile at 80 °C (3.14). This increase in selectivity is likely
due to the large increase in the size of iodine over bromine atoms, and was consistent for both mono- and di-iodination reactions between NIS and BDT [Figure 3-9]. If, however, the reaction was conducted in neat CHCl₃, ~5% iodination at the 3 position of BDT was observed by GC-MS. This suggests that use of larger, bulkier alkylsilyl groups could improve the selectivity of the bromination reactions, but this would come at the cost of solubility and increased price of starting materials.

The isomers obtained by halogenation reactions were inseparable without further reaction. It was only possible to separate the isomers by chromatography after subsequent cross-coupling reactions. This was less of an issue with iodo derivatives since isomeric mixtures could be suppressed, but mono-iodination products did contain about 5% unreacted TIPS-BDT and 5% 4,8-diiodo-BDT (3.15), both of which could be separated after further reaction. In the case of di-iodination of BDT, no unreacted BDT, mono-iodo product (3.14) or isomers were observed. The 4,8-diiodo-BDT (3.15) could be purified by chromatography on silica gel using hexanes as eluent and recrystallized from hexanes [Figure 3-10, a].

**Figure 3-10:** Crystal structure diagrams of diiodo-TIPS-BDT and acetyl-TIPS-BDT, (a) Crystal structure of 4,8-diiodo benzo[1,2-b:4,5-b′]dithiophene showing disorder, (b) crystal structure of 4-acetyl benzo[1,2-b:4,5-b′]dithiophene showing disorder
Friedel-Crafts acylation was possible by reaction of TIPS-BDT with acetyl chloride and aluminum chloride in methylene chloride [**Figure 3-9**]. The product was purified by silica gel chromatography using 1:1 hexanes:methylene chloride as eluent to yield 4-acetyl TIPS-BDT (3.16) as the major product, which was recrystallized from hexanes to acquire the structure [**Figure 3-10, b**]. GC-MS analysis shows the minor products to be desilylated BDT and acetylated, desilylated BDT. The order of addition of reagents did not have any effect on the yield or ratio of products from the reaction, though it may be possible to reduce the formation of byproducts by judicious choice of solvent and reagents.

### 3.3 Mono-substituted BDT based acceptors

Beginning from mono-halogenated TIPS-BDT, we could exchange the halogen atom for a 3,5-di(2-ethylhexyloxy) benzene (DEHOB) solubilizing substituent via Suzuki coupling [**Figure 3-11**]. The 3,5-di(2-ethylhexoxy) benzene pinacolato borane (DEHOB-Bpin, 3.18) was synthesized from 3,5-dimethoxy bromobenzene by demethylation, alkylation with 2-ethylhexyl bromide and finally Suzuki-Miyaura coupling to exchange the bromide for the pinacolato boron group to achieve the DEHOB-Bpin. This molecule was then used for Suzuki coupling with iodo-TIPS-BDT to achieve the DEHOB substituted TIPS-BDT (3.19). The tri(iso-propyl)silyl groups were removed from DEHOB-TIPS-BDT by reaction with tetrabutylammonium fluoride to yield the key desilylated BDT intermediate (DEHOB-BDT, 3.20).

DEHOB-BDT could be used in the synthesis of a variety of molecules as a substitution for various similar fluorene or similar groups often employed in organic semiconductor materials. In future examinations of the mono-substituted BDT unit may also employ a
wider variety of solubilizing units because of the wide variety of potential substitution reactions available for aryl halogens. Only the DEHOB derivative of the unit is described here and further derivatization for incorporation in larger molecules is described.

**Figure 3-11:** Synthesis of key intermediate DEHOB-BDT, i.) 1. BBr₃, 2. K₂CO₃, 2-ethylhexyl bromide, ii.) (Bpin)₂, KOAc, PdCl₂(PPh₃)₂, iii.) Pd₂dba₃, PPh₃, K₂CO₃, iv.) TBAF

**Figure 3-12:** Synthesis of mono-substituted benzodithiophene based acceptor molecule (DEHOB-BDT-BT-ID), i.) 1. n-BuLi, 2. Me₃SnCl, 3. Br-BT-CHO, Pd₂dba₃, PPh₃, ii.) 1,3-indanedione, Hunig’s base

DEHOB-BDT was lithiated using n-butyl lithium, then quenched with trimethyltin chloride solution yielding a stannane which was employed in a Stille coupling reaction
with 3-bromo-6-formyl benzothiadiazole (Br-BT-CHO) [Figure 3-12]. This aryl aldehyde (3.21) was then used in a Knoevenagel reaction with to synthesize the acceptor molecule, DEHOB-BDT-BT-ID (3.22). From $^1$H-NMR data, it was observed that two very similar and inseparable regioisomers were formed from the substitution on the benzodithiophene moiety. Due to the reduction in symmetry of the molecule by mono-substitution on the central ring, there is a difference between substitution at the 2 or 6 position of the BDT unit.

**Figure 3-13:** UV-vis and electrochemical properties of DEHOB-BDT-BT-ID, (a) Normalized UV-visible spectrum of DEHOB-BDT-BT-ID, (b) Cyclic voltammogram (black solid trace) and differential pulse voltammogram (dashed red trace) in THF solution with 0.1 M Bu$_4$NPF$_6$ electrolyte support.

The UV-visible spectrum of DEHOB-BDT-BT-ID (3.22) [Figure 3-13, a] shows a broad, featureless absorption profile. The absorption cutoff is ~625 nm in the visible region, which corresponds to absorption of a larger portion of the solar spectrum as compared to PC$_{60}$BM, which has an absorption cutoff of ~450 nm.$^{22}$ From voltammetry [Figure 3-13, b], two reversible reductions and one reversible oxidation are observed for 3.22. The oxidation appears irreversible from the cyclic voltammogram, but appears reversible from
the differential pulse voltammogram. This could be a result of sluggish kinetics for the oxidation of the molecule, leading to smoothing of the CV but not in the pulsed DPV method. HOMO and LUMO energies were estimated by comparison against the ferrocene/ferrocnium (Fc/Fc⁺) oxidation pair by internal standard, and found to be -5.72 eV and -3.72 eV, respectively, by calculation.¹⁴ These energies should provide sufficient energy offsets for exciton dissociation in BHJ active layers when mixed with P3HT (HOMO = -4.7 eV and LUMO = -2.8 eV).²²⁻²³ From these energy values, a $V_{OC}$ potential of 0.68 eV was calculated for OPV devices of 3.22 and P3HT.

![Figure 3-14: BHJ OPV device characteristics of P3HT donor and DEHOB-BDT-BT-ID acceptor with 1:1 and 1:2 ratios as cast and annealed, (a) J-V curves, (b) $V_{OC}$ (black data) and $J_{SC}$ (blue data), and (c) $PCE_{MAX}$ (black data) and FF (blue data). All data from Loo group at Princeton University](image)

From OPV data of devices fabricated with DEHOB-BDT-BT-ID acceptor and P3HT donor [Figure 3-14], the calculated $V_{OC}$ and measured $V_{OC}$ (~0.65 V) values are observed to be in rather close agreement. Fill factors for devices were quite low (0.38 average) because of high series resistance ($R_S$) and low shunt ($R_P$) resistance, observed by the slopes at the X-axis and Y-axis, respectively. In addition to these device issues, the $J_{SC}$ was also low (2.50 mA/cm² average) which may be a result of poor film morphology and unfavorable transfer
kinetics within the bulk heterojunction. These poor device characteristics lead to an overall low $\text{PCE}_{\text{MAX}}$ of 0.61 % on average.

The device performance was still much improved compared to the previous similar anthrathiophene derivative, however. It is difficult to determine why this is the case, but it may be due to the steric hindrance around the anthrathiophene unit as compared to the mono-substituted BDT unit. The lack of the second solubilizing unit in the BDT case introduces the possibility for close contacts between adjacent molecules at the electron rich region of the molecule. This may seem trivial, but increased $\pi$-contact often improves charge transport.

### 3.4 Large BDT based molecular donors

A class of small-molecule organic semiconductor donor molecules with a bent molecular geometry that has been developed for BHJ OPV device applications.\(^7, 24-25\) These molecules have a central DTS unit with variety of multicomponent aromatic substituents. The use of DTS is what lends the bent geometry to these molecules and the high performance of these materials has been attributed to this bending of the molecule.\(^7\)

What is particularly interesting about these materials is the crystal packing, due to molecules exhibiting inter-stack contacts, the nature and extent of which depend on the aryl substituents employed.\(^24\) This interaction between stacks is potentially advantageous for transmission of charge carriers, leading to passage of charges around defects and reduction of charge trapping in devices. The strength of intermolecular contacts has also been to some degree attributed to the degree of bend in the molecules and examined by atom substitution in the position occupied by silicon in DTS, whereby increasing the size
of this atom, more bend is induced in the molecule and closer plane to plane distances are observed.\textsuperscript{7}

![Structures of the linearized molecular donors, DG1 and DG2, and a literature comparison molecule, T1](image)

**Figure 3-15**: Structures of the linearized molecular donors, DG1 and DG2, and a literature comparison molecule, T1

We can now incorporate DEHOB-BDT into these molecular systems to study the effect of linearizing a bent molecule. If bending of these molecules is beneficial, linearizing the molecule should decrease the performance of devices when comparing the bent and linear molecules. To carry the analogy further, we can also study the effect of symmetrical substitution of solubilizing groups around the center of these larger molecules by also synthesizing the 4,8-diaryl benzodithiophene unit. By increasing the steric bulk on the center of the molecule, we should be able to disrupt π-stacking interactions in this region of the molecule, which should also disrupt the 1-D or columnar stacking motifs observed in some desymmetrized molecules,\textsuperscript{3} thus hindering OPV device performance characteristics. These two linearized molecules were synthesized and device performance characteristics compared to a literature molecule (T1) [Figure 3-15].\textsuperscript{26}
The symmetrically substituted benzodithiophene unit was synthesized by way of functionalization of benzo[1,2-b:4,5-b’]bithiophene 4,8-quinone (BDT-Qn, 3.23) [Figure 3-16]. The synthesis of BDT-Qn is well known and simple, and multi-gram quantities can be prepared. The 2 and 6 positions of the thiophenes in BDT-Qn must also be protected to facilitate clean reactions with aryl lithium reagents. The pKa of these carbons are lower than those of aryl protons and without protection, proton exchange readily occurs leading to significantly messier reactions and low yields. With protection of the thiophene units, addition of the aryl lithium followed by deoxygenation by SnCl$_2$ gives the diaryl TMS protected BDT (3.25) in good yields. The trimethylsilyl groups were then removed by reaction with tetrabutylammonium fluoride to obtain 4,8-bis{3,5-di(2-ethylhexyloxy)benzene} benzo[1,2-b:4,5-b’]dithiophene (bDEB-BDT, 3.26).

The fluoro-benzothiadiazole bithiophene aryl unit employed in the large molecular donors was synthesized by literature methods. Crystal structure analysis of this unit shows many intermolecular π-π contacts with various heteroatom close contacts additionally [Figure 3-17, c]. This suggests that these units may contribute significantly π-stacking in aggregates, and to explore these interactions further, a smaller derivative
molecule incorporating this unit was synthesized [Figure 3-18]. This synthesis proceeds via a Heck coupling between ethyl acrylate and 3-bromo-4-fluoro-6-(5’-hexyl-2,2’-bithiophene) benzothiadiazole to achieve ethyl 3-acrylo-4-fluoro-6-(5’-hexyl-2,2’-bithiophene) benzothiadiazole (EA-FBT-bTh, 3.27).

![Synthesis diagram](image)

**Figure 3-17**: Crystal structure diagrams of FBT-bTh based molecules, (a) Br-FBT-bTh and (b) EA-FBT-bTh, and crystal packing diagrams of (c) Br-FBT-bTh and (d) EA-FBT-bTh showing close contacts (red dashed lines).

![Synthesis diagram](image)

**Figure 3-18**: Synthesis of Ethyl 3-acrylo-4-fluoro-6-(5’-hexyl-2,2’-bithiophene) benzothiadiazole from 3-bromo-6-(5’-hexyl-2,2’-bithiophene) benzothiadiazole. Ethyl acrylate, Pd<sub>3</sub>dba<sub>3</sub>, PPh<sub>3</sub>, 110 °C

Crystallographic analysis of EA-FBT-bTh demonstrates a similar π-contact network [Figure 3-17, d] to that seen in the parent compound. This may be indicative of the advantageous intermolecular interactions of molecules incorporating FBT-bTh unit being largely driven by these end-groups. The central unit is essentially directing these
interactions, where the bent central units direct the packing of adjacent molecules, and

the curved nature of the DTS unit directs the aryl substituents away from the central 2-
ethylhexane solubilizing groups, allowing room for the 1-D stacking.

**Figure 3-19:** Synthesis of large mono- and di-substituted BDT based molecular donors DG1 and DG2, i.) 1. n-BuLi, THF, -78 °C, 2. Me3SnCl, 3. Br-FBT-bTh, Pd2dba3, PPh3

The synthesis of the large molecular donors was straightforward from the mono- and di-substituted BDT cores previously synthesized [Figure 3-19]. The BDT unit was lithiated twice with n-butyl lithium at -78 °C in tetrahydrofuran, after which it was quenched with trimethyldim chloride to form the distannane. This distannane was then purified by chromatography on neutralized silica gel and used in Stille couplings with Br-FBT-bTh to synthesize the product donor molecules. These molecules were purified by a three-step process of filtration through a thick pad of silica using 1:1 hexanes:chloroform as eluent, followed by size exclusion chromatography with SX-10 Bio-beads and toluene eluent.
Finally, the molecules were purified by silica gel chromatography using 1:2 hexanes:chloroform for DG1 and 2:1 hexanes:chloroform for DG2.

We expected that straightening the core of this molecule should result in restriction of the packing arrangements between adjacent molecules, disrupting the 1-D packing motif seen for T1, but potentially resulting in a motif akin to columnar stacking. The addition of a second solubilizing unit to the core BDT unit should further disrupt the packing efficiency and allow only for end-group overlap. Unfortunately, it was not possible to grow x-ray quality crystals of these materials despite many conditions and methods being investigated, making it impossible to confirm these hypotheses. We are limited to physical properties and device characteristics to investigate the effect of straightening the core and symmetrizing the solubilizing units.

Figure 3.20: UV-vis and electrochemical properties of DG1 and DG2, (a) UV-vis spectra of DG1 (solution in DCM [black] and film [black dot dash]) and DG2 (solution in DCM [red] and film [red dot dash]), (b) differential pulse voltammograms of DG1 (solid line) and DG2 (dashed line).

The solution UV-visible spectra of DG1 and DG2 show very similar profiles [Figure 3-20, a], as expected from near-identical chromophores. There is a broad, featureless
absorption profile with a long wavelength cutoff of around 620 nm, which is a decrease in the cutoff wavelength energy of about 0.15 eV compared to T1. The film UV-vis shows significant aggregation effects with the stokes shift of about 50 nm between the solution and film spectra and the J-aggregate peak around 650 nm in the film spectra, which is a hypsochromic shift of ~50 nm compared to T1. From the DPV data [Figure 3-20], the LUMO (-3.26 eV) was calculated from the reduction potential of -0.94 V when compared against the Fc/Fc+ redox couple. The oxidation potentials were not clearly defined, as seen in the DPV figure, and the HOMO (-5.26 eV) was instead estimated from the energy of the optical gap (2.0 eV). These HOMO and LUMO values are close to the values found for T1 (-5.12 eV and -3.34 eV, respectively).

Devices were fabricated at KAUST using 2:3 donor:PC71BM blends that were dissolved in chlorobenzene with a concentration of 35 mg/mL. Different concentrations 1,8-diiodooctane additive (DIO) was added into solution and the solution stirred at 80 °C overnight. The hot solution was spin-cast on PEDOT:PSS substrates and the fresh films were thermally annealed at 75 °C for 10 min before transferred into evaporation for Ca/Al deposition. These devices were then tested for OPV response [Figure 3-21].

Of the two BDT cores, DG1 performed the best with the same DIO concentration as optimized T1 (0.4% DIO), while DG2 showed no photovoltaic response in any of the devices. DG1 OPV devices demonstrated lower short circuit current density, fill factor and overall power conversion efficiency (J_sc = 5.98 mA/cm^2, FF = 56.9%, PCE = 2.9%) compared to T1 (J_sc = 13.98 mA/cm^2, V_oc = 0.81 V, FF = 65.5%, PCE = 7.4%) although open circuit voltage was slightly larger for DG1 (V_oc = 0.86 V) compared to T1 (0.806 V). In the case of
DG2, the lack of photovoltaic behavior likely stems from the significant disruption of π-stacking due to the steric crowding around the center of the molecule, leading to an inability to transport charge in the BHJ films. The case of DG1 is less clear as to the effects on photovoltaic characteristics. The hypsochromic shift in the light absorption profile for DG1 compared to T1 would suggest that a slight decrease in J_{SC} between devices fabricated from these materials is inevitable, though a decrease in J_{SC} of nearly 60% for DG1 on this basis alone is unlikely, implying that issues of film microstructure and charge transport efficiency play a significant role in the observed differences.

**Figure 3-21:** Devices characteristics of molecular donors with [6,6]-phenyl-C71-butyric acid methyl ester (PC71BM) acceptor and various percentages of 1,8-diiodooctane (DIO), (a) J-V curves of DG1 with various concentrations of DIO, (b) device characteristic comparisons of T1 (blue), DG1 (orange) with various concentrations of DIO and DG2 (green). Data from the Amassian group at KAUST

These results may be a confirmation of the theory put forward by Bazan *et al* that curvature of the molecular donors contributes to the degree of intermolecular interactions. The more linear nature of the core of DG1 would decrease the degree of interdigitation of the molecules in extended networks in aggregate, reducing charge
transport efficiency and decreasing defect tolerance. Considering the high performance of other BDT small molecules found in the literature,\textsuperscript{15} the end groups employed here maybe not be appropriate for OPV materials based on BDT.

3.5 Conclusions

The substitution of linear core units for bent units in molecular structures has shown to have deleterious effects on the device performance of the materials. Materials with symmetrical solubilizing motifs, e.g. anthrathiophene and disubstituted benzodithiophene, are affected more so than the desymmetrized BDT unit. This effect is likely due to the steric crowding around the central unit, which is disrupting to the ability of molecules to π-stack in aggregates.

With the advent of direct electrophilic aromatic substitution of BDT, we are now able to incorporate a desymmetrized BDT unit into organic semiconductors. This allows for directional placement of solubilizing units and the ability to compare this unit to the wide variety of directionally solubilized units available in the literature and investigate the properties of these materials. Our initial application of this approach, e.g. modeling the T1 molecule, demonstrates the potential for this method. Straightening the core of this molecule was expected to depress the OPV performance as compared to T1, which was observed. This experiment, compared to the symmetrical donor molecule DG2, demonstrated that changing the substitution pattern around the center of the molecule has increasingly negative effects on OPV performance, stemming from increasing steric bulk and restriction of intermolecular interactions.
3.6 Experimental

Bulk solvents were purchased from Fisher Scientific or Pharmco-Aaper. Reagents and starting materials were purchased from one of the major chemical suppliers, i.e. Sigma Aldrich, Oakwood Chemical, Fisher Scientific etc. Thiophene-4,5-dicarboxaldehyde and 3-bromo-6-formylbenzothiadiazole were prepared previously by other Anthony lab members. Trimethylsilyl acetylene and tri(iso-propyl)silyl acetylene were purchased from GFS chemicals.

NMR spectra were collected using either a Varian Unity 400 MHz. Chemical shifts are reported as compared to solvent reference values. GC-MS spectra were collected using an Agilent 6890N GC with 5973 MSD or a Bruker SCION SQ GC-MS. MALDI-TOF mass spectra were collected with a Bruker Daltonics MALDI-TOF MS in negative ion mode and EI mass spectrometry was collected with a JEOL JMS-700T mass spectrometer by the University of Kentucky Mass Spectrometry facility. Cyclic voltammetry and differential pulse voltammetry were collect using a BAS-CV 50W potentiostat using 0.1 M Bu₄NPF₆ in DCM for FRED (3.4) or tetrahydrofuran as electrolyte solution and ferrocene as an internal standard.

2-iodo-thiophene-4,5-dicarboxaldehyde (3.1)

In a 250 mL round bottom flask, 7.22 g (51.5 mmol) of thiophene-2,3-carboxaldehyde was dissolved in 125 mL of chloroform. 9.16 g (36.1 mmol) of I₂ and 15.5 g of BTI (36.1 mmol) were dissolved in the reaction solution. The reaction mixture was stirred at room temperature for 16 hours. Excess iodine was quenched by addition of Na₂S₂O₃ in portions until removal of the red/purple iodine color was observed. The organic and aqueous
layers were separated and the organic layer was dried with MgSO₄, filtered and the solvent removed in vacuo. The solid was purified by silica gel column chromatography using 4:1 hexanes:ethyl acetate as eluent. The tan solid was recrystallized from hexanes/ethyl acetate to give 6.40 g (46%) of 3.1 as tan needles. ¹H NMR (400 MHz, CDCl₃): 7.76 ppm (d, 1 H, J = 1.2 Hz), 10.22 ppm (d, 1 H, 1.2 Hz), 10.31 ppm (d, 1 H, J = 1.2 Hz); ¹³C NMR (100 MHz, CDCl₃): 86.34 ppm, 124.89 ppm, 138.72 ppm, 139.37 ppm, 144.31 ppm, 152.62 ppm, 181.12 ppm, 183.11 ppm; GC-MS (m/z): M = 266 Da.

2-iodo-5,10-thienotetracene quinone (3.2)

In a 50 mL round bottom flask, 0.56 g of 2-iodo-thiophene-4,5-dicarboxaldehyde (2.09 mmol) and 0.34 g of 1,4-dihydroxynaphthalene (2.09 mmol) were dissolved in 2 mL of hot ethanol. Five drops of 15% NaOH was added to the solution with vigorous stirring. A precipitate evolved from the solution. The reaction mixture was filtered and washed successively with methanol, acetone and finally ether. The resultant yellow powder was dried under ambient conditions. 0.55 g (67%) of a yellow powder was collected and used without further purification. MALDI-TOF (m/z): M = 390 Da.

2-iodo-5,10-bistri(iso-butyl)silylethynyl thienotetracene (3.3)

In a flame dried 250 mL round bottom flask, 2.30 g of tri(iso-butyl)silyl acetylene (10.3 mmol) was dissolved in 20 mL of n-heptane and cooled to 0 °C. 3.99 mL of 2.5 M n-BuLi (9.98 mmol) was added drop-wise to the reaction solution and stirred for 30 minutes. The reaction solution was diluted with 70 mL of n-heptane. 1.00 g of 2-iodo-5,10-thienotetracene quinone (2.56 mmol) was added to the reaction solution, followed by 10
mL of dry THF. The reaction mixture was brought to room temperature and stirred for 16 hours. The reaction was quenched with water, extracted with DCM and the combined organic solution washed with water. The organic solution was dried with MgSO$_4$, filtered and the solvent evaporated *in vacuo*. The resultant yellow oil was run through a thick pad of silica using hexanes as eluent to remove excess acetylene, followed by methylene chloride to collect the ethynylated thienotetracene diol as a yellow oil.

The ethynylated thienotetracene diol was dissolved in 30 mL of THF and 30 mL of 10% HCl. 2.60 g SnCl$_2$·2H$_2$O (11.5 mmol) was added to the reaction mixture along with 20 mL of THF and stirred for 1 hour. The solution was extracted with hexanes (3x 50 mL) and the combined organic solution was washed with water (3x 50 mL). The organic solution was dried with MgSO$_4$, filtered and the solvent removed *in vacuo*. The resultant orange solid was run through a thick pad of silica using hexanes as eluent. 1.54 g (74%) of orange solid was collected after removal of the solvent. $^1$H NMR (400 MHz, CDCl$_3$, ppm): 0.88 (d, 12 H, J = 6.8 Hz), 1.11 (d, 36 H, J = 6.8 Hz), 2.09 (m, 6 H), 7.55-7.58 (m, 2 H), 7.64 (s, 1 H), 8.56-8.60 (m, 2 H), 8.98 (s, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): 25.4, 26.52, 26.55, 83.8, 103.5, 103.6, 108.2, 108.6, 117.8, 118.7, 119.1, 119.9, 126.6, 126.8, 127.3, 129.7, 130.0, 132.4, 132.6, 133.6, 140.8, 143.5; MALDI-TOF (m/z): M = 804.32 Da.

2,3’-(6’-dicyanovinylbenzothiadiazole)-5,10-bistri(iso-buty1)silylethynyl anthrathiophene (3.4)

In a flame dried 100 mL round bottom flask, 0.5 g of 2-iodo-5,10-bistri(iso-buty1)silylethynyl thienotetracene (0.62 mmol) was dissolved in 20 mL of n-heptane. To
this solution was added 0.4 mL of 2.5 M n-BuLi (1.0 mmol) at room temperature and the reaction stirred for 1 hour. 0.32 mL of tributylstannous chloride was added to the solution and the reaction mixture stirred another 1 hour. The reaction mixture was extracted with hexanes (3x 50 mL) and the combined organic solution was dried with MgSO₄, filtered and the solvent removed in vacuo. The resultant orange oil was used in the next step without purification.

In a dried round bottom flask, the previous stannane was dissolved in 20 mL of toluene. 0.15 g of 3-bromo-6-carboxaldehydebenzothiadiazole (0.62 mmol) was added to the solution. The reaction solution was degassed with a steady stream of nitrogen for 30 minutes. 0.11 g of Pd(PPh₃)₄ (0.093 mmol) was added and the reaction was degassed an additional 10 minutes. The reaction mixture was heated to 90 °C for 16 hours. After cooling to room temperature, the solution was washed with water (3x 50 mL) and the organic solution was dried using MgSO₄, filtered and the solvent removed in vacuo. The product was purified by silica gel column chromatography using 1:1 hexanes: DCM as eluent.

The formyl benzothiadiazole thienotetracene intermediate was dissolved in 20 mL of dichloroethane. 0.09 g of malononitrile (1 mmol) and 12 drops of triethylamine were added to the reaction mixture and stirred for 1 hour. The solvent was removed in vacuo and the product was purified by silica gel column chromatography using 1:1 hexanes:methylene chloride. The resulting green solid was recrystallized from dichloroethane to yield 86 mg (15% over 3 steps) of dark green crystals. ¹H NMR (400 MHz, CDCl₃, ppm): 1.02-1.07 (m, 12 H), 1.26-1.31 (m, 36 H), 2.18-2.27 (m, 6 H), 7.21-7.22
(d, 1 H, J = 7.4 Hz), 7.32 (s, 1 H), 7.60-7.62 (m, 2 H), 7.95 (d, 1 H, J = 7.4 Hz), 8.22 (s, 1 H), 8.32 (s, 1 H), 8.37 (br s, 2 H), 8.46 (s, 1 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), ppm): \(^{13}\)C NMR (100 MHz, CDCl\(_3\), ppm): ; MALDI-TOF (m/z): M = 888 Da.

**1,4-dibromo-2,5-diiodobenzene (3.5)**

In a 500 mL round bottom flask, 19.5 g of p-dibromobenzene (82.7 mmol) and 250 mL of concentrated sulfuric acid were combined and heated to 50 °C. 46.2 g of I\(_2\) (182 mmol) was added in 5 g portions over a 2-hour period. The reaction mixture was brought to 135 °C for 96 hours with occasional scraping of sublimed iodine back into the reaction. The reaction mixture was cooled to room temperature and poured into 300 mL ice water. The aqueous suspension was cooled to 0 °C and extracted with chloroform (2x 50 mL). The large disk of product in the flask was dissolved in chloroform and the organic solutions combined. Excess iodine was quenched by addition of 15% potassium hydroxide until the purple/pink iodine color was removed. The organic solution was separated from the aqueous solution and then dried with MgSO\(_4\), filtered and the solvent removed in vacuo. The pink solid was washed with hexanes to remove residual iodine, and the resultant white solid was recrystallized from chloroform yielding 21.4 g (53%) of 3.5 as white needles. \(^1\)H NMR (400 MHz, CDCl\(_3\), ppm): 8.02 (s, 2 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), ppm): 101.3, 129.2, 142.3; GC-MS (m/z): M = 485 Da.

**1,4-dibromo-2,5-bistrimethylsilylethynyl benzene (3.6)**

A 250 mL round bottom flask was charged with 120 mL of benzene and oxygen was removed from solution with a steady stream of nitrogen. To the flask was added 10.0 g of
1,4-dibromo-2,5-diiodobenzene (20.5 mmol), 0.10 g of trans-dichlorobistriphenylphosphine palladium (0.14 mmol), 0.020 g of copper(I) iodide (0.11 mmol) and 4.23 g of trimethylsilyl acetylene (43.1 mmol). Lastly, 10.0 mL of triethylamine (71.7 mmol) was added dropwise to the reaction mixture. The reaction mixture was stirred at room temperature for 24 hours, after which the solvent was removed in vacuo. The crude residue was purified by filtration on a thick pad of silica using hexanes as eluent. The collected pale yellow powder was further purified by rinsing with 20 mL methanol to remove the yellow byproduct. After drying at ambient conditions, 3.6 was collected as 6.21 g colorless powder (70 %). \(^1\)H NMR (400 MHz, CDCl\(_3\)): 0.27 ppm (s, 18 H), 7.66 ppm (s, 2 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): -0.1 ppm, 101.6 ppm, 103.2 ppm, 123.9 ppm, 126.6 ppm, 136.6 ppm; GC-MS (m/z): M = 426 Da + 428 Da + 430 Da.

2,6-bistrimethylsilyl benzo[1,2-b:4,5-b’]dithiophene (3.7)\(^{18}\)

In a nitrogen flushed, flame-dried 500 mL round bottom flask, 4.56 g of 1,4-dibromo-2,5-bistrimethylsilylethynyl benzene (10.7 mmol) was dissolved in 150 mL of dry diethyl ether and cooled to -78 °C. To the solution was added 25.0 mL of 1.7 M t-BuLi (42.5 mmol) dropwise over a period of 30 minutes. After addition, the reaction was warmed to room temperature and 0.68 g of sulfur powder (21.2 mmol) was added to the flask in one portion. The solution was then heated to reflux for 30 minutes, then cooled back to room temperature. 60 mL of absolute ethanol was added slowly and the reaction mixture was stirred at room temperature for 24 hours. The product was extracted with chloroform (3x 50 mL) and the organic solution was washed with water (3x 50 mL) and 50 mL of brine, dried with MgSO\(_4\) and the solvent removed in vacuo. The crude product was purified by
filtration through a thick pad of silica using hexanes as eluent to yield 2.63 g colorless powder (73%). $^1$H NMR (400 MHz, CDCl$_3$): 0.40 ppm (s, 18 H), 7.46 ppm (s, 2 H), 8.26 ppm (s, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): -0.5 ppm, 116.0 ppm, 129.8 ppm, 139.2 ppm, 140.8 ppm, 143.7 ppm; GC-MS (m/z): M = 334 Da.

**4-nitro-2,6-bistrimethylsilyl benzo[1,2-b:4,5-b’]dithiophene (3.8)**

A 100 mL round bottom flask was charged with 1.00 g of 2,6-bistrimethylsilyl benzo[1,2-b:4,5-b’]dithiophene (2.99 mmol) and 20 mL of acetic anhydride. The solution was heated to 75 °C and a solution of 0.79 g of cupric nitrate trihydrate (3.27 mmol) in 40 mL of acetic anhydride was added dropwise. The resultant green solution was heated at 75 °C for 2 hours, then cooled to room temperature. After cooling, the reaction mixture was poured into 200 mL of ice water and stirred for 1 hour. The precipitate was collected by filtration and purified by filtration through a thick pad of silica using 1:1 hexanes:methylene chloride as eluent. **3.8** was collected as 1.00 g of orange powder (88%). $^1$H NMR (400 MHz, CDCl$_3$): 0.45 ppm (s, 9 H), 0.46 ppm (s, 9 H), 7.51 ppm (s, 1 H), 8.42 ppm (s, 1 H), 8.53 ppm (d, 1 H, J = 0.8 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$): -0.24 ppm, -0.21 ppm, 123.3 ppm, 125.1 ppm, 129.6 ppm, 129.8 ppm, 134.0 ppm, 139.0 ppm, 140.3 ppm, 143.4 ppm, 147.9 ppm, 152.2 ppm; GC-MS (m/z): M = 379 Da.

**4-nitro benzo[1,2-b:4,5-b’]dithiophene (3.9)**

In a 50 mL round bottom flask, 0.50 g of 7-nitro-2,5-bistrimethylsilyl-trans-benzodithiophene (1.32 mmol) was dissolved in 15 mL of DCM. With vigorous stirring, 2.90 mL of 1.0 M tetrabutylammonium fluoride (2.90 mmol) was added to the flask and
stirred for 15 minutes. The reaction mixture was poured onto a thick pad of silica and run through the silica using 2:1 hexanes DCM as eluent. Recrystallization of 3.9 from ethanol/benzene yielded 50 mg (16%) product as yellow needles. $^1$H NMR (400 MHz, DMSO-$d_6$, ppm): 7.67 (d, 1 H, $J = 6.0$ Hz), 7.96 (d, 1 H, $J = 5.6$ Hz), 8.32-8.33 (m, 2 H), 9.05 (s, 1 H); $^{13}$C NMR (100 MHz, DMSO-$d_6$, ppm): 127.9, 129.1, 131.4, 137.1, 137.7, 140.1, 141.5, 144.0, 144.66; GC-MS ($m/z$): $M = 235$ Da; MP Range: 234-238 °C.

1,4-dibromo-2,5-bistri(iso-propyl)silylethynyl benzene (3.10)

A 500 mL round bottom flask was charged with 200 mL of benzene and oxygen was removed from solution with a steady stream on nitrogen. To the flask was added 10.0 g of 1,4-dibromo-2,5-diiodo benzene (20.5 mmol), 0.15 g of trans-dichlorobistriphenylphosphine palladium (0.21 mmol), 0.05 g of copper(I) iodide (0.26 mmol) and 9.7 mL of tri(iso-propyl)silyl acetylene (43.2 mmol). Lastly, 10.0 mL of triethylamine (71.7 mmol) was added dropwise to the reaction mixture. The reaction mixture was stirred at room temperature for 24 hours, after which the solvent was removed in vacuo. The crude residue was purified by filtration on a thick pad of silica using hexanes as eluent. The collected pale yellow powder was further purified by rinsing with 20 mL methanol to remove the yellow byproduct. After drying at ambient conditions, 3.10 was collected as 11.44 g of colorless powder (93%). $^1$H NMR (400 MHz, CDCl$_3$): 1.13 ppm (s, 42 H), 7.67 ppm (s, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): 11.3 ppm, 18.6 ppm, 99.8 ppm, 103.3 ppm, 123.7 ppm, 126.7 ppm, 136.5 ppm; GC-MS ($m/z$): $M = 594$ Da + 596 Da + 598 Da.
2,6-bistri(iso-propyl)silyl benzo[1,2-b:4,5-b’]dithiophene (3.11)

In a nitrogen flushed, flame-dried 500 mL round bottom flask, 10.0 g of 1,4-dibromo-2,5-bis tri(iso-propyl)silylethynyl benzene (16.8 mmol) was dissolved in 150 mL of dry tetrahydrofuran and cooled to -78 °C. To the solution was added 47.9 mL of 1.4 M s-BuLi in cyclohexane (67.0 mmol) dropwise over a period of 30 minutes. After addition, the reaction mixture was warmed to room temperature and 1.08 g of sulfur powder (33.7 mmol) was added to the flask in one portion. The solution mixture was then heated to 80 °C for 1 hour, then cooled back to room temperature. 80 mL of absolute ethanol was added slowly and the reaction mixture was stirred at room temperature for 24 hours. 25 mL of saturated ammonium chloride was added to the reaction and a white precipitate formed. The suspension was poured over 300 mL of water and stirred for 15 minutes. The resultant slurry was filtered and washed with 100 mL of methanol. The filtrate was dried in a vacuum oven at 40 °C for 4 hours to yield 6.11 g of a colorless powder (72%) which was used without further purification. \(^1\)H NMR (400 MHz, CDCl\(_3\)): 1.17 ppm (d, 36 H, J = 7.4 Hz), 1.43 ppm (spt, 6 H, J = 7.4 Hz), 7.51 ppm (s, 2 H), 8.30 ppm (s, 2 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): 11.8 ppm, 18.6 ppm, 115.5 ppm, 131.4 ppm, 138.3 ppm, 138.9 ppm, 140.6 ppm; GC-MS (m/z): M = 502 Da.

4-bromo-2,6-bistri(iso-propyl)silyl benzo[1,2-b:4,5-b’]dithiophene (3.12)

A 250 mL round bottom flask, equipped with a magnetic stir bar, was charged with 5.0 g of 2,6-bistri(iso-propyl)silyl benzo[1,2-b:4,5-b’]dithiophene (9.94 mmol), 1.95 g of N-bromosuccinimide (10.9 mmol) and 100 mL of chloroform. The resultant suspension was
heated to reflux for 16 hours, after which the reaction mixture was cooled to room
temperature and the solvent removed in vacuo. The crude residue was purified by
filtration through a thick pad of silica using hexanes as eluent to yield 5.59 g of a colorless
powder as a mix of 3.12 with 5% of 3.11 and 15% 3-bromo-2,6-bistri(iso-propyl)silyl
benzo[1,2-b:4,5-b’]dithiophene. \(^1\)H NMR (400 MHz, CDCl\(_3\)): 1.16-1.19 ppm (m, 18 H), 1.41-
1.48 ppm (m, 6 H), 7.60 ppm (s, 1 H), 7.62 ppm (s, 1 H), 8.24 (s, 1 H); \(^1\)C NMR (100 MHz,
CDCl\(_3\)): 13.7 ppm, 20.5 ppm, 108.8 ppm, 114.8 ppm, 131.1 ppm, 132.0 ppm, 132.3 ppm,
138.1 ppm, 139.1 ppm, 139.2 ppm, 140.1 ppm, 141.2 ppm; GC-MS (m/z): M = 580 Da.

**4,8-dibromo-2,6-bistri(iso-propyl)silyl benzo[1,2-b:4,5-b’]dithiophene (3.13)**

A 50 mL round bottom flask equipped with a magnetic stir bar, was charged with 0.5
g of 2,6-bistri(iso-propyl)silyl benzo[1,2-b:4,5-b’]dithiophene (1.00 mmol), 0.37 g of N-
bromosuccinimide (2.10 mmol) and 10 mL of chloroform. The resultant suspension was
heated to 80 °C for 16 hours, after which the reaction mixture was cooled to room
temperature and the solvent removed in vacuo. The crude residue was purified by
filtration through a thick pad of silica using hexanes as eluent to yield 0.62 g colorless
powder as a mix of 3.13 with 15% 4,7-dibromo-2,6-bistri(iso-propyl)silyl benzo[1,2-b:4,5-
b’]dithiophene and 5% 3,7-dibromo-2,6-bistri(iso-propyl)silyl benzo[1,2-b:4,5-
b’]dithiophene. \(^1\)H NMR (400 MHz, CDCl\(_3\)): 1.16 ppm (d, 36 H, J = 7.4 Hz), 1.39-1.48 ppm
(m, 6 H), 7.69 ppm (s, 2 H); \(^1\)C NMR (100 MHz, CDCl\(_3\)): 11.8 ppm, 18.6 ppm, 108.0 ppm,
132.0 ppm, 138.2 ppm, 140.9 ppm, 142.7 ppm; GC-MS (m/z): M = 658 Da.
**4-iodo-2,6-bistri(iso-propyl)silyl benzo[1,2-b:4,5-b']dithiophene (3.14)**

A 50 mL round bottom flask equipped with a magnetic stir bar, was charged with 0.5 g of 2,6-bistri(iso-propyl)silyl benzo[1,2-b:4,5-b']dithiophene (1.0 mmol), 0.25 g of N-iodosuccinimide (1.1 mmol), 5 mL of chloroform and 5 mL of acetonitrile. 10 drops of trifluoroacetic acid was added to the flask and the resultant suspension was heated to 80 °C for 16 hours, after which the reaction mixture was cooled to room temperature and the solvent removed *in vacuo*. The crude residue was purified by filtration through a thick pad of silica using hexanes as eluent to yield 0.57 g of a colorless powder as 3.14 with 15% of 3.11 and 5% 4,8-diiodo-2,6-bistri(iso-propyl)silyl benzo[1,2-b:4,5-b']dithiophene. \(^1\)H NMR (400 MHz, CDCl\(_3\)): 1.15-1.18 (m, 36 H), 1.40-1.47 (m, 6 H), 7.53 ppm (s, 1 H), 7.76 ppm (s, 1 H), 8.24 (s, 1 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): 11.78 ppm, 11.80 ppm, 18.6 ppm, 81.6 ppm, 115.8 ppm, 132.8 ppm, 134.8 ppm, 137.6 ppm, 138.7 ppm, 139.4 ppm, 139.6 ppm, 141.6 ppm, 147.7 ppm; GC-MS (m/z): \(M = 627\) Da.

**4,8-diiodo-2,5-bistri(iso-propyl)silyl benzo[1,2-b:4,5-b']dithiophene (3.15)**

A 50 mL round bottom flask equipped with a magnetic stir bar was charged with 0.5 g of 2,6-bistri(iso-propyl)silyl benzo[1,2-b:4,5-b']dithiophene (1.0 mmol), 0.50 g of N-bromosuccinimide (2.2 mmol), 5 mL of chloroform and 5 mL of acetonitrile. 10 drops of trifluoroacetic acid was added to the flask and the resultant suspension was heated to 80 °C for 16 hours, after which the reaction mixture was cooled to room temperature and the solvent removed *in vacuo*. The crude residue was purified by filtration through a thick pad of silica using hexanes as eluent to yield 0.75 g of 3.15 (99%) as a pale, yellow powder.
The compound was further purified by recrystallization from hexanes to yield 0.39 g of pale, yellow prisms (51%). $^1$H NMR (400 MHz, CDCl$_3$): 1.17 ppm (d, 36 H, J = 7.4 Hz), 1.43 ppm (spt, 6 H, J = 7.4 Hz), 7.78 ppm (s, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): 11.8 ppm, 18.6 ppm, 82.3 ppm, 136.3 ppm, 139.9 ppm, 140.3 ppm, 146.2 ppm; GC-MS (m/z): M = 754 Da; MP Range: 285-292 °C.

**4-acetyl-2,6-bistri(iso-propyl)silyl benzo[1,2-b:4,5-b′]dithiophene (3.16)**

A 100 mL round bottom flask was charged with 0.50 g of 2,6-bistri(iso-propyl)silyl benzo[1,2-b:4,5-b′]dithiophene (1.0 mmol), 20 mL of methylene chloride and 0.08 mL of acetyl chloride (1.1 mmol) at 0 °C. To this solution was added 0.15 g of anhydrous aluminum chloride (1.1 mmol) and the reaction mixture was stirred for 1 hour at room temperature. The dark solution was then poured into 100 mL ice water and stirred for 1 hour. The layers were separated and the aqueous solution extracted once with 20 mL methylene chloride. The combined organic layer was dried with MgSO$_4$, filtered and the solvent removed *in vacuo*. The resultant residue was purified by filtration through a thick pad of silica using 1:1 hexanes:methylene chloride as eluent to yield **3.16** as 0.39 g of a yellow solid (71%). This material was then recrystallized from hexanes to yield 0.25 g of yellow needles (45%). $^1$H NMR (400 MHz, CDCl$_3$): 1.17 ppm (t, 36 H, J = 7 Hz), 1.46 ppm (spt, 6 H, 7.4 Hz), 2.98 ppm (s, 3H), 7.56 ppm (s, 1 H), 8.06 ppm (s, 1 H), 8.50 ppm (s, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$): 11.78 ppm, 11.82 ppm, 18.6 ppm, 18.7 ppm, 32.1 ppm, 120.7 ppm, 125.5 ppm, 130.8 ppm, 131.0 ppm, 137.6 ppm, 139.4 ppm, 141.6 ppm, 142.0 ppm, 142.1 ppm, 142.3 ppm, 198.1 ppm; GC-MS (m/z): M = 544 Da; MP Range: 185-190 °C.
3,5-di(2-ethylhexoxy) bromobenzene (3.17)\(^\text{21}\)

A flame dried, nitrogen purged 1 L round bottom flask was charged with 25.0 g of 3,5-dimethoxy bromobenzene (115 mmol) and 100 mL methylene chloride. The solution was cooled to -78 °C and 230 mL of 1.0 M boron tribromide in methylene chloride (230 mmol) was added dropwise over 2 hours. The reaction mixture was warmed to room temperature and stirred for 72 hours. The reaction mixture was then cooled back to -78 °C and 200 mL of methanol was added dropwise to the flask and the reaction mixture was kept at -78 °C for 1 hour. The solution was slowly warmed to room temperature and stirred for 16 hours, after which the solution was washed with brine (3x 100 mL) and the brine solution extracted once with 100 mL ethyl acetate. The combined organic phases were dried with MgSO\(_4\), filtered and the solvent removed \textit{in vacuo}. The crude material was filtered through a thick pad of silica using 2:1 hexanes:ethyl acetate as eluent and the concentrated material was dried in a vacuum oven at 80 °C for several hours. The resultant thick oily solid was used directly.

A 500 mL round bottom flask was charged with the 3,5-dihydroxy bromobenzene intermediate and 200 mL of acetonitrile. To this solution was added 77.84 g of 1-bromo-2-ethyl hexane (403 mmol) and 79.47 g of potassium carbonate (575 mmol) and the reaction mixture was heated to 80 °C for 96 hours. The reaction mixture was then cooled to room temperature, diluted with 200 mL of water and extracted with methylene chloride (3x 100 mL). The combined organic phase was dried with MgSO\(_4\), filtered and the solvent removed \textit{in vacuo}. The crude product was filtered through a thick pad of silica using 4:1 hexanes:ethyl acetate as eluent, then unreacted 1-bromo-2-ethyl hexane was
distilled off the product via kugelrohr at 50 °C. The resultant orange oil was then further purified by column chromatography using 4:1 hexanes:ethyl acetate as eluent to yield 44.09 g (92%) of 3.17 as a clear, yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): 0.90-0.94 ppm (m, 12 H), 1.29-1.54 ppm (m, 16 H), 1.70 ppm (spt, 2 H, J = 6.1 Hz), 3.80 ppm (dd, 4 H, J$_1$ = 5.7 Hz, J$_2$ = 1.4 Hz), 6.38 ppm (t, 1 H, J = 2.2 Hz), 6.65 ppm (d, 2 H, J = 2.2 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$): 11.1 ppm, 14.1 ppm, 23.0 ppm, 23.8 ppm, 29.0 ppm, 30.5 ppm, 39.3 ppm, 70.7 ppm, 100.5 ppm, 110.1 ppm, 122.8 ppm, 161.0 ppm; GC-MS (m/z): M = 412 Da.

3,5-di(2-ethylhexyloxy)benzene pinacolatoboron (3.18)

A 500 mL round bottom flask was charged with 10.0 g of 3,5-di(2-ethylhexyloxy) bromobenzene (24.2 mmol) and 200 mL of acetonitrile, then oxygen was removed from solution by a stream of nitrogen gas. To the oxygen free solution was added 9.21 g of bispinacolato diboron (36.3 mmol), 7.13 g of potassium acetate (72.6 mmol) and 0.85 g of trans-dichloro bistriphenylphosphine palladium (1.21 mmol). The solution was then heated to 80 °C for 16 hours. After cooling to room temperature, the solution was diluted with 200 mL water and extracted with methylene chloride (3x 100 mL). The combined organic phases were dried with MgSO$_4$, filtered and the solvent removed in vacuo. The crude product was twice filtered through a thick pad of silica using 1:1 hexanes:methylene chloride as eluent to yield 8.78 g of a yellow oil (78%). $^1$H NMR (400 MHz, CDCl$_3$): 0.87-0.94 ppm (m, 12 H), 1.27-1.54 (m, 28 H), 1.66-1.72 (m, 2 H), 3.85 ppm (dd, 4 H, J$_1$ = 5.5 Hz, J$_2$ = 2 Hz), 6.57 ppm (s, 1 H), 6.93 ppm (d, 2 H, J = 2 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$): 11.1 ppm, 14.0 ppm, 23.0 ppm, 24.0 ppm, 24.8 ppm, 29.1 ppm, 30.6 ppm, 39.6 ppm, 70.5 ppm, 83.7 ppm, 105.1 ppm, 112.4 ppm, 134.7 ppm, 160.2 ppm; GC-MS (m/z): M = 460 Da.
4-{3,5-di(2-ethylhexyloxy) benzene} 2,6-bistri(iso-propyl)silyl benzo[1,2-b:4,5-b’]dithiophene (3.19)

A 75 mL pressure tube was charged with 2.8 g of 4-iodo-2,6-bistri(iso-propyl)silyl benzo[1,2-b:4,5-b’]dithiophene (4.5 mmol) and 30 mL of tetrahydrofuran. Oxygen was removed from solution using a stream of nitrogen while 10 mL of 2 M potassium carbonate in water solution was added to the tube. To the biphasic solution was added 4.1 g of 3,5-di(2-ethylhexoxy) benzene pinacolatoboron (9.0 mmol), 0.21 g of tris(dibenzylideneacetone)dipalladium(0) (0.23 mmol) and 0.24 g of triphenylphosphine (0.90 mmol). The tube was sealed and heated to 100 °C for 48 hours. The reaction mixture was then cooled to room temperature and extracted with methylene chloride (3x 50 mL). The combined organics were washed with water (3x 50 mL), dried with MgSO₄, and the solvent removed in vacuo. The crude product was purified by filtration through a thick pad of silica using 9:1 hexanes:methylene chloride as eluent, followed by silica gel flash chromatography using 3% methylene chloride in hexanes as eluent. 3.19 was collected as 2.11 g of a colorless oil (56%) which slowly solidifies on standing. ¹H NMR (400 MHz, CDCl₃): 0.87-0.98 ppm (m, 12 H), 1.14 ppm (dd, 36 H, J₁ = 7.4 Hz, J₂ = 2.7 Hz), 1.27-1.57 ppm (m, 22 H), 1.77 ppm (spt, 2 H, J = 6.2 Hz), 3.89 ppm (d, 4 H, J = 5.5 Hz), 6.59 ppm (m, 1 H), 6.94 ppm (m, 2 H), 7.56 ppm (s, 1 H), 7.59 ppm (s, 1 H), 8.28 ppm (s, 1 H); ¹³C NMR (100 MHz, CDCl₃): 11.1 ppm, 11.8 ppm, 14.1 ppm, 18.6 ppm, 23.1 ppm, 23.9 ppm, 29.0 ppm, 30.6 ppm, 39.4 ppm, 70.6 ppm, 102.1 ppm, 107.5 ppm, 114.8 ppm, 130.1 ppm, 131.3 ppm, 131.9 ppm, 136.8 ppm, 137.7 ppm, 138.6 ppm, 139.2 ppm, 140.4 ppm, 141.2 ppm, 141.5 ppm, 160.7 ppm; GC-MS (m/z): M = 835 Da.
4-{3,5-di(2-ethylhexyloxy) benzene} benzo[1,2-b:4,5-b']dithiophene (3.20)

A 100 mL round bottom flask was charged with 3.0 g of 4-{3,5-di(2-ethylhexyloxy) benzene} 2,6-bistri(iso-propyl)silyl benzo[1,2-b:4,5-b']dithiophene (3.59 mmol) and 50 mL of methylene chloride. To this solution was added 9.0 mL of 1.0 M tetrabutylammonium fluoride in tetrahydrofuran (9.0 mmol) and the reaction was stirred at room temperature for 16 hours under a blanket of nitrogen. The solution was filtered directly through a thick pad of silica using methylene chloride as eluent. 3.20 was collected as 2.0 g of a viscous, colorless oil (quantitative). $^1$H NMR (400 MHz, CDCl$_3$): 0.94-1.01 ppm (m, 12 H), 1.33-1.63 ppm (m, 16 H), 1.80 ppm (spt, 2 H, J = 5.5 Hz), 3.94 ppm (d, 4 H, J = 5.5 Hz), 6.66 ppm (t, 1 H, J = 2.3 Hz), 6.89 ppm (d, 2 H, J = 2.3 Hz), 7.42 ppm (d, 1 H, J = 5.9 Hz), 7.44 ppm (s, 2 H), 7.47 ppm (d, 1 H, J = 5.9 Hz), 8.30 ppm (s, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$): 11.1 ppm, 14.1 ppm, 23.0 ppm, 23.9 ppm, 29.1 ppm, 30.5 ppm, 39.4 ppm, 70.7 ppm, 101.6 ppm, 107.6 ppm, 116.0 ppm, 122.7 ppm, 123.3 ppm, 126.5 ppm, 127.5 ppm, 131.4 ppm, 135.6 ppm, 137.0 ppm, 137.6 ppm, 137.8 ppm, 140.8 ppm, 160.8 ppm; GC-MS (m/z): M = 522 Da.

6'-formyl-2,3' -benzothiadiazole-4-{3,5-di(2-ethylhexyloxy) benzene} benzo[1,2-b:4,5-b']dithiophene (3.21)

A flame-dried, nitrogen flushed 150 mL pressure tube was charged with 0.70 g of 4-{3,5-di(2-ethylhexyloxy) benzene} benzo[1,2-b:4,5-b']dithiophene (1.34 mmol) and 50 mL of tetrahydrofuran. The solution was cooled to -78 °C and 0.50 mL of 2.5 M n-butyl lithium in hexane (1.34 mmol) was added dropwise. The reaction was stirred at -78 °C for 30 minutes, followed by the addition of 1.6 mL of 1.0 M trimethyltin chloride in
tetrahydrofuran. The reaction mixture was kept at -78 °C for 30 minutes, then warmed to room temperature for 1 hour. Oxygen was removed from solution by a stream of nitrogen. To the solution was added 0.65 g of 3-bromo-6-formyl benzothiadiazole (2.68 mmol), 0.03 g of tris(dibenzylideneacetone)palladium(0) (0.027 mmol) and 0.06 g of triphenylphosphine (0.21 mmol). The nitrogen needle was then removed, the tube sealed and the reaction mixture heated to 80 °C for 64 hours. The reaction was cooled to room temperature and extracted with methylene chloride (3x 20 mL), washed with water (3x 50 mL), the organic solution dried with MgSO₄ and the solvent removed in vacuo. The residue was purified by filtration through a thick pad of silica using 1:1 hexanes:methylene chloride as eluent. 3.21 was collected as 0.40 g of a dark red, oily solid (43%). ¹H NMR (400 MHz, CDCl₃, ppm): 0.88-0.99 (m, 12 H), 1.31-1.60 (m, 16 H), 1.75-1.84 (m, 2 H), 3.94-3.98 (m, 4 H), 6.65 (t, 0.33 H, J = 2.2 Hz), 6.68 (t, 0.67 H, 2.2 Hz), 6.83 (d, 0.67 H, J = 2.0 Hz), 6.93 (d, 1.64 H, J = 2.3 Hz), 7.28 (d, 0.67 H, J = 5.5 Hz), 7.33 (d, 0.33 H, J = 5.5 Hz), 7.43 (d, 0.33 H, J = 5.5 Hz), 7.47 (d, 0.67 H, J = 5.5 Hz), 7.79 (d, 1 H, J = 7.4 Hz), 8.00 (m, 1.67 H), 8.07 (s, 0.33 H), 8.61 (s, 0.33 H), 8.71 (s, 0.67 H), 10.54 (s, 0.33 H), 10.57 (s, 0.67); ¹³C NMR (100 MHz, CDCl₃, ppm): 11.2, 14.1, 23.1, 24.0, 29.2, 30.6, 39.4, 70.8, 101.6, 102.0, 107.6, 107.7, 114.7, 115.4, 117.3, 112.8, 123.4, 125.4, 125.6, 125.78, 125.82, 127.2, 127.9, 128.1, 129.0, 131.0, 131.7, 131.8, 132.4, 132.6, 132.7, 136.0, 136.8, 137.0, 137.5, 137.9, 138.0, 138.1, 138.3, 138.7, 138.9, 140.21, 140.26, 152.23, 152.31, 153.5, 160.9, 188.06, 188.10; MALDI-TOF (m/z): M = 684.2 Da.
DEHOB-BDT-BT-ID (3.22)

A 50 mL round bottom flask was charged with 0.22 g of 6'-formyl-2,3’-benzothiadiazole-7-{3,5-di(2-ethylhexoxy) benzene} benzo[1,2-b:4,5-b’]dithiophene (0.32 mmol) and 10 mL of 1,2-dichloroethane. 0.09 g of indane-1,3-dione (0.64 mmol) and 10 drops of triethylamine were added to the flask and the reaction mixture was stirred vigorously for 3 hours. The reaction mixture was then filtered through a thick pad of silica using methylene chloride as eluent to yield 3.22 as 0.26 g of a dark red solid (99%). $^1$H NMR (400 MHz, CDCl$_3$, ppm): 0.84-1.06 (m, 12 H), 1.26-1.67 (m, 16 H), 1.83-1.89 (m, 2 H), 4.03-4.07 (m, 4 H), 6.67 (t, 0.25 H, J = 2.3 Hz), 6.70 (t, 0.75 H, J = 2.3 Hz), 6.81 (d, 0.5 H, J = 2.1 Hz), 6.92 (d, 1.5 H, J = 2.1 Hz), 6.98 (d, 0.75 H, J = 5.4 Hz), 7.12 (d, 0.25 H, J = 5.4 Hz), 7.18 (d, 0.25 H, J = 5.4 Hz), 7.20 (d, 0.75 H, J = 5.4 Hz), 7.45-7.54 (m, 3 H), 7.62 (d, 0.5 H, J = 6.7 Hz), 7.73 (d, 1.5 H, J = 6.7 Hz), 8.24 (s, 0.25 H), 8.31 (s, 0.25 H), 8.34 (s, 0.75 H), 8.43 (s, 0.75 H), 9.27 (d, 1 H, J = 7.9 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): 11.3, 14.2, 22.7, 23.2, 24.0, 29.2, 30.7, 31.59, 39.5, 70.9, 101.7, 102.25, 107.6, 107.7, 115.3, 117.3, 122.69, 122.77, 123.3, 124.2, 126.2, 126.4, 126.8, 127.5, 127.9, 128.5, 129.46, 129.49, 130.65, 130.78, 132.5, 134.51, 134.63, 135.9, 136.6, 137.25, 137.34, 137.40, 137.9, 138.1, 138.4, 138.7, 139.2, 139.6, 140.13, 140.20, 142.1, 150.9, 155.41, 155.44, 160.86, 160.89, 188.54, 188.57, 188.80, 188.85; MALDI-TOF (m/z): M = 812.3 Da.

4,8-benzo[1,2-b:4,5-b’]dithiophene quinone (3.23)

In a 500 mL round bottom flask, 60 g of AgNO$_3$ (353 mmol) was dissolved in 100 mL of water. In a separate flask, 30 g of NaOH (750 mmol) was dissolved in 100 mL of water and
cooled to room temperature. The sodium hydroxide solution was added slowly to the silver nitrate solution to produce Ag$_2$O as a dark brown precipitate. The oxidation solution was cooled to 0 °C and 20.0 g of thiophene-3-carboxaldehyde was added slowly to the Ag$_2$O slurry. The reaction mixture was brought to room temperature and stirred for 1 hour. The reaction mixture was filtered and the dark brown filtrate was washed with 200 mL water. The combined aqueous solution was acidified to pH 2 using concentrated HCl. The voluminous white precipitate was filtered and washed with 200 mL water. The white solid was dried on top of an oven for 16 hours to yield 20.69 g (90%) of white powder as thiophene-3-carboxylic acid.

10.28 g of thiophene-3-carboxylic acid (80.2 mmol) was dissolved in 250 mL of methylene chloride in a 500 mL round bottom flask. This solution was cooled to 0 °C and 13.8 mL of oxalyl chloride (160.4 mmol) was added drop-wise to the solution. After addition of oxalyl chloride, the solution was stirred for 1 hour at 0 °C. 1 mL of dry dimethyl formamide was added to the solution in small portions and stirred for 2 hours at 0 °C. The solution was warmed slowly to room temperature and stirred for 16 hours. The reaction mixture was dried with MgSO$_4$, filtered and the solvent was removed \textit{in vacuo}. The resulting white solid was used in the subsequent reaction without purification.

The thiophene-3-carboxylic acid chloride intermediate was dissolved in 100 mL of methylene chloride in a 250 mL round bottom flask. Separately, 16.8 mL of diethylamine (160 mmol) was dissolved in 50 mL of methylene chloride and this solution was added drop-wise to the acid chloride solution at 0 °C. The reaction mixture was stirred at 0 °C for 1 hour, and then brought to room temperature and stirred an additional hour. The
solution was washed with water (3x 100 mL), and then dried with MgSO₄, filtered and the solvent removed in vacuo. The collected oil was purified by vacuum distillation. The N,N-diethyl thiophene-3-carboxamide distilled at an internal temperature of 76-79 °C to yield 11.87 g (80% over 2 steps) of light yellow oil. GC-MS (m/z): M = 183 Da.

In a flame dried 250 mL round bottom flask, 5.00 g of N,N-diethylthiophene-3-carboxamide (27.3 mmol) was dissolved in 100 mL of dry THF and cooled to 0 °C. 11.5 mL of 2.5 M n-BuLi (28.7 mmol) was added drop-wise to the reaction solution. The reaction mixture was brought to room temperature and stirred for 1 hour. The reaction mixture was poured into 300 mL ice water and stirred for 15 minutes. The solution was filtered and washed with 200 mL water, followed by methanol, acetone and ether. The light green solid was dried at ambient conditions for 16 hours and 1.79 g of 4,8-benzo[1,2-b:4,5-b’]dithiophene quinone (59%) was collected as light green powder. ¹H NMR (400 MHz, DMSO-d₆, ppm): 7.60 (d, 2 H, J = 5.1 Hz), 8.12 (d, 2 H, J = 5.1 Hz); ¹³C NMR (100 MHz, DMSO-d₆, ppm): 131.4, 140.8, 147.7, 149.5, 179.3; GC-MS (m/z): M = 220 Da.

2,6-bistrimethylsilyl benzo[1,2-b:4,5-b’]dithiophene 4,8-quinone (3.24)

A flame dried, nitrogen purged 500 mL round bottom flask was charged with 2.0 g of benzo[1,2-b:4,5-b’]dithiophene 4,8-quinone (9.08 mmol) and 200 mL of dry THF. To this suspension was added 19.7 g of trimethylsilyl chloride (182 mmol), followed by slow addition of 31.8 mL of lithium hexamethyldisilazide (31.8 mmol). The reaction was stirred for 36 hours at room temperature, then quenched by slow addition of 30 mL of water. The solution was diluted with an additional 200 mL of water and extracted with...
methylene chloride (3x 50 mL). The combined organic phase was dried with MgSO₄, filtered and the solvent removed in vacuo. The crude product was then purified by filtration through a thick pad of silica using 1:1 hexanes:methylene chloride as eluent to yield 2.0 g of a bright yellow, crystalline solid (60%). ¹H NMR (400 MHz, CDCl₃): 0.38 ppm (s, 18 H), 7.72 ppm (s, 2 H); ¹³C NMR (100 MHz, CDCl₃): -0.48 ppm, 132.7 ppm, 143.7 ppm, 149.0 ppm, 151.5 ppm, 174.7 ppm; GC-MS (m/z): M = 364 Da.

4,8-bis{3,5-di(2-ethylhexyloxy) benzene} 2,6-bistrimethylsilyl benzo[1,2-b:4,5-b’]dithiophene (3.25)

A flame dried, nitrogen purged 250 mL round bottom flask was charged with 3.40 g of 3,5-di(2-ethylhexyloxy) bromobenzene (8.23 mmol) and 100 mL of n-heptane and cooled to 0 ℃. 11.5 mL of 1.4 M sec-butyl lithium in cyclohexane (16.2 mmol) was added dropwise to the reaction mixture and kept at 0 ℃ for 30 minutes. The reaction mixture was brought to room temperature and 1.0 g of 2,6-bistrimethylsilyl benzo[1,2-b:4,5-b’]dithiophene 4,8-quinone (2.74 mmol) was added in one portion, 10 mL of dry THF was added and the reaction was stirred for 64 hours at room temperature. The reaction was then carefully quenched by the addition of 0.5 mL of water and the solvent removed in vacuo. The crude mixture was dissolved in 100 mL of acetonitrile and 10 mL of THF, 2.78 g of tin(II) chloride dihydrate (12.3 mmol) was added and the solution heated to 80 ℃ for 2 hours. The reaction mixture was then cooled to room temperature, diluted with 200 mL of water and extracted with methylene chloride (3x 75 mL). The combined organic solution was dried with MgSO₄, filtered and the solvent removed in vacuo. The crude product was purified by filtration through a thick pad of silica using 9:1 hexanes:methylene chloride as eluent, followed by column chromatography using 19:1
hexanes:methylene chloride to yield 1.76 g of a pale-yellow oil (64%). $^1$H NMR (400 MHz, CDCl$_3$, ppm): 0.34 (s, 18 H), 0.90-0.98 (m, 24 H), 1.28-1.55 (m, 32 H), 1.79 (m, 4 H), 3.92 (d, 8 H, J = 5.5 Hz), 6.62 (s, 2 H), 6.88 (s, 4 H), 7.53 (s, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): -0.4, 11.1, 14.1, 23.1, 23.9, 29.1, 30.6, 39.4, 70.8, 101.7, 107.8, 129.89, 129.94, 137.3, 141.2, 141.5, 143.7, 160.7; MALDI-TOF (m/z): M = 998.6 Da.

4,8-bis{3,5-di(2-ethylhexyloxy) benzene} benzo[1,2-b:4,5-b']dithiophene (3.26)

A 100 mL round bottom flask was charged with 1.50 g of 4,8-bis{3,5-di(2-ethylhexyloxy) benzene} 2,6-bistrimethylsilyl benzo[1,2-b:4,5-b']dithiophene (1.50 mmol) and 30 mL of methylene chloride. To this solution was added 4.5 mL of 1.0 M tetrabutylammonium fluoride in THF (4.50 mmol) and the solution was stirred for 16 hours under a blanket of nitrogen. The solvent was then removed in vacuo and the residue was purified by flash chromatography using 20% methylene chloride in hexanes as eluent. 3.26 was collected as 0.68 g of a pale-yellow oil (52%). $^1$H NMR (400 MHz, CDCl$_3$, ppm): 0.90-0.99 (m, 24 H), 1.29-1.58 (m, 32 H), 1.78-1.80 (m, 4 H), 3.92 (d, 8 H, J = 5.9 Hz), 6.63 (s, 2 H), 6.88 (s, 4 H), 7.42-7.47 (m, 4 H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): 11.2, 14.1, 23.1, 23.9, 29.1, 30.6, 39.4, 70.8, 101.7, 107.8, 123.1, 127.2, 130.6, 135.9, 137.9, 140.9, 160.8; EI-MS (m/z): M = 854 Da.

Ethyl 3-acrylo-4-fluoro-6-(5’-hexyl-2,2′-bithiophene) benzothiadiazole (3.27)

A 75 mL pressure tube was charged with 30 mL of toluene and oxygen was removed from solution by a stream of nitrogen. To the tube was added 0.68 g of 3-bromo-4-fluoro-6-(5’-hexyl-2,2′-bithiophene) benzothiadiazole (1.41 mmol), 0.3 mL of ethyl acrylate (2.82
mmol), 0.06 g of tris(dibenzylideneacetone)dipalladium(0) (0.071 mmol), 0.07 g of triphenylphosphine (0.28 mmol) and 0.6 mL of triethylamine (4.23 mmol). The tube was then sealed and heated to 110 °C for 96 hours. The reaction mixture was cooled to room temperature and washed with water (3x 50 mL), dried with MgSO₄ and the solvent removed in vacuo. The residue was purified by filtration through a thick pad of silica using 1:1 hexanes:methylene chloride as eluent. 3.27 was collected as 0.47 g of a dark red solid (66%). The product was recrystallized by slow evaporation from 1,2-dichloroethane to collect dark red needles. ¹H NMR (400 MHz, CDCl₃, ppm): 0.89 (t, 3 H, J = 6.3 Hz), 1.30-1.40 (m, 9 H), 1.68 (quin, 2 H, J = 7.4 Hz), 2.80 (t, 2 H, 7.6 Hz), 4.3 (q, 2 H, 7.2 Hz), 6.71 (d, 1 H, J = 3.1 Hz), 7.09 (d, 1 H, J = 3.5 Hz), 7.14 (d, 1 H, 3.9 Hz), 7.51-7.60 (m, 2 H), 8.04 (d, 1 H, J = 3.9 Hz), 8.11 (d, 1 H, J = 16.4 Hz); ¹³C NMR (100 MHz, CDCl₃, ppm): 14.1, 14.3, 22.5, 28.7, 30.2, 31.5, 60.6, 111.0, 111.1, 114.6, 114.9, 123.9, 124.1, 124.2, 124.4, 125.1, 129.0, 129.1, 130.3, 131.81, 131.85, 135.37, 135.40, 141.8, 146.9, 149.6, 153.8, 153.9, 161.3, 163.8, 167.2; ¹⁹F NMR (377 MHz, CDCl₃, ppm): -108.88 (d, 1 F, J = 11.9 Hz); El-MS (m/z): M = 500 Da; MP Range: 188-203 °C.

DG1 (3.28)

A flame-dried, nitrogen purged 100 mL round bottom flask was charged with 0.66 g of 4-\{3,5-di(2-ethylhexyloxy) benzene\} benzo[1,2-b:4,5-b′]dithiophene (1.26 mmol) and 25 mL of dry tetrahydrofuran. The solution was cooled to -78 °C, 1.3 mL of 2.5 M n-butyl lithium in hexane (3.15 mmol) was added dropwise and the reaction mixture was stirred for 30 minutes. 3.8 mL of 1.0 M trimethyltin chloride in tetrahydrofuran (3.8 mmol) was added dropwise and the reaction mixture was warmed to room temperature and stirred
for 16 hours. The solvent was then removed in vacuo and the residue filtered through a thick pad of triethylamine neutralized silica gel using 19:1 hexanes:triethylamine as eluent. The bistrimethyl stannane was collected as a colorless oil and used directly.

The bistrimethyl stannane was dissolved in 10 mL of toluene in a pressure tube and oxygen was removed from solution by a stream of nitrogen. To this solution was added 1.27 g of 3-bromo-4-fluoro-6-(6′-hexyl-2,2′-bithiophene)-benzothiadiazole (2.65 mmol), 0.06 g of tri(dibenzylidene-acetone)dipalladium(0) (0.063 mmol) and 0.07 g of triphenylphosphine (0.252 mmol). The tube was then sealed and heated to 110 °C for 96 hours. The reaction mixture was cooled to room temperature and diluted with 20 mL of toluene. The toluene solution was washed with water (3x 50 mL), dried with MgSO₄ and the solvent removed in vacuo. The residue was purified by filtration through a thick pad of silica using a ramp of solvent mixtures from 1:1 hexanes:chloroform to 1:2 hexanes:chloroform as eluent, size exclusion chromatography on S-X Bio-beads with tetrahydrofuran solvent and silica gel chromatography using 1:2 hexanes:chloroform as eluent. **DG1** was collected as 1.12 g of a dark-purple solid (67%). ¹H NMR (400 MHz, CDCl₃, ppm): 0.84-1.04 (m, 18 H), 1.21-1.69 (m, 30 H), 1.82-1.85 (m, 2 H), 2.74-2.78 (m, 4 H), 3.97 (d, 4 H, J = 5.5 Hz), 6.6 (d, 3 H, J = 9.8 Hz), 6.92 (d, 3 H, 13.3 Hz), 7.48 (d, 1 H, J = 5.1 Hz), 7.52 (d, 1 H, J = 5.1 Hz), 7.88 (m, 2 H), 8.00 (s, 1 H), 8.40 (s, 1 H), 8.47 (s, 1 H); ¹³C NMR (100 MHz, CDCl₃, ppm): 26.8, 29.3, 29.6, 37.9, 38.6, 39.4, 44.2, 44.6, 45.0, 45.20, 45.22, 46.1, 46.30, 46.33, 46.8, 54.9, 86.3, 117.6, 122.8, 124.8, 125.0, 129.3, 129.6, 137.8, 138.2, 139.4, 140.8, 143.0, 143.1, 144.4, 147.15, 147.23, 147.74, 147.8, 149.43, 149.48, 149.8.
DG2 (3.29)

A flame-dried, nitrogen purged 100 mL round bottom flask was charged with 0.68 g of 4,8-bis{3,5-di(2-ethylhexyloxy) benzene} benzo[1,2-b:4,5-b']dithiophene (0.79 mmol) and 10 mL of dry tetrahydrofuran. The solution was cooled to -78 °C, 0.7 mL of 2.5 M n-butyllithium in hexane (1.75 mmol) was added dropwise and the reaction mixture was stirred for 30 minutes. 2.0 mL of 1.0 M trimethyltin chloride in tetrahydrofuran (2.0 mmol) was added dropwise and the reaction mixture was warmed to room temperature and allowed to stir for 16 hours. The solvent was then removed in vacuo and the residue filtered through a thick pad of triethylamine neutralized silica gel using 19:1 hexanes:triethylamine as eluent. The bistrimethyl stannane was collected as a pale-yellow oil and used directly.

The bistrimethyl stannane was dissolved in 10 mL of toluene in a pressure tube and oxygen was removed from solution by a stream of nitrogen. To this solution was added 0.74 g of 3-bromo-4-fluoro-6-(6'-hexyl-2,2'-bithiophene)-benzothiadiazole (1.5 mmol), 0.03 g of tri(dibenzylideneacetone)dipalladium(0) (0.037 mmol) and 0.04 g of triphenylphosphine (0.15 mmol). The tube was then sealed and heated to 110 °C for 72 hours. The reaction was cooled to room temperature and diluted with 20 mL of chloroform. The organic solution was washed with water (3x 50 mL), dried with MgSO$_4$ and the solvent removed in vacuo. The residue was purified by filtration through a thick pad of silica using toluene as eluent, size exclusion chromatography on S-X Bio-beads with
tetrahydrofuran solvent and silica gel chromatography using 2:1 hexanes:chloroform as eluent. DG2 was collected as 0.46 g of a dark-purple solid (38%). $^1$H NMR (400 MHz, CDCl$_3$, ppm): 0.87-0.90 (m, 24 H), 0.97 (t, 12 H, J = 6.8 Hz), 1.24-1.70 (m, 42 H), 1.78-1.84 (m, 4 H), 2.74 (t, 4 H, J = 7.6 Hz), 3.97 (d, 8 H, J = 5.5 Hz), 6.63-6.66 (m, 4 H), 7.02-7.05 (m, 6 H), 7.09 (d, 2 H, J = 3.1 Hz), 7.59 (s, 1 H), 7.62 (s, 1H), 7.95 (d, 2 H, J = 3.5 Hz), 8.57 (s, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): 26.5, 29.35, 29.40, 37.9, 38.4, 39.3, 44.1, 44.4, 45.5, 45.9, 46.7, 46.8, 54.8, 86.1, 117.6, 123.1, 126.2, 126.3, 130.7, 131.1, 139.0, 139.3, 140.2, 141.5, 141.6, 141.9, 144.6, 145.7, 148.9, 149.5, 150.8, 151.7, 153.9, 155.8, 156.2, 161.7, 164.8, 168.8, 168.9, 173.8, 176.1, 176.3; MALDI-TOF (m/z): M = 1654.6 Da.

3.7 References


4 Benzo[2,3-b:5,6-b’]diindolizine Based Organic Semiconductors

Over the past several decades, acenes have been shown to be successful semiconducting materials and possess interesting photoelectronic properties. Pentacene is an archetypal example of such acene materials. The addition of various ethynyl groups to the central rings of the acene improve solubility and control solid state ordering, while the use of ethynyl groups also improves stability by reducing the tendency of the acene to form endoperoxides. Substitution of other functional groups to the periphery of the acene, either electron donating or withdrawing groups, affects the solubility and electronic properties of the acene, such as promoting n-type or p-type properties.

Acenes can be further modified by substitution of one or more fused benzene rings with heterocycles. The substitution of one or more of the benzene rings in the acene chromophore with another variety of aromatic group greatly affects the stability and electronic properties of the chromophore. A series of N-heteroacenes has been developed which employ the use of pyridine or pyrazine moieties [Figure 4-1]. This general motif is affected by the substitution of CH groups on the acene with nitrogen atoms, where these N-heteroacenes generally show deepened HOMO and LUMO energies compared to the corresponding carbocyclic acenes, leading to ambipolar or even n-type transport properties. This effect extends to the first triplet state energy in these molecules, often leading to improved singlet fission.

N-heteroarenes that incorporate the nitrogen atom at bridgehead positions of the polycyclic aromatic framework via indolizine moieties [Figure 4-1] are the focus here, as opposed to incorporating pyridine or pyrazine moieties. This motif is achieved by the
substitution of one bridgehead carbon with nitrogen and the removal of a CH group from an adjacent fused ring. Indolizine is formally aromatic and isoelectronic with naphthalene because of the nitrogen lone pair being fully incorporated into the π-electron system.

**Figure 4-1**: Structures of pyridine, pyrazine and indolizine with representative structures of pentacene analogues incorporating these simple N-heteroaromatic structures

Over the past several years, several organic chromophores that absorb and emit light in the visible spectrum have been developed that incorporate indolizine moieties. Most of these examples focus primarily on the highly fluorescent nature of the materials and applications related to this property. However, Delcamp et al demonstrated the potential use of indolizine based molecules in optoelectronic devices, i.e. dye-sensitized solar cells, demonstrating charge generation and charge transport is possible with these molecules. The indolizine moieties in this example are strong electron donors incorporated into a push-pull π-conjugated system as opposed to electron accepting units as demonstrated by azaacenes.

Our intention is to develop poly(N-heterocyclic) compounds that possess the electron rich character of indolizine and may possess properties like existing N-heteroacenes, e.g.
n-type or ambipolar semiconductor behavior. With the nitrogen placed at the bridgehead position, the non-bonding electron pair of the nitrogen should be fully incorporated into the aromatic framework. We have developed a route to synthesize N-heteroatomic aromatic compounds that have the indolizine moiety fused into the chromophore. We chose to begin with symmetric derivatives of this new architecture to simplify synthesis and facilitate control over solid state ordering.

4.1 Synthesis and Optical Properties

![Diagram of synthesis](image)

**Figure 4-2**: Synthesis of 1,4-bis-ethynyl benzo[2,3-b:5,6-b’]diindolizine, i.) 1. methyl acrylate, DABCO, 2. Ac₂O, ii.) TMEDA, KHMDS, iii.) 1. RCCLi, 2. SnCl₂. Adapted with permission from Granger, D. B.; Mei, Y.; Thorley, K. J.; Parkin, S. R.; Jurchescu, O. D.; Anthony, J. E. *Org. Lett.* 2016, 18, 6050. Copyright 2016 American Chemical Society.

Design of the benzodiindolizine chromophore incorporates many of the features present in previous acene chromophores. We incorporated the indolizine moieties into a dibenzoanthracene-like framework through a quinoidal intermediate and subsequent ethynylation to attach solubilizing groups and direct the solid-state packing [Figure 4-2]. The synthesis proceeds through methyl 2-indolizinate (4.1) via a Baylis-Hillman reaction.
between 2-formylpyridine and methyl acrylate, followed by an intramolecular annulation in acetic anhydride. The subsequent benzo[2,3-b:5,6-b’]diindolizine quinone (4.2) was obtained via an intermolecular nucleophilic annulation reaction. This quinone was then functionalized by ethynylation and aromatization to yield ethynyl substituted BDI (4.3a-g).

**Figure 4-3:** Structural and optical comparison of TIPS-BDI and two other 5-ring molecules and electrochemical properties of TIPS-BDI, (a) Structure of benzobisbenzothiophene (left), benzodiindolizine (center) and pentacene (right), (b) Ultraviolet-visible spectrum of TIPS-BDI (purple dot dashed line), TES-BBBT (orange trace) and TIPS-Pentacene (blue dashed line), (c) Cyclic voltammetry (black dashed line), Differential pulse voltammetry (blue trace) of TIPS-BDI. Adapted with permission from Granger, D. B.; Mei, Y.; Thorley, K. J.; Parkin, S. R.; Jurchescu, O. D.; Anthony, J. E. *Org. Lett.* **2016**, *18*, 6050. Copyright 2016 American Chemical Society.
Several derivatives of ethynyl BDI were prepared from the BDI quinone (4.3a-g). It was immediately apparent that the optoelectronic properties of the molecule were significantly different from those of 1,4-triethylsilylethynyl benzo[2,3-b: 5,6-b']bisbenzothiophene (TES-BBBT) [Figure 4-3, a]. The solution color of the BDI molecules was blue with strong red fluorescence instead of the expected yellow color of anthracene analogs. This result suggests an electronic energy gap like pentacene, which is demonstrated by the UV-visible spectrum of ethynyl BDI. [Figure 4-3, b]

In addition to UV-visible data, cyclic voltammetry was measured for the TIPS-BDI molecule [Figure 4-3, c]. The oxidation of the molecule appears to be irreversible from the CV, however, DPV (blue line) shows the oxidation of BDI to be quasi-reversible, while the reduction of BDI appears reversible in both cases. The first oxidation potential of TIPS-BDI overlaps with the ferrocene/ferrocenium (Fc/Fc⁺) redox pair, placing the BDI highest occupied molecular orbital (HOMO) at -4.83 eV. The reduction pair from differential pulse voltammetry was used to calculate the approximate lowest unoccupied molecular orbital (LUMO) energy of -2.63 eV compared to Fc/Fc⁺. The electrochemically measured frontier molecular orbital (FMO) energy gap is 2.20 eV which compares well to the optical gap of about 2 eV. It was necessary to measure the electrochemistry in tetrahydrofuran (THF) due to the reactivity of the BDI chromophore in chlorinated solvents because of residual acidic components of those solvents.

To better understand the optoelectronic properties of the BDI chromophore, DFT calculations were undertaken at the B3LYP/6-31G(d) level of theory after AM1 geometry minimization on the GAMESS DFT software. From the chemical structure, we see that
the molecule has only one sextet, located on the central ring, differentiating the BDU molecules from BBBT which has three sextets located at the central ring and the two peripheral benzo groups. This difference allows for a contiguous ring current across the entire BDI chromophore, which is borne out by the HOMO orbitals calculated by DFT [Figure 4-4]. The BDI chromophore is more like the pentacene chromophore in this respect, while the LUMO of BDI very closely resembles the LUMO of BBBT.

Figure 4-4: DFT calculated molecular orbitals, (a) Silylethynyl-BBT LUMO, (b) Silylethynyl-BBT HOMO, (c) Silylethynyl-BDI LUMO, (d) Silylethynyl-BDI HOMO, (e) Silylethynyl-Pentacene LUMO, (f) Silylethynyl-Pentacene HOMO. Adapted with permission from Granger, D. B.; Mei, Y.; Thorley, K. J.; Parkin, S. R.; Jurchescu, O. D.; Anthony, J. E. Org. Lett. 2016, 18, 6050. Copyright 2016 American Chemical Society.
In addition to benzodiindolizine molecules exhibiting blue/purple color due to absorption of orange and green light, red fluorescence is apparent. In concentrated solutions of BDI molecules, it is difficult to separate the absorption from emission by visual inspection. Dilute solutions demonstrate strong fluorescence which is measurable via fluorimeter.

To measure the fluorescence quantum yield of TIPS-BDI, a dilute solution of TIPS-BDI was prepared along with a dilute solution of rubrene as a fluorescence standard. Rubrene has a reported fluorescence quantum yield ~100% in toluene,\textsuperscript{14} which was the solvent used for the fluorescence measurements of both TIPS-BDI and rubrene. Comparison of the two spectra was simplified, per Equation 4-1,\textsuperscript{15} by using identical solvent and excitation wavelengths for the measurements.

\[
\varphi_s = \varphi_r \frac{A_r(\lambda_r)I_r(\lambda_r)\eta_r^2 D_s}{A_s(\lambda_s)I_s(\lambda_s)\eta_s^2 D_r}
\]

(4-1)

Since identical excitation wavelengths were used, the intensity of light at the excitation wavelength \((I_r)\) can be removed from the calculation. Additionally, the refractive index of the solvent \((\eta)\) was also removed from the calculation. The absorption of each species \((A)\), was constant for excitation at 545 nm, but varied for the excitation at 509 nm and so was considered for this measurement [Figure 4-5]. The areas under the fluorescence spectra \((D)\) were calculated for each species to yield the fluorescence quantum yield \((\varphi)\).
Figure 4-5: Absorption (solid lines) and fluorescence (dashed lines) spectra of rubrene (red lines) and TIPS-BDI (blue lines), Left: Excitation at 545 nm, Right: Excitation at 509 nm. Adapted with permission from Granger, D. B.; Mei, Y.; Thorley, K. J.; Parkin, S. R.; Jurchescu, O. D.; Anthony, J. E. Org. Lett. 2016, 18, 6050. Copyright 2016 American Chemical Society.

From this relative measurement, a fluorescence quantum yield of 32% was measured for TIPS-BDI using two separate wavelengths; 509 nm and 545 nm. Pentacene derivatives substituted with ethynyl groups at the 6 and 13 positions have fluorescence quantum yields less than 10%. Increases in fluorescence quantum for BDI compared to pentacene is unsurprising considering the highly fluorescent nature of other indolizine based materials.

4.2 Crystal Engineering

As has been demonstrated with various pentacene derivatives, the solid-state ordering of BDI can be influenced by tuning the size and volume of the trialkysilyl groups employed for solubility. We targeted a 2-D “brickwork” arrangement in relation to the central BDI chromophore. This packing arrangement has been demonstrated to be best for organic field effect transistors (OFET) when using trialkysilyl substituted polycyclic aromatic hydrocarbons. The trialkysilyl groups tend to interact with the substrate of the device and the 2-D π-stacking is directed along the gap between the source and drain.
electrodes.\textsuperscript{18} This orientation allows charge carriers to move through the active material with the most possible routes.

To determine the substitution pattern required to achieve the 2-D “brickwork” motif, we started by synthesizing the tri(iso-propyl)silyl (TIPS) ethynyl BDI derivative. Considering that TIPS pentacene packs in the targeted 2-D motif, TIPS was a logical first choice for the BDI framework because of the comparable size of the two chromophores. From this starting point, we can change the trialkylsilyl substituent and determine the effect on solid state packing to achieve the targeted packing motif. The TIPS derivative packs in a 1-D slip stack motif [Figure 4-6], rather than the target 2-D stacking motif.

![Figure 4-6: Crystal structure diagrams of TIPS-BDI (a) structure, (b) 1-D crystal packing diagram, tri(iso-propyl)silyl groups and protons omitted for clarity](image)

Since the TIPS group did not yield a 2-D packing motif, smaller groups were employed in lieu of the tri(iso-propyl)silyl group. Both trimethylsilyl and tert-butyl groups were used as solubilizing groups, to similar effect [Figure 4-7]. In both cases, a 1-D slip-stack arrangement like that of TIPS-BDI is observed. Contrary to the TIPS-BDI case, however,
TMS-BDI and tBu-BDI both exhibit a 90° rotation of the central chromophore with respect to adjacent 1-D π-stacks.

The intended 2-D “brickwork” motif was finally realized using triethylsilyl groups. Crystals of this material appeared markedly different from previous derivatives, growing as plates rather than needles. This crystal geometry is indicative of 2-D packing motifs, but not definitive. The structure obtained by x-ray diffraction confirmed the 2-deminsional π-stacking arrangement of the central BDI chromophore [Figure 4-8].

Figure 4-7: Crystal structure diagrams of TMS-BDI and tBu-BDI, (a) structure of TMS-BDI, (b) TMS-BDI 1-D crystal packing diagram, trimethylsilyl groups and protons omitted for clarity, (c) structure of tBu-BDI, (d) tBu-BDI 1-D crystal packing diagram, tert-butyl groups and protons omitted for clarity
Figure 4-8: Crystal structure diagrams of TES-BDI, (a) structure, (b) 2-D crystal packing diagram, triethylsilyl groups and protons omitted for clarity

To gauge the potential effectiveness of TES-BDI for FET application, transfer integrals were calculated via DFT based on crystal structures using Gaussian 09\(^{19}\) (B3LYP/6-31(G)) employing the method by Valeev.\(^{20}\) HOMO couplings were 19 meV and 31 meV and found to be comparable to TIPS pentacene, 4 meV and 29 meV.\(^{21}\) Transfer integrals for the LUMO coupling of TES-BDI were significantly higher, 34 meV and 49 meV, as expected for systems similar to aza-acenes\(^{6,11}\) yet no electron mobility was observed as a result of poor LUMO alignment between the material and device contacts.\(^{22}\)

To improve the transfer integrals, it is necessary to fine-tune the crystal packing. This could potentially be achieved by increasing/decreasing the length of one or more of the ethyl groups of the TES moiety. Using this approach, we can shift the molecular displacement and the plane to plane distance of the BDI chromophores. Changes in molecular displacement and plane to plane distance also change the orbital overlap between \(\pi\)-stacking molecules. Increasing orbital overlap increases transfer integrals between molecules and should increase mobility in the bulk material.
We found that increasing the size of the alkylsilyl group by one atom reduced the transfer integrals compared to TES-BDI and was accompanied by an increase in the long axis slip and reduced orbital overlap. Both allyldiethylsilyl (ADES) and n-propyldiethylsilyl (PDES) groups were inspected, to similar effect, where the general packing motif between the three molecules was largely unchanged and the 2-D packing was retained [Figure 4-9]. Switching from TES to ADES reduced the HOMO coupling to 9 meV and 18 meV and switching to PDES reduced the HOMO coupling further to 4 meV and 16 meV.

**Figure 4-9:** Crystal structure diagrams of ADES-BDI and PDES-BDI, (a) structure of ADES-BDI, (b) ADES-BDI 2-D crystal packing diagram, allyldiethylsilyl groups and protons omitted for clarity, (c) ORTEP structure of PDES-BDI, (d) PDES-BDI 2-D crystal packing diagram, n-propyldiethylsilyl groups and protons omitted for clarity.
Reducing the size of the alkylsilyl groups had a much different effect on the crystal packing of the BDI chromophore, where diethylmethylsilyl groups (DEMS) disrupted the 2-D packing motif and led to a rubrene-like herringbone packing motif [Figure 4-10]. This change in solid state packing was also evident from crystal geometry, as the 2-D ordered materials were thin plates and the DEMS-BDI material crystallized as blocks. Calculated HOMO transfer integrals were strong in the direction of the 1-D slip-stacks, 45 meV, and weak at the herringbone edge-to-face contacts, 3 meV.

4.3 Stability Studies

It was expected that the BDI chromophore should not be acid sensitive because of the nitrogen lone pair being incorporated into the π-electrons of the ring system. Unexpectedly, the BDI molecules are quite sensitive to acidic conditions. This sensitivity requires special reaction conditions and neutralization of silica when conducting chromatography.
Figure 4-11: Optical response of TMS-BDI to acid and base treatment, (a) UV-visible spectra of TMS-BDI (black trace), after addition of trifluoroacetic acid (red dot dash) and after addition of triethylamine (blue dashed line), (b) TIPS-BDI solution in toluene (left), after addition of 3 drops trifluoroacetic acid (center), and after addition of 3 drops triethylamine (right). Adapted with permission from Granger, D. B.; Mei, Y.; Thorley, K. J.; Parkin, S. R.; Jurchescu, O. D.; Anthony, J. E. Org. Lett. 2016, 18, 6050. Copyright 2016 American Chemical Society.

It is interesting to note that the acid/base chemistry of BDI is reversible, and though the various BDI derivatives reacted with acids to form new chemical species, the addition of base, such as trimethylamine, regenerates the BDI chromophore [Figure 4-11]. This effect was found to be consistent with mineral acids in addition to trifluoroacetic acid. The regeneration of the chromophore observed visually was confirmed by the reemergence of the UV-vis spectrum of the BDI chromophore.

Stability toward light and interaction with other chemical species commonly used in optoelectronic devices is also important. Acenes react with fullerenes to form 4 + 2 Diels-Alder adducts when mixed together, either in solution or solid state. This reactivity precludes the use of acene derivatives, such as TIPS pentacene, in conjunction with fullerenes or their derivatives for device applications. Any chemical reaction between the
components of a device, either in the bulk or at interfaces, changes the physical properties of the materials, which can lead to reduced effectiveness of the devices.

Figure 4-12: Comparison of reactivity of TIPS-BDI (left) and TIPS pentacene (right) with C60 in toluene at room temperature. Adapted with permission from Granger, D. B.; Mei, Y.; Thorley, K. J.; Parkin, S. R.; Jurchescu, O. D.; Anthony, J. E. Org. Lett. 2016, 18, 6050. Copyright 2016 American Chemical Society.

To gauge whether the BDI chromophore reacts with fullerenes, a dilute solution in toluene was formulated with an absorbance of less than 1 AU. To this solution was added 10 mg PC60BM and kept at room temperature in the dark. The absorbance of this solution was measured at the time of mixing, and after 30 minutes, 1 hour and 72 hours and compared to the absorbance of neat solutions of TIPS-BDI and PC60BM [Figure 4-12, a]. From the series, we observed that BDI does not react appreciably with PC60BM at these time scales.

The larger acenes also decompose in the presence of light to form 4 + 4 cycloaddition adducts. A dilute solution of TIPS-BDI in oxygen free toluene was monitored periodically while exposed to a 75 W light source to gauge solution stability toward light [Figure 4-12,
Under these conditions, the half-life of the BDI chromophore is on the order of 4-5 minutes, while under similar conditions TIPS-Pn has a half-life of about 15 minutes.

### 4.4 Device Characterization

Device fabrication using benzodiindolizines was undertaken by Joshua Mei of the Jurchescu group at Wake Forest University. Initially, dissolution of TES-BDI in high boiling solvents, such as chlorobenzene and tetralin, was incomplete at a 2% weight by volume (w/v) concentration. Heating the solution to 70 °C for 1 hour improved the solubility sufficiently that films could be deposited.

**Figure 4-13**: Films from coating processes using TES-BDI, drop casting using 0.2% w/v solution, (a) Chlorobenzene, (b) 4:1 chlorobenzene: tetralin, spin coating from 2% w/v solution in chlorobenzene, (c) Untreated Au, (d) TFBT treated Au

Drop casting was attempted with less concentrated solutions (0.2% w/v) [Figure 4-13, a-b]. Instead of uniform films, scaling and small isolated domains formed from the solution. Uniform films with large domains and few boundaries are the ideal target for
deposition methods for OFET devices. Spin coating of 2\% w/v solutions showed increased uniformity in film formation [Figure 4-13, c-d]. Treating the gold electrodes with pentafluorobenzene thiol (PFBT) further improved the film uniformity [Figure 4-13, d], and film uniformity is paramount for reliable and reproducible device fabrication and performance.

![Spin coating TES-BDI and PDES-BDI from 2\% w/v solution with various ratios of chlorobenzene and tetralin, TES-BDI (a) 8:1, (b) 4:1, (c) 3:1, (d) 2:1, PDES-BDI (e) 4:1, (f) 8:1](image)

**Figure 4-14:** Spin coating TES-BDI and PDES-BDI from 2\% w/v solution with various ratios of chlorobenzene and tetralin, TES-BDI (a) 8:1, (b) 4:1, (c) 3:1, (d) 2:1, PDES-BDI (e) 4:1, (f) 8:1

Film uniformity was increased by spin coating 2\% w/v solutions of solvent blends of chlorobenzene and tetralin [Figure 4-14]. Screening of various ratios of solvent blends of chlorobenzene and tetralin shows that 4:1 mixtures of these solvents [Figure 4-14, b] produced films with the largest grain sizes. Ratios with higher and lower tetralin content produced films with smaller grain sizes and decreased film uniformity and produced devices with no transistor properties when using TES-BDI. The devices fabricated by spin casting from 4:1 solution mixtures produced devices with transistor response for both
TES-BDI and PDES-BDI. The latter performed better with films spin cast from 8:1 chlorobenzene:tetralin [Figure 4-14, f].

**Figure 4-15**: Device characteristics of TES-BDI and PDES-BDI spin cast films, TES-BDI from 4:1 chlorobenzene:tetralin (a), (b), TES-BDI from 8:1 chlorobenzene:tetralin (c), (d) and PDES-BDI from 8:1 chlorobenzene:tetralin (e), (f). Adapted with permission from Granger, D. B.; Mei, Y.; Thorley, K. J.; Parkin, S. R.; Jurchescu, O. D.; Anthony, J. E. *Org. Lett.* 2016, 18, 6050. Copyright 2016 American Chemical Society.

Field effect transistor device architecture consisted of the BDI molecule film on top of bottom contact PFBT treated gold electrodes with cytop dielectric on the gate electrode, the fabrication of which has been reported previously.25 These devices show a maximum hole mobility (μ) of 0.05 cm²/Vs with on/off ratios in the 10⁵ regime for TES-BDI films spin cast from 4:1 chlorobenzene:tetralin [Figure 4-15, a]. Mobility measurements as high as 0.1 cm²/Vs were found for TES-BDI spin cast from 8:1 chlorobenzene:tetralin [Figure 4-15, b], though the output curves show device behavior that is not ideal. Devices fabricated from PDES-BDI solutions in 8:1 chlorobenzene:tetralin show hole mobility of 0.08 cm²/Vs, with on/off ratios also in the 10⁵ regime [Figure 4-15, c].
The device performance for these materials is limited due to their poor film forming properties. Small grains with high boundary area reduce the charge transport efficiency between the source and drain electrodes by increasing resistance to current flow.\textsuperscript{26} To improve device characteristics, it is necessary to improve the film morphology of the materials resulting in larger grain sizes with fewer interelectrode boundaries, though currently no conditions have been found that achieve this goal.

![Figure 4-16](image)

**Figure 4-16:** DEMS-BDI film casting and device characteristics, (a) drop casting using 0.1% w/v solution in methylene chloride (b) device characteristics, (c) drop casting using 0.1% w/v solution in 1:1 methylene chloride:chlorobenzene, (d) device characteristics, (e) spin coating using 1% w/v solution in 1:1 methylene chloride:chlorobenzene, (f) device characteristics

This film forming issue is exacerbated for devices fabricated using DEMS-BDI as the active material. This material forms films with highly segregated domains, leading to incomplete bridging of the gap between the source and drain electrodes [Figure 4-16]. Devices fabricated by drop-casting using methylene chloride showed very poor FET response with mobility of $10^{-6}$ cm$^2$/Vs and on/off ratios of 10, while drop-casting and spin-casting from 1:1 methylene chloride:chlorobenzene showed slightly improved response
with hole mobilities on the order of $10^{-5}$ and $10^{-4}$, respectively, and on/off ratios on the order of $10^2$.

4.5 Conclusions

We have developed a new class of extended polycyclic N-heteroaromatic compounds by incorporating indolizine moieties into a bent fused aromatic framework. Benzo[2,3-b:5,6-b’]diindolizine molecules show physical properties much closer to linear pentacene than bent benzo[2,3-b:5,6-b’]bisbenzothiophene, due to the placement of the heteroatoms. The placement of the nitrogen atoms at bridgehead positions allows for the ring current of the central unit to pass around the entire BDI chromophore, leading to pentacene-like absorption and emission profiles. These molecules also demonstrate increased fluorescence compared to ethynyl pentacenes as well as reversible acid/base chemistry which is not destructive to the BDI chromophore.

The use of substituted ethynyl groups as solubilizing groups on the central ring allowed for the control and tuning of solid state arrangements, where the use of triethysilyl ethynyl groups produced the 2-D “brick-work” packing arrangement. Expanding the silyl group to allyldiethyl or propylidiethyl reproduced this 2-D stacking motif with slight long axis slip expansion, leading to lower orbital overlap. Ethynyl groups smaller or larger than these generates various 1-D “slip-stack” packing motifs, including a packing motif like the 1-D herringbone packing of rubrene for the diethylmethylsilyl molecule.

The 2-D BDI materials tend to form non-uniform films with small domains, though spin coating from various chlorobenzene/tetralin mixtures produces films with measurable
transistor properties. Maximum hole mobilities for these materials was 0.1 cm$^2$/Vs for TES-BDI and 0.08 cm$^2$/Vs for ADES-BDI with on/off ratios at $10^5$ for both materials. DEMS-BDI films were much less suitable for FET devices than the 2-D materials, with small domains and grains and little coverage of the transistor electrode gap. This lead to devices with very small hole mobilities, $10^{-4}$ cm$^2$/Vs max, and low on/off ratios also, $10^2$. Improved processing conditions could lead to better films with larger grains and fewer boundaries, and would thus improve performance of FET devices.

However, poor solubility of the materials is the likely cause of the inadequate film morphology in these devices. The solubility cannot be improved upon by substitution of the solubilizing groups, as this would alter the solid-state ordering and disrupt the packing motifs. We can, on the other hand, apply the strategy employed in the design of BDI to the synthesis of new chromophores with new and interesting molecular architectures.

4.6 Experimental

Bulk solvents were purchased from VWR (methylene chloride, hexanes and acetone) or Pharmco-Aaper (diethyl ether). Anhydrous tetrahydrofuran, methyl acrylate, potassium 1,1,1,3,3,3-hexamethyldisilizide, N,N,N',N’-tetramethylethlenediamine, 2-formyl pyridine, n-butyl lithium solution and tert-butyl acetylene were purchased from Sigma Aldrich. Trimethylsilyl acetylene, triethylsilyl acetylene and tri(iso-propyl)silyl acetylene were purchased from GFS Chemicals. All other silyl acetylenes were synthesized by addition of Grignard reagents to commercial chlorosilanes.

Proton and carbon NMR spectra were collected using a 400 MHz Varian Unity spectrometer. Chemical shifts of each spectrum are reported in ppm and referenced to
their corresponding deuterated solvents as listed. GC-MS was measured using a Bruker Scion-SQ GC-MS with an EI source. LDI-TOF was measured at the UK mass spectroscopy center using a Bruker Daltonics MALDI-TOFMS ultraflex TOF/TOF in negative ion mode with no matrix. MALDI-TOF samples were analyzed by the UIUC mass spectroscopy center using a Bruker Daltonics MALDI-TOFMS flex with DHB matrix in positive ion mode. UV-visible spectra were measured using a StellarNet Inc Black-Comet UV-vis or Hewlett Packard 8453 UV-vis spectrophotometer. Fluorescence spectra were collected using a StellarNet Inc Silver-Nova spectrophotometer with a SL1-LED excitation source. Fluorescence quantum yield comparison spectra were collected using a Horiba Scientific Fluoromax-4 fluorimeter; excitation wavelength of 545nm and 509nm, excitation slit width of 2nm and emission slit width of 5nm. Cyclic voltammetry and differential pulse voltammetry were measured using a BAS CV-50W potentiostat at a scan rate of 20 mV/s with a button glassy carbon working electrode, a platinum wire counter electrode and an Ag/AgCl reference electrode. A solution of 0.1 M Bu$_4$NPF$_6$ in tetrahydrofuran was used as a supporting electrolyte solution under a blanket of N$_2$ with Fc/Fc$^+$ as an internal reference. Melting points were obtained by differential scanning calorimetry (DSC), measured using a TA Instruments DSC Q100 with a ramp rate of 10 °C/minute.

**Methyl 2-indolizinate (4.1)$^{10}$**

A 50 mL round bottom flask was purged with nitrogen, then charged with 9.8 mL of 2-formyl pyridine (103 mmol) and 19.5 mL of methyl acrylate (217 mmol). To this solution was added 1.7 g of diazo[2.2.2]bicyclooctane (12.5 mmol). The reaction mixture was stirred at room temperature for 16 hours, after which the reaction mixture was filtered
through a thick pad of silica using ethyl acetate as eluent. The solvent was removed and the residue was taken up in 50 mL of acetic anhydride. The solution was heated to 120 °C for 2 hours with constant stirring. The acetic anhydride and acetic acid were removed *in vacuo*. The remaining solid was filtered through a thick pad of silica using dichloromethane as eluent. The product was collected as 8.31 g (46%) of a colorless powder. $^1$H NMR (400.38 MHz, CDCl$_3$, ppm): 3.86 (3H), 6.51 (1H, ddd, $J_1 = 6.5$ Hz, $J_2 = 6.5$ Hz, $J_3 = 1.2$ Hz), 6.66 (1H, ddd, $J_1 = 9.2$ Hz, $J_2 = 6.5$ Hz, $J_3 = 1.2$ Hz), 6.80 (1H, br s), 7.34 (1H, dt, $J_1 = 9.2$ Hz, $J_2 = 1.2$ Hz), 7.78 (1H, br s), 7.84 (1H, dt, $J_1 = 6.5$ Hz, $J_2 = 1.2$ Hz); $^{13}$C NMR (100.68 MHz, CDCl$_3$, ppm): 51.45, 100.40, 112.26, 115.82, 118.11, 119.62, 120.28, 125.33, 132.76, 165.55; MS (GC-MS, EI): 175.1 Da; MP Range: 101-104 °C (ref. 10: 99-100 °C from hexane).

1,4-Benzo[2,3-b:5,6-b']diindolizine quinone (4.2)

A 500 mL round bottom flask was flame dried and purged with nitrogen. The flask was charged with 5.00 g of methyl 2-indolizinate (28.5 mmol) and 150 mL dry of diethyl ether. The subsequent solution was cooled to 0 °C and 12.9 mL of N,N,N′,N′-tetramethylethylenediamine (85.5 mmol) was added slowly to the flask. A solution of 8.53 g of potassium 1,1,1,3,3,3-hexamethyldisilazide (42.8 mmol) in 50 mL of dry diethyl ether was added dropwise to the flask via cannula. The reaction was kept at 0 °C for 1 hour, then brought to room temperature for 16 hours with constant stirring. The diethyl ether was then removed *in vacuo*. Water was added to the flask and the resulting suspension was filtered. The solid was washed with water until the filtrate ran clear. The solid was then washed with methanol until the solvent ran clear, then were washed with 50 mL of
acetone. The collected dark red, insoluble solid was dried under atmospheric conditions for 24 hours to yield 2.13 g of dark red powder (52%). MS (LDI-TOF): 286.1 Da.

1,4-bis(tri-iso-propylsilylethynyl)-benzo[2,3-b:5,6-b’]diindolizine (4.3a)

A flame-dried, nitrogen purged 250 mL round bottom flask was flushed with nitrogen, then charged with 5.2 mL of TIPS acetylene (23.2 mmol) and 60 mL of dry THF. The solution was cool to 0 °C with an ice water bath. 8.8 mL of 2.5 M n-BuLi in hexanes (22.0 mmol) was added dropwise to the flask. The reaction solution was kept at 0 °C with constant stirring for 30 minutes. To this solution was added 0.43 g of 1,4-benzo[2,3-b: 5,6-b’]diindolizine quinone (1.5 mmol) in one portion. The reaction was brought to room temperature for 16 hours. A solution of 2.9 g of SnCl₂ 2H₂O (13.1 mmol) in 20 mL of 10% aqueous HCl was added to the flask and stirring continued for 1 hour. The solution was extracted using 50 mL of hexanes and the organic layer was washed with water (3 x 50 mL). The hexanes solution was dried with MgSO₄, filtered and the solvent removed in vacuo. The resulting residue was filtered through a thick pad of silica using dichloromethane as eluent, yielding 0.38 g of a dark blue solid (41%) which was crystallized from hexanes. ¹H NMR (400.38 MHz, CS₂/d₆-DMSO, ppm): 1.33 (36H, s), 6.39 (2H, t, J = 6.8 Hz), 6.82 (2H, s), 6.92 (2H, dd, J₁ = 9.2 Hz, J₂ = 6.8 Hz), 7.41 (2H, d, J = 9.2 Hz), 9.85 (2H, d, J = 7.4 Hz); ¹³C NMR (100.68 MHz, CS₂/d₆-DMSO, ppm): 13.66, 20.76, 93.83, 98.91, 104.74, 105.98, 108.20, 120.69, 124.60, 128.10, 128.34, 131.38, 139.09; Elemental Analysis: C 77.47%, H 8.56%, N 4.54% (theoretical: C 77.86%, H 8.49%, N 4.54%); MS (MALDI-TOF, DHB): 616.447 Da; MP Range: 215-227 °C.
1,4-bis(tert-butylethynyl)-benzo[2,3-b:5,6-b’]diindolizine (4.3b)

A flame-dried, nitrogen purged 250 mL round bottom flask was flushed with nitrogen, then charged with 2.5 mL of tert-butyl acetylene (20.3 mmol) and 60 mL of dry THF. The solution was cool to 0 °C with an ice water bath. 7.5 mL of 2.5 M n-BuLi in hexanes (18.8 mmol) was added dropwise to the flask. The reaction solution was kept at 0 °C with constant stirring for 30 minutes. To this solution was added 0.50 g of 1,4-benzo[2,3-b:5,6-b’]diindolizine quinone (1.7 mmol) in one portion. The reaction was brought to room temperature for 16 hours. A solution of 1.7 g of SnCl₂·2H₂O (7.5 mmol) in 10 mL of saturated ammonium chloride was added to the flask and stirring continued for 2 hours. The solution was extracted using 50 mL methylene chloride. The methylene chloride solution was dried with MgSO₄, filtered and the solvent removed in vacuo. The resulting residue was filtered through a thick pad of triethylamine neutralized silica using 9:1 hexanes:dichloromethane as eluent, yielding 0.27 g of a dark purple solid (38%) which was crystallized from acetone. ¹H NMR (400.38 MHz, CS₂/d₆-DMSO, ppm): 1.61 (18H, s), 6.40 (2H, t, J = 6.8 Hz), 6.78 (2H, s), 6.88 (2H, dd, J₁ = 8.8 Hz, J₂ = 6.8 Hz), 7.38 (2H, d, J = 9.0 Hz), 9.67 (2H, d, J = 7.4 Hz); ¹³C NMR (100.38 MHz, CS₂/d₆-DMSO, ppm): 30.45, 32.75, 78.64, 93.72, 98.61, 107.83, 110.49, 120.65, 124.18, 127.94, 128.24, 130.84, 138.74; Elemental Analysis: C 86.62%, H 6.70%, N 6.75% (theoretical: C 86.50%, H 6.78%, N 6.72%); MS (MALDI-TOF, DHB): 416.476 Da; MP Range: 239-253 °C.

1,4-bistrimethylsilylethynyl-benzo[2,3-b:5,6-b’]diindolizine (4.3c)
A flame-dried, nitrogen purged 100 mL round bottom flask was flushed with nitrogen, then charged with 1.0 mL of trimethylsilyl acetylene (7.0 mmol) and 30 mL of iso-octane. The solution was cool to 0 °C with an ice water bath. 2.4 mL of 2.5 M n-BuLi in hexanes (6.0 mmol) was added dropwise to the flask. The reaction solution was kept at 0 °C with constant stirring for 30 minutes. To this solution was added 0.25 g of 1,4-benzo[2,3-b: 5,6-b’]diindolizine quinone (0.87 mmol) in one portion, followed by 3 mL of dry tetrahydrofuran. The reaction was brought to room temperature for 16 hours. The reaction was quenched with 10 drops of water and the solvent was removed in vacuo. The residue was run through a thick pad of triethylamine neutralized silica using hexanes as eluent to remove residual TMS acetylene, followed by methylene chloride to collect the diethynyl diol. The diol was taken up in 50 mL of tetrahydrofuran and 10 mL of water to which 0.79 g of SnCl₂·2H₂O (3.5 mmol) was added to the solution. After 1 hour of vigorous stirring, the solution was extracted using 50 mL of ethyl acetate and the organic layer was washed with water (3 x 50 mL). The ethyl acetate solution was dried with MgSO₄, filtered and the solvent removed in vacuo. The resulting residue was filtered through a thick pad of triethylamine neutralized silica using 9:1 hexanes:methylene chloride as eluent, yielding 0.37 g of a purple solid (94 %) which was crystallized from acetone. ^1H NMR (400.38 MHz, d₆-acetone, ppm): 0.43 (18H, s), 6.59 (2H, dd, J₁ = 7.4 Hz, J₂ = 6.8 Hz), 6.94 (2H, s), 7.03 (2H, dd, J₁ = 9 Hz, J₂ = 6.8 Hz), 7.59 (2H, d, J = 9 Hz), 9.82 (2H, d, J = 7.4 Hz); ^13C NMR (100.68 MHz, d₆-acetone, ppm): 0.03, 92.15, 97.73, 102.69, 107.65, 108.06, 119.98, 124.20, 127.14, 127.30, 130.14, 139.08; Elemental Analysis: C 74.72%, H
6.23%, N 6.15% (theoretical: C 74.95%, H 6.29%, N 6.24%); MS (MALDI-TOF, DHB): 448.267 Da; MP Range: 242-264 °C.

1,4-bis(triethylsilylethynyl)-benzo[2,3-b:5,6-b’]diindolizine (4.3d)

A flame-dried, nitrogen purged 100 mL round bottom flask was flushed with nitrogen, then charged with 1.25 mL of triethylsilyl acetylene (6.97 mmol) and 30 mL of iso-octane. The solution was cool to 0 °C with an ice water bath. 1.4 mL of 2.5 M n-BuLi in hexanes (6.0 mmol) was added dropwise to the flask. The reaction solution was kept at 0 °C with constant stirring for 30 minutes. To this solution was added 0.25 g of 1,4-benzo[2,3-b:5,6-b’]diindolizine quinone (0.87 mmol) in one portion, followed by 3 mL of dry tetrahydrofuran. The reaction was brought to room temperature for 16 hours. The reaction was quenched with 10 drops of water and the solvent was removed in vacuo. The residue was run through a thick pad of triethylamine neutralized silica using hexanes as eluent to remove residual TES acetylene, followed by methylene chloride to collect the diethynyl diol. The diol was taken up in 50 mL of tetrahydrofuran and 15 mL of water to which 0.88 g of SnCl2·2H2O (3.9 mmol) was added to the solution. After 1 hour of vigorous stirring, the solution was extracted using 50 mL of methylene chloride and the organic layer was washed with water (3 x 50 mL). The methylene chloride solution was dried with MgSO4, filtered and the solvent removed in vacuo. The resulting residue was filtered through a thick pad of triethylamine neutralized silica using hexanes as eluent, yielding 0.32 g of a purple solid (69%) which was crystallized from acetone. 1H NMR (400.38 MHz, d6-acetone, ppm): 0.89 (12H, q, J = 7.8 Hz), 1.19 (18H, t, J = 7.8 Hz), 6.58 (2H, ddd, J1 = 7.2 Hz, J2 = 6.4 Hz, J3 = 1.2 Hz), 6.96 (2H, s), 7.04 (2H, ddd, J1 = 9.2 Hz, J2 = 6.4 Hz, J3 = 1.2 Hz),
7.60 (2H, d, J = 9.2 Hz), 9.91 (2H, dd, J₁ = 7.2 Hz, J₂ = 1.2 Hz); ¹³C NMR (100.68 MHz, d₆-acetone, ppm): 6.10, 9.01, 93.08, 98.77, 104.90, 106.33, 108.95, 120.99, 125.20, 128.12, 128.28, 131.29, 140.02; Elemental Analysis: C 76.59%, H 7.74%, N 5.37% (theoretical: C 76.64%, H 7.57%, N 5.26%); MS (MALDI-TOF, DHB): 532.374 Da; MP Range: 191-204 °C.

**1,4-bis(n-propyldiethylsilylethynyl)-benzo[2,3-b:5,6-b’]diindolizine (4.3e)**

A flame-dried, nitrogen purged 100 mL round bottom flask was flushed with nitrogen, then charged with 0.80 g of n-propyldiethylsilyl acetylene (5.18 mmol) and 25 mL of iso-octane. The solution was cool to 0 °C with an ice water bath. 1.9 mL of 2.5 M n-BuLi in hexanes (4.75 mmol) was added dropwise to the flask. The reaction solution was kept at 0 °C with constant stirring for 30 minutes. To this solution was added 0.15 g of 1,4-benzo[2,3-b: 5,6-b’]diindolizine quinone (0.52 mmol) in one portion, followed by 3 mL of dry tetrahydrofuran. The reaction was brought to room temperature for 16 hours. The reaction was quenched with 10 drops of water and the solvent was removed *in vacuo*. The residue was run through a thick pad of triethylamine neutralized silica using hexanes as eluent to remove residual PDES acetylene, followed by methylene chloride to collect the diethynyl diol. The diol was taken up in 30 mL of tetrahydrofuran and 5 mL of water to which 0.53 g of SnCl₂·2H₂O (2.34 mmol) was added to the solution. After 1 hour of vigorous stirring, the solution was extracted using 50 mL of hexanes and the organic layer was washed with water (3 x 50 mL). The hexanes solution was dried with MgSO₄, filtered and the solvent removed *in vacuo*. The resulting residue was filtered through a thick pad of triethylamine neutralized silica using hexanes as eluent, yielding 0.28 g of a purple solid (95%) which was crystallized from acetone. ¹H NMR (400.38 MHz, CS₂/d₆-DMSO, ppm):
1H NMR (400.38 MHz, d6-acetone, ppm): 0.89 (8H, q, J = 8 Hz), 1.20 (12H, t, J = 8 Hz), 1.93 (4H, d, J = 8 Hz), 4.98 (2H, d, J = 10.4 Hz), 5.07 (2H, t, J = 6.8 Hz), 6.41 (2H, t, J = 6.8 Hz), 6.81 (2H, s), 6.92 (2H, dd, J1 = 8.4 Hz, J2 = 6.8 Hz), 7.42 (2H, d, J = 9.4 Hz), 9.78 (2H, d, J = 7.2 Hz); 13C NMR (100.68 MHz, CS2/d6-DMSO, ppm): 7.37, 9.93, 17.33, 19.94, 20.46, 93.86, 98.83, 105.36, 106.01, 108.19, 120.71, 124.57, 128.04, 128.25, 131.18, 139.12; Elemental Analysis: C 77.30%, H 8.19%, N 5.05% (theoretical: C 77.09%, H 7.91%, N 4.99%); MS (MALDI-TOF, DHB): 560.437 Da; MP Range: 140-160 °C.

1,4-bis(allyldiethylsilylethynyl)-benzo[2,3-b:5,6-b']diindolizine (4.3f)

A flame-dried, nitrogen purged 50 mL round bottom flask was flushed with nitrogen, then charged with 0.59 g of allyldiethylsilyl acetylene (3.9 mmol) and 15 mL of iso-octane. The solution was cool to 0 °C with an ice water bath. 1.4 mL of 2.5 M n-BuLi in hexanes (3.5 mmol) was added dropwise to the flask. The reaction solution was kept at 0 °C with constant stirring for 30 minutes. To this solution was added 0.10 g of 1,4-benzo[2,3-b: 5,6- b']diindolizine quinone (0.35 mmol) in one portion, followed by 2 mL of dry tetrahydrofuran. The reaction was brought to room temperature for 16 hours. The reaction was filtered and 25 mL of tetrahydrofuran and 4 mL of water was added to the solution. 0.36 g of SnCl2·2H2O (1.6 mmol) was added to the solution and stirring continued for 1 hour. The solution was extracted using 50 mL of hexanes and the organic layer was washed with water (3 x 50 mL). The hexanes solution was dried with MgSO4, filtered and the solvent removed in vacuo. The resulting residue was filtered through a thick pad of triethylamine neutralized silica using hexanes as eluent, yielding 0.14 g of a dark blue solid (71%) which was crystallized from acetone. 1H NMR (400.38 MHz, d6-acetone, ppm): 0.89 (8H, q, J = 8 Hz), 1.20 (12H, t, J = 8 Hz), 1.93 (4H, d, J = 8 Hz), 4.98 (2H, d, J = 10.4 Hz), 5.07
(2H, d, J = 16.8 Hz), 5.99 (2H, hx, J = 9.2 Hz), 6.56 (2H, t, J = 6.4 Hz), 6.97 (2H, s), 7.02 (2H, dd, J₁ = 9.2, J₂ = 8.8), 7.59 (2H, d, J = 8.8), 9.87 (2H, d, J = 7.6); ¹³C NMR (100.68 MHz, d₆-acetone, ppm): 6.20, 8.93, 22.00, 93.14, 98.68, 105.26, 105.74, 109.04, 115.66, 120.97, 125.25, 128.24, 131.31, 136.04, 140.07; Elemental Analysis: C 77.54%, H 7.40%, N 5.03% (theoretical: C 77.64%, H 7.24%, N 5.03%); MS (MALDI-TOF, DHB): 556.368 Da; MP Range: 148-163 °C.

1,4-bis(diethylmethylsilylethynyl)-benzo[2,3-b:5,6-b’]diindolizine (4.3g)

A flame-dried, nitrogen purged 50 mL round bottom flask was flushed with nitrogen, then charged with 0.61 g of diethylmethylsilyl acetylene (4.8 mmol) and 20 mL of iso-octane. The solution was cool to 0 °C with an ice water bath. 1.3 mL of 2.5 M n-BuLi in hexanes (3.3 mmol) was added dropwise to the flask. The reaction solution was kept at 0 °C with constant stirring for 30 minutes. To this solution was added 0.14 g of 1,4-benzo[2,3-b:5,6-b’]diindolizine quinone (0.49 mmol) in one portion, followed by 2 mL of dry tetrahydrofuran. The reaction was brought to room temperature for 16 hours. The reaction was quenched with 10 drops of water and the solvent was removed in vacuo. The residue was run through a thick pad of triethylamine neutralized silica using hexanes as eluent to remove residual DEMS acetylene, followed by methylene chloride to collect the diethynyl diol. The diol was taken up in 30 mL tetrahydrofuran and 10 mL of water to which 0.43 g of SnCl₂·2H₂O (1.9 mmol) was added to the solution. After 1 hour of vigorous stirring, the solution was extracted using 100 mL ethyl acetate and the organic layer was washed with brine (3 x 50 mL). The ethyl acetate solution was dried with MgSO₄, filtered and the solvent removed in vacuo. The resulting residue was filtered through a thick pad
of triethylamine neutralized silica using 9:1 hexanes:methylene chloride as eluent, yielding 0.22 g of a purple solid (50%) which was crystallized from acetone. $^1$H NMR (400.38 MHz, d$_6$-acetone, ppm): 0.38 (6H, s), 0.89 (8H, m), 1.21 (12H, t, J = 7.4 Hz), 6.58 (2H, t, J = 6.8 Hz), 6.95 (2H, s), 7.04 (2H, dd, $J_1$ = 9.2 Hz, $J_2$ = 6.4 Hz), 7.60 (2H, d, J = 9.2 Hz), 9.88 (2H, d, J = 7.2 Hz); $^{13}$C NMR (100.68 MHz, d$_6$-acetone, ppm): -3.29, 7.87, 8.90, 93.09, 98.73, 104.43, 107.07, 108.96, 120.96, 125.17, 128.10, 128.26, 131.21, 140.01; Elemental Analysis: C 75.93%, H 7.20%, N 5.41% (theoretical: C 76.14%, H 7.19%, N 5.55%); MS (MALDI-TOF, DHB): 504.361 Da; MP Range: 212-232 °C.

4.7 References


Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.


5 (2.2.3) Cyclazine Capped Acenes

Expanding on the molecular design of indolizine containing organic semiconductors, we targeted a building block that would allow for more generalized inclusion of the indolizine moiety. There are several potential building blocks reported in the literature with varying complexity which are built from simpler azaarenes [Figure 5-1].\(^1\)\(^-\)\(^3\) Pyridine can be used to synthesize indolizine units\(^1\) and indolizine can be used to synthesize a tricyclic unit referred to as cyclazine.\(^2\) Other cyclazines\(^3\) and more complicated units such as ullaizine\(^4\) can also be synthesized by similar methods, but are not the focus here.

![Figure 5-1: General structures of pyridine, indolizine and (2.2.3) cyclazine](image)

The (2.2.3) cyclazine unit was chosen for inspection because of the relative simplicity compared to larger more complex cyclazines or other azaarenes.\(^3\)\(^-\)\(^4\) In addition, there is potentially more versatility over synthesis of bent indolizine molecules, which generally involve the reaction of 1,4-acenequinones with pyridine.\(^5\) Methods of introducing 1,2-dicarbonyl groups on (2.2.3) cyclazine molecules are known\(^2a\) and these carbonyl groups can be modified for use in further synthetic steps to extend the aromatic framework via aldol condensation.

It was expected that molecules incorporating any of these varieties of N-heterocyclic aromatic groups should demonstrate extended absorption and emission profiles like that observed for benzo[2,3-b: 5,6-b’]diindolizine (BDI) described in chapter 4. Although these
molecules will not be linear in ring attachment around the azaarene units, the placement of the nitrogen atoms at bridgehead positions may allow the electrons in the $\pi$-system to complete the ring current around the whole of the molecule as shown for BDI. To elucidate these properties, a series of molecules incorporating the (2.2.3) cyclazine unit were synthesized and their properties investigated.

In addition to the unimolecular electronic properties, we are also interested in the bulk properties of these molecules, primarily singlet fission (SF) properties. Heterocyclic aromatic analogs of polycyclic aromatic hydrocarbons have been demonstrated to affect the alignment of the first singlet ($S_1$) and first triplet ($T_1$) excited states of molecules. In many of the investigated frameworks, substitution of nitrogen atoms for a CH pair induces a number of changes in the electronic characteristics of molecules that are beneficial to singlet fission. The placement of the nitrogen atom reduces the $S_0$, $S_1$ and $T_1$ energies, but affects the $S_1$ and $T_1$ to greater extent, resulting in a slightly less exoergic of SF process though retaining exoergicity. This reduces non-radiative losses and should result in increased SF efficiency, which has been observed in azaacenes. All of the azaarene molecules that have had their SF properties investigated have the nitrogen placed in peripheral positions, but comparison to molecules with bridgehead nitrogen may prove interesting.

### 5.1 Synthesis of 1,2-diformyl (2.2.3) cyclazine

To synthesize the prime intermediate 1,2-diformyl (2.2.3) cyclazine, it was necessary to first synthesize unsubstituted indolizine. This unsubstituted indolizine is an efficient partner in $8\pi + 2\pi$ cycloadditions, per literature synthetic methods. Although there are
many synthetic methods to produce unsubstituted indolizine, many of these are low yielding\textsuperscript{2a,8} or require outdated methods and equipment which was unavailable.\textsuperscript{9}

![Diagram]

\textbf{Figure 5-2:} Synthesis of 1,2-diformyl (2.2.3) cyclazine, i.) 1. methyl chloroacetate, 2. methyl acrylate, triethylamine, MnO\textsubscript{2}, Δ, ii.) 1. KOH, ethanol, reflux, 2. HCl, reflux, iii.) 1. dimethyl acetylenedicarboxylate, 2. MnO\textsubscript{2}, iv.) 1. DIBAL-H, 2. MnO\textsubscript{2}

Other reports in the literature suggest indolizines substituted by carboxylate groups at the C1 and C3 positions can readily be decarboxylated, while carboxylate groups at the indolizine C2 position are not readily removed.\textsuperscript{10} We were able to synthesize indolizine substituted with carboxylate groups at the indolizine C1 and C3 positions (5.1) in quantities greater than 15 g [\textbf{Figure 5-2}] via modified literature procedures.\textsuperscript{11} Conditions to remove these carboxylate groups via saponification followed by decarboxylation under acidic conditions, similar to literature methods,\textsuperscript{10} were employed to obtain unsubstituted indolizine (5.2) in multi-gram quantities. The unsubstituted indolizine was then used in a modified literature $8\pi + 2\pi$ cycloaddition\textsuperscript{2} with dimethyl acetylenedicarboxylate,
followed by oxidation with activated manganese(IV) dioxide in one pot to synthesize dimethyl (2.2.3) cyclazine-1,2-dicarboxylate (5.3) in good yield.

![Image](image.png)

**Figure 5-3**: Crystal structures and UV-vis spectra of indolizine and cyclazine diester, (a) crystal structure of indolizine showing disorder, (b) crystal structure of dimethyl (2.2.3) cyclazine-1,2-dicarboxylate showing disorder, (c) UV-visible spectra of indolizine and dimethyl (2.2.3) cyclazine-1,2-dicarboxylate

The diester intermediate was then reduced to the dicarbinol using di(iso-butyld)aluminum hydride. It was not possible to rigorously purify the diol due to low solubility and high polarity of the molecule which makes chromatography difficult. Thus, the diol was not purified prior to oxidation with MnO₂ in toluene at 120 °C. The dialdehyde product was more easily purified to yield a fibrous yellow-orange solid in good yields.

From the visible spectrum of indolizine and dimethyl (2.2.3) cyclazine-1,2-dicarboxylate [Figure 5-3], we observed a significant bathochromic shift, ~70 nm, on expansion of the ring system from the bicyclic to tricyclic compounds. This can be attributed to the increase in conjugation in the tricyclic compound. It is not obvious if the nitrogen lone pair is participating in the π-electron system, though the planar geometry
around the nitrogen atom is suggestive of inclusion of the nitrogen lone pair in the π-system.

5.2 Covalent charge transfer complex of naphthoquinone and indolizine

To expand on the 8+2 cycloaddition reaction between indolizine and electron deficient unsaturated aliphatic molecules, indolizine was mixed with naphthoquinone [Figure 5-4]. A new chemical species was observed by thin layer chromatography, which was originally thought to be the cycloaddition adduct. Activated MnO$_2$ was added to the reaction and upon addition the solution turned dark blue. This blue material was collected and purified by silica gel chromatography and recrystallized from acetone to yield blue needles.

![Figure 5-4: Intended product (left) and actual product of the reaction (right) between indolizine and naphthoquinone, i.) 1. Toluene, 2. MnO$_2$](image)

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![Figure 5-4: Intended product (left) and actual product of the reaction (right) between indolizine and naphthoquinone, i.) 1. Toluene, 2. MnO$_2$](image)

Figure 5-5: (a) Crystal structure and (b) UV-vis spectrum of 3,2'-indolizino-naphthoquinone

![Figure 5-5: (a) Crystal structure and (b) UV-vis spectrum of 3,2'-indolizino-naphthoquinone](image)
From the crystal structure [Figure 5-5, a], it was found that the product of the reaction was not a fully annulated indolizine-containing molecule. The structure has only one new sigma bond between the C2 position of the naphthoquinone and the C3 position of the indolizine. The molecule is not planar due to the steric interaction between the internal protons on each segment of the compound, and the dark color of the compound is suggestive of a charge transfer complex, which is further suggested by the broad, featureless absorption profile in the visible region [Figure 5-5, b]. From these results, it seems unlikely that this reaction scheme will be successful using geometrically constrained dienophiles, as has been the case in previously published works with similar molecules.2a

5.3 9,10-Bistri(iso-propyl)silylethynyl anthra[2,3-cd]indolizine synthesis and properties

![Synthetic route to 9,10-bistri(iso-propyl)silylethynyl anthra[2,3-cd]indolizine (TIPS-AIA)](image)

Figure 5-6: Synthetic route to 9,10-bistri(iso-propyl)silylethynyl anthra[2,3-cd]indolizine (TIPS-AIA), i.) THF, EtOH, KOH, ii.) 1. TIPSCCl, 2. SnCl2

A larger framework based on the (2.2.3) cyclazine was accomplished by aldol condensation of the dialdehyde with 1,4-dihydroxynaphthalene [Figure 5-6]. This produced the anthra[cd]indolizine-9,10-quinone (5.6) which could be ethynylated and aromatized to yield the 9,10-bistri(iso-propyl)silylethynyl anthra[cd]indolizine (5.7). The
TIPS derivative is the only derivative to be synthesized to date, though the synthesis of other ethynyl derivatives should be straightforward.

**Figure 5-7:** Crystal structure diagrams of TIPS-AIA and a comparison to TES-tetracene, (a) crystal structure asymmetric unit of TIPS-AIA, (b) pair-wise stacking unit of TES-tetracene with protons and triethylsilyl groups omitted for clarity, (c) relation of two stacking pairs of TIPS-AIA with protons and tri(iso-propyl)silyl groups omitted for clarity, (d) 90° rotation on the z-axis of the two stacking pairs shown in part c

Crystals of TIPS-AIA were grown from hexanes as dark green cubes. The molecules crystallize as segregated pairs, with herringbone/edge-to-face interactions between pairs. With the lack of π-interactions between the stacks, the electronic coupling between pairs should be minimal as well. Thus, the TIPS-AIA derivative is not likely to be appropriate for optoelectronic devices such a field effect transistors and photovoltaics. Although, devices that are not reliant on mobility such as light emitting diodes may be a better fit for molecules with this molecular arrangement. Additionally, the derivative
could be helpful to determine singlet fission properties of the AIA chromophore, including efficiency and time scale of fission in the material.

**Figure 5-8:** UV-vis and fluorescence spectra of TIPS-AIA and TIPS-anthracene, (a) UV-visible (blue trace) and fluorescence (red trace) spectra of TIPS-AIA, (b) UV-visible spectrum of 9,10-bistri(iso-propyl)silylethynyl anthracene

The UV-visible spectrum shows that TIPS-AIA exhibits some of the character usually associated with acenes [Figure 5-8]. Vibrational fine structure is observed in the visible region between 500 and 650 nm. However, it must be stated that there is significant broadening of these features in the spectrum, leading to a combination between the absorption characteristics of anthracene [Figure 5-8, b] and (2.2.3) cyclazine [Figure 5-3, c]. The addition of (2.2.3) cyclazine to anthracene produces a bathochromic shift of close to 150 nm and shifts the absorption cutoff of TIPS-AIA to around 650 nm compared to ~450 nm for 9,10-bistri(iso-propyl)silylethynyl anthracene [Figure 5-8, b]. Despite the vibrational features in the absorption spectrum, the fluorescence spectrum demonstrates no vibrational structure and instead has a broad featureless emission peak with $\lambda_{\text{max}}$ of ~670 nm, corresponding to a Stokes shift of 70 nm.
Cyclic voltammetry of TIPS-AIA shows two weak oxidations and one strong reduction [Figure 5-9]. The oxidation pair corresponding to the HOMO of the molecule, 0.633 V, appears to be quasi-reversible from the cyclic voltammogram and overlaps with the ferrocene/ferrocenium oxidation pair. The reduction pair seen in the voltammogram, -1.17 V, corresponds to the LUMO of the molecule. From these values and the measured Fc/Fc+ oxidation pair, 0.614 V, the HOMO and LUMO of the molecule were estimated to be -4.82 eV and -3.02 eV, respectively, by calculation.\textsuperscript{12}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure5_9.png}
\caption{Cyclic voltammetry of TIPS-AIA in THF solution with 0.1 M Bu$_4$NPF$_6$ electrolyte support}
\end{figure}

5.4 Larger N-heterocyclic aromatic molecules

To further extend the acene portion of this series of molecules, 1,2-diformyl (2.2.3) cyclazine was reacted with 1,4-dihydroxyanthracene and 1,4-cyclohexane dione in aldol condensations [Figure 5-10]. The aldol condensations were good yielding, yet ethynylation reactions were not successful. Very little of the intended product was formed in all ethynylation reactions of these quinones, with only \textasciitilde20 mg of dimerized material collected as identified by MALDI-TOF. All attempts to improve the reaction and prevent dimerization reactions were unsuccessful.
Despite the tendency for dimerization of these molecules, the presence of an extended polycyclic aromatic chromophore is still observed from the dark green solution color and spectroscopic characterization [Figure 5-11]. The absorption spectra for both molecules show similar bathochromic shifts from the respective base acenes as was observed for TIPS-AIA versus anthracene. This effect pushes the absorption profile for the AIT chromophore just above 700 nm with emission $\lambda_{\text{max}}$ around 760 nm.

Figure 5-10: Synthetic route to TIPS-AIT (top) and TIBS-DAIA (bottom), i.) 1,4-dihydroxy anthracene, THF, EtOH, 15% KOH, ii.) 1. TIPSClLi, 2. SnCl$_2$, iii.) 1,4-cyclohexane dione, THF, EtOH, 15% KOH, iv.) 1. TIBSClLi, 2. SnCl$_2$

The DAIA molecule with two cyclazine end caps shows additional bathochromic shift of the absorption spectrum of anthracene [Figure 5-11, b] relative to the singly capped
AIA molecule. This additional shift of the spectrum pushes the absorption cutoff wavelength over 700 nm with emission $\lambda_{\text{max}}$ at 720 nm. This data suggests that the positioning of nitrogen atoms in bridgehead positions of polycyclic aromatic systems expands the ring currents of non-linear molecules with judicious placement of these groups.

**Figure 5-11:** UV-vis and fluorescence spectra of TIPS-AIT and TIBS-DAIA, (a) UV-visible (black trace) and fluorescence (black dashed line) spectra of TIPS-AIT, (b) UV-visible (black trace) and fluorescence (black dashed line) spectra of TIBS-DAIA

### 5.5 DFT Calculations of Cyclazine based Molecules

To elucidate the structure of the frontier molecular orbitals (FMO) of these various cyclazine based molecules, density functional theory (DFT) calculations were undertaken at the B3LYP/6-31G(d) level of theory after AM1 geometry minimization on the GAMESS DFT software for the molecules with (2.2.3) cyclazine end-caps [Figure 5-12]. From the calculations, it was found that the acene portions of the molecules largely conform to the orbital structures observed for acenes generally in both the HOMO and LUMO orbitals of the molecules. The cyclazine portion of the molecules have orbital structure like that of the acene portion of the molecules in the HOMOs and appears to be an extension of the
motif. Conversely, the LUMO of the molecules have very little contribution from the cyclazine units.

The FMO trend is consistent across all the molecules investigated here for both HOMO and LUMO orbitals as seen in Figure 5-12. This includes the case of both potential DAIA isomers listed as Anti DAIA and Syn DAIA which show minor differences in orbital structure despite the differences in ring placement. It is also apparent that there is significant electron density on the nitrogen atoms in these molecules, further suggesting that the nitrogen lone pair may be participating in the π-electron system as noted for BDI.

![DFT calculated frontier molecular orbitals of AIA, DAIA (syn- and anti-isomers) and AIT](image)

Figure 5-12: DFT calculated frontier molecular orbitals of AIA, DAIA (syn- and anti-isomers) and AIT

5.6 Conclusions

We have conceived of a route to incorporate (2.2.3) cyclazine into extended aromatic frameworks. This class of molecules utilizes aldol condensations with 1,2-diformyl (2.2.3) cyclazine and 1,4-dihydroxyacenes to synthesize quinones that can then be ethynylated to produce fully conjugated systems. This synthetic scheme works particularly well for the
tetracene sized derivative referred to as AIA. Larger derivatives, similar in size to pentacene, are significantly less stable after ethynylolation and aromatization where only dimerization products were collected.

These molecules do, however, retain acene-like UV-vis light absorption properties despite the break in linearity in ring fusion. This is like that seen for BDI and is likely a result of inclusion of the nitrogen atoms at bridgehead positions in the framework. In addition, the increase in conjugation by inclusion of a tricyclic unit, as opposed to a benzenoid ring, leads to significant bathochromic shifting of the absorption spectrum for these molecules.

Future work with these molecules will center on synthesis of new and stable derivatives of the AIA and AIT molecules by substitution on the terminal benzenoid ring. The use of sterically bulky groups on the AIT molecules such as di(iso-butyl)dioxolane groups may prevent the molecules from dimerizing and the use of electron withdrawing groups such as fluorine atoms may lower the HOMO energy of the molecule sufficiently to make the Diels-Alder energetics unfavorable. Similar substitution schemes will be targeted for the AIA molecule to affect the triplet energy of the molecules for comparison in singlet fission experiments.

5.7 Experimental

Bulk solvents were purchased from VWR (methylene chloride, hexanes and acetone) or Pharmco-Aaper (diethyl ether). Anhydrous tetrahydrofuran, methyl acrylate, n-butyl lithium solution and manganese(IV) dioxide were purchased from Sigma Aldrich. Tri(iso-propyl)silyl acetylene was purchased from GFS Chemicals. Tri(iso-butyl)silyl acetylene was
synthesized by addition of ethynyl magnesium chloride to commercial tri(iso-butyl) chlorosilane.

Proton and carbon NMR spectra were collected using a 400 MHz Varian Unity spectrometer. Chemical shifts of each spectrum are reported in ppm and referenced to their corresponding deuterated solvents as listed. GC-MS was measured using a Bruker Scion-SQ GC-MS with an EI source. MALDI-TOF samples were analyzed by the UIUC mass spectroscopy center using a Bruker Daltonics MALDI-TOFMS flex with DHB matrix in positive ion mode. UV-visible spectra were measured using a StellarNet Inc Black-Comet UV-vis or Hewlett Packard 8453 UV-vis spectrophotometer. Fluorescence spectra were collected using a StellarNet Inc Silver-Nova spectrophotometer with a SL1-LED excitation source. Cyclic voltammetry and differential pulse voltammetry were measured using a BAS CV-50W potentiostat at a scan rate of 20 mV/s with a button glassy carbon working electrode, a platinum wire counter electrode and an Ag/AgCl reference electrode. A solution of 0.1 M Bu₄NPF₆ in tetrahydrofuran was used as a supporting electrolyte solution under a blanket of N₂ with Fc/Fc⁺ as an internal reference. Melting points were obtained by differential scanning calorimetry (DSC), measured using a TA Instruments DSC Q100 with a ramp rate of 10 °C/minute.

**Dimethyl indolizine-1,3-dicarboxylate (5.1)**

In a 100 mL round bottom flask, 16.2 mL of anhydrous pyridine (0.20 mol) was combined with 17.6 mL of methyl chloroacetate (0.21 mol). The mixture was stirred at room temperature under a blanket of nitrogen for 96 hours. The solid cake was broken
up and filtered with ether (4x 50 mL). The ether was evaporated from the solid in a vacuum oven at room temperature to yield 36.45 g colorless solid (99%) which was used without purification.

A 500 mL round bottom flask was charged with 250 mL of toluene, 20.0 g of methyl N-pyridylacetate (109.6 mmol), 50 mL of methyl acrylate (0.50 mol), 76.2 g of activated MnO₂ 58% Mn (0.88 mol) and 17 mL of triethylamine (0.13 mol). The suspension was heated to 90 °C under N₂ for 2 hours and filtered hot. The filtrate was washed with 250 mL of hot toluene and the combined solution concentrated in vacuo. The crude product was purified by filtration through a thick pad of silica using methylene chloride as eluent. 5.1 was collected as 19.25 g of a pale yellow solid (>70%) as a mixture with 10% methyl indolizinecarboxylate. A pure analytical sample was recrystallized from hexanes as colorless needles. ¹H NMR (400 MHz, CDCl₃, ppm): 3.78-3.88 (m, 6 H), 6.94 (t, 1 H, J = 7.0 Hz), 7.26 (m, 1 H), 7.92 (s, 1 H), 8.28 (d, 1 H, J = 9.0 Hz), 9.46 (d, 1 H, J = 7.0 Hz); ¹³C NMR (100 MHz, CDCl₃, ppm): 51.12, 51.34, 104.9, 114.38, 114.42, 119.5, 124.2, 125.6, 127.8, 139.0, 161.4, 164.5; GC-MS (m/z): M = 233 Da; MP Range: 186-189 °C.

**Indolizine (5.2)¹⁰**

A 250 mL round bottom flask was charged with 6.0 g of dimethyl indolizine-1,3-dicarboxylate (25.7 mmol), 120 mL of ethanol and 9.0 g of potassium hydroxide (0.16 mol). The resultant suspension was heated to 95 °C for 16 hours, after which it was cooled to room temperature and the solids dissolved with 50 mL of water. The dicarboxylic acid was then precipitated by addition of concentrated hydrochloric acid to solution pH 1. The
solid was collected by filtration and washed with 100 mL of 10% HCl to remove traces of ethanol. The dicarboxylic acid was then dissolved in 100 mL of 15% KOH poured into a 500 mL round bottom flask where the solution was brought to pH 1 with concentrated HCl. The suspension was heated to 100 °C for 1 hour, when the evolution of carbon dioxide ceased. The solution was cooled to room temperature and brought to pH 14 with 15% KOH. The aqueous solution was extracted with methylene chloride (3x 50 mL), the combined solution dried with MgSO₄ and the solvent removed in vacuo. The crude product was purified by filtration through a thick pad of silica using methylene chloride as eluent. The title compound was collected as 3.21 g of a colorless crystalline solid (quantitative). Unsubstituted indolizine degrades slowly under standard conditions and should be used immediately. ¹H NMR (400 MHz, CDCl₃, ppm): 6.47-6.50 (m, 2 H), 6.69 (t, 1 H, J = 7.6 Hz), 6.86 (s, 1 H), 7.33 (br s, 1 H), 7.42 (d, 2 H, 9.0 Hz), 7.93 (d, 1 H, 6.3 Hz); ¹³C NMR (100 MHz, CDCl₃, ppm): 99.0, 110.3, 112.1, 113.7, 116.9, 119.2, 125.3, 113.0; GC-MS (m/z): M = 117 Da; MP Range: 72-75 °C.

**Dimethyl (2.2.3) cyclazine-1,2-dicarboxylate (5.3)²a**

In a 500 mL round bottom flask, 3.21 g of indolizine (25.7 mmol) was dissolved in 150 mL of toluene and oxygen was removed by a steady stream of N₂. To this solution was added 4.1 mL of dimethyl acetylene-dicarboxylate and the reaction mixture was stirred at room temperature under N₂ for 16 hours. 17.87 g of activated MnO₂ 58% Mn (0.206 mol) was added to the flask and the suspension stirred at room temperature for 1 hour. The suspension was then filtered, the filtrate washed with 150 mL of toluene and the solvent removed in vacuo. The crude product was purified by silica gel column
chromatography using 2:1 hexanes:ethyl acetate as eluent. The pure product was collected as 3.67 g of an orange-red crystalline solid (55%). $^{1}$H NMR (400 MHz, CDCl$_3$, ppm): 3.98 (s, 3 H), 4.02 (s, 3 H), 7.30 (d, 1 H, $J$ = 5.1 Hz), 7.63 (d, 1 H, 4.7 Hz), 7.74 (t, 1 H, $J$ = 7.8 Hz), 7.86 (d, 1 H, $J$ = 7.4 Hz), 8.30 (d, 1 H, $J$ = 8.2 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): 51.7, 52.5, 112.3, 115.1, 115.8, 117.4, 120.5, 121.4, 124.8, 127.1, 129.5, 131.9, 164.1, 164.6; El-MS ($m/z$): 257.1 Da; MP Range: 90-95 °C.

1,2-Diformyl (2.2.3) cyclazine (5.4)

A flame-dried, nitrogen flushed 500 mL round bottom flask was charged with 3.0 g of dimethyl (2.2.3) cyclazine (11.7 mmol) and 90 mL of methylene chloride. The solution was cooled to -78 °C and 70.0 mL of 1.0 M di(iso-butyl)aluminum hydride in hexanes (70.0 mmol) was added dropwise to the flask. The reaction mixture was kept at -78 °C for 1 hour, then brought to room temperature slowly and stirred at room temperature for 16 hours. The flask was cooled to 0 °C and carefully quenched by the addition of 5 mL of 15% KOH over 30 minutes. The solution was then diluted with 200 mL of 15% KOH and extracted with ethyl acetate (3x 100 mL). The combined organic solution was dried with MgSO$_4$, filtered and the solvent removed in vacuo. The crude dicarbinol was partially purified by filtration through a thick pad of silica using methylene chloride as eluent to remove by products, followed by 4:1 methylene chloride:acetone to collect the diol.

The dicarbinol intermediate was loaded into a 250 mL round bottom flask and dissolved in 100 mL of toluene at 90 °C. To this solution was added 8.14 g of activated MnO$_2$ 58% Mn (93.6 mmol) and the reaction kept at 90 °C for 16 hours. The suspension...
was filtered hot and washed with 150 mL of hot 1,2-dichloroethane. The solvent was removed in vacuo and the solid purified by filtration through a thick pad of silica using 9:1 methylene chloride:acetone as eluent to yield 1.29 g of orange fibers (55%). $^1$H NMR (400 MHz, CDCl$_3$, ppm): 7.57 (d, 1 H, 4.7 Hz), 7.90 (d, 1 H, 5.1 Hz), 8.02 (t, 1 H, J = 7.8 Hz), 8.10 (d, 1 H, J = 7.4), 8.59 (d, 1 H, J = 7.8 Hz), 10.78 (s, 1 H), 10.92 (s, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): 116.9, 118.5, 119.0, 121.40, 121.45, 126.2, 127.3, 128.0, 129.7, 132.5, 185.8, 187.8; El-MS (m/z): 197.0 Da.

3,2'-Indolizino-naphthoquinone (5.5)

A 50 mL round bottom flask was charged with 0.45 g of indolizine (3.8 mmol) and 20 mL of toluene and cooled to 0 °C. To this solution was added 0.60 g of naphthoquinone (3.8 mmol). The solution was stirred vigorously for 30 minutes at 0 °C and 0.99 g of MnO$_2$ 58% Mn (11.4 mmol) was added in one portion. The reaction mixture was brought to room temperature and filtered. The filtrate was washed with 20 mL of methylene chloride and the combined organic solution was concentrated in vacuo. The residue was purified by filtration through a thick pad of silica using methylene chloride as eluent. The blue solid was recrystallized from 1,2-dichloroethane to yield 0.25 g of thin purple needles (24%). $^1$H NMR (400 MHz, CDCl$_3$, ppm): 6.63 (d, 1 H, J = 4.3 Hz), 6.68 (t, 1 H, J = 6.5 Hz), 6.89 (dd, 1 H, $J_1 = 7$ Hz, $J_2 = 8.2$ Hz), 7.18 (s, 1 H), 7.38 (d, 1 H, J = 4.3 Hz), 7.47 (d, 1 H, J = 8.6 Hz), 7.75 (m, 2 H), 8.14 (m, 2 H), 8.38 (d, 1 H, J = 6.6); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): 103.7, 112.4, 119.8, 120.8, 122.8, 125.6, 125.7, 126.5, 126.5, 127.0, 132.3, 132.6, 133.3, 133.9, 137.9, 138.8, 184.6, 184.8; El-MS (m/z): 274.2 Da; MP Range: 200-220 °C.
Anthra[2,3-cd]indolizine-9,10-quinone (5.6)

1,4-Dihydroxy naphthalene was prepared by adding a solution of 2.20 g of sodium dithionite (12.7 mmol) in 30 mL of water to a suspension of 0.5 g of 1,4-naphthoquinone (3.16 mmol) in 50 mL of diethyl ether and 20 mL of methylene chloride. This biphasic solution was then stirred for 16 hours, after which the layers were separated and the organic layer was dried with magnesium sulfate, filtered and the solvent removed in vacuo. The crude hydroquinone was used without purification.

The 1,4-dihydroxy naphthalene intermediate and 0.41 g of 1,2-diformyl (2.2.3) cyclazine (2.08 mmol) were combined in a 100 mL round bottom flask. The flask was heated to 81 °C and 60 mL of tetrahydrofuran, 20 drops of 15% KOH and 10 mL of ethanol were added. The reaction mixture was kept at 81 °C for 16 hours. The reaction mixture was cooled, filtered and the filtrate washed successively with 50 mL of methanol, 50 mL of acetone and 50 mL of ether. The solid was dried at ambient conditions for 24 hours to yield 0.55 g of an insoluble purple powder (54%). MALDI-TOF (m/z): 321.1 Da.

9,10-bistri(iso-propyl)silylethynyl anthra[2,3-cd]indolizine (5.7)

A flame dried, nitrogen purged 100 mL round bottom flask was charged with 1.75 mL of tri(iso-propyl)silyl acetylene (7.78 mmol) and 50 mL of hexanes. The solution was cooled to 0 °C and 2.8 mL of 2.5 M n-butyl lithium in hexanes (7.02 mmol) was added slowly to the flask. The reaction was stirred at 0 °C for 30 minutes, then 0.50 g of anthra[2,3-cd]indolizine-9,10-quinone (1.56 mmol) was added in one portion. The reaction mixture was brought to room temperature and 10 mL of dry tetrahydrofuran was
added to the flask. The reaction mixture was kept at room temperature for 16 hours, then the reaction was quenched with 1 mL of water. The solvent was removed in vacuo and the residue was purified by filtration through a thick pad of silica using hexanes to collect residual acetylene, followed by 1:1 hexanes:methylene chloride to collect the acene diol.

The acene diol intermediate was dissolved in 50 mL of tetrahydrofuran and 20 mL of water, to which 1.58 g of tin(II)chloride dehydrate was added in one portion. The solution was stirred at room temperature for 1 hour, after which the solution was extracted with methylene chloride (3x 50 mL). The combined organic solutions were washed with water (3x 50 mL), dried with MgSO₄ and the solvent removed in vacuo. The crude product was purified by filtration through a thick pad of silica using 9:1 hexanes:methylene chloride as eluent. The title compound was collected as 0.85 g of a dark-red to purple solid (83%) and recrystallized from hexanes to yield 0.50 g of dark green blocks (49%). ¹H NMR (400 MHz, CDCl₃, ppm): 1.35-1.37 (m, 42 H), 7.55-7.67 (m, 5 H), 7.89 (d, 1H, 7 Hz), 7.93 (d, 1 H, 8.6 Hz), 8.72 (d, 2 H, J = 8.2 Hz), 9.39 (s, 1 H), 9.78 (s, 1 H); ¹³C NMR (100 MHz, CDCl₃, ppm): 27.0, 34.3, 119.2, 119.4, 119.9, 120.69, 120.76, 121.6, 126.3, 130.8, 132.1, 133.6, 135.0, 135.3, 137.0, 137.6, 141.6, 142.3, 142.5, 142.7, 143.6, 144.4, 145.2, 146.8, 147.2, 147.4, 148.0; MALDI-TOF (m/z): 652.5 Da; MP Range: 220-225 °C.

Tetraceno[2,3-cd]indolizine-5,12-quinone (5.8)

1,4-Dihydroxy anthracene was prepared by adding a solution of 1.67 g of sodium dithionite (9.61 mmol) in 50 mL of water to a suspension of 0.5 g of 1,4-anthraquinone (2.40 mmol) in 100 mL of diethyl ether and 30 mL of methylene chloride. This biphasic
solution was then stirred for 16 hours, after which the layers were separated and the organic layer was dried with magnesium sulfate, filtered and the solvent removed in vacuo. The crude hydroquinone was used without purification.

The 1,4-dihydroxy anthracene intermediate and 0.47 g of 1,2-diformyl (2.2.3) cyclazine (2.40 mmol) were combined in a 100 mL round bottom flask. The flask was heated to 81 °C and 50 mL of tetrahydrofuran, 20 drops of 15% KOH and 10 mL of ethanol were added. The reaction mixture was kept at 81 °C for 48 hours. The reaction mixture was cooled, filtered and the filtrate washed successively with 50 mL of methanol, 50 mL of acetone and 50 mL of ether. The solid was dried at ambient conditions for 24 hours to yield 0.57 g of an insoluble red solid (63%). MALDI-TOF (m/z): M = 372.2 Da.

5,12-bistri(iso-propyl)silylethynyl tetraceno[2,3-cd]indolizine (5.7)

A flame dried, nitrogen purged 100 mL round bottom flask was charged with 0.60 mL of tri(iso-propyl)silylacetylene (2.69 mmol) and 25 mL of hexanes. The solution was cooled to 0 °C and 0.97 mL of 2.5 M n-butyl lithium in hexanes (2.43 mmol) was added slowly to the flask. The reaction mixture was stirred at 0 °C for 30 minutes, then 0.20 g of tetraceno[2,3-cd]indolizine-5,12-quinone (0.54 mmol) was added in one portion. The reaction mixture was brought to room temperature and 5 mL of dry tetrahydrofuran was added to the flask. The reaction mixture was kept at room temperature for 16 hours, then quenched with 10 drops of water. The solvent was removed in vacuo and the residue was purified by filtration through a thick pad of silica using hexanes to collect residual acetylene, followed by 1:1 hexanes:methylene chloride to collect the acene diol.
The acene diol intermediate was dissolved in 35 mL of methanol to which a solution of 0.55 g of tin(II)chloride dihydrate (2.43 mmol) was added in one portion. The solution was stirred at room temperature for 1 hour, after which a green solid was collected by filtration. The solid was washed with 50 mL of methanol and dried under ambient conditions for 24 hours. 5.7 was collected as 0.30 g of a green solid. Attempts to purify by chromatography or recrystallization resulted in no product being collected. Absorption characteristics likely from dimers were seen by UV-vis even in fresh solutions.

**Anthra[2,3-cd: 6,7-cd]diindolizine-9,10-quinone (5.10)**

A 100 mL round bottom flask was charged with 0.15 g of 1,2-diformyl (2.2.3) cyclazine (0.76 mmol) and 0.043 g of 1,4-cyclohexanedione (0.38 mmol). These reagents were dissolved in 20 mL of tetrahydrofuran and 5 mL of ethanol at reflux, and 10 drops of 15% KOH were added to the solution. The reaction mixture was stirred at room temperature for 16 hours, then filtered. The filtrate was washed successively with 50 mL of methanol, 50 mL of acetone and 50 mL of ether. The solid was dried at ambient conditions to yield 0.11 g of a dark red solid (66%). MALDI-TOF (m/z): 434.10 Da.

**9,10-bistri(iso-butyl)silyl ethynyl anthra[2,3-cd: 6,7-cd]diindolizine (5.11)**

A flame dried, nitrogen purged 50 mL round bottom flask was charged with 0.29 g of tri(iso-butyl)silyl acetylene (1.27 mmol) and 10 mL of hexanes. The solution was cooled to 0 °C and 0.46 mL of 2.5 M n-butyl lithium in hexanes (1.14 mmol) was added slowly to the flask. The reaction mixture was stirred at 0 °C for 30 minutes, then 0.11 g of anthra[2,3-cd: 6,7-cd]diindolizine-9,10-quinone (0.25 mmol) was added in one portion. The reaction
mixture was brought to room temperature and 4 mL of dry tetrahydrofuran was added to the flask. The reaction mixture was kept at room temperature for 16 hours, then the reaction was quenched with 0.5 mL of water. The solvent was removed \textit{in vacuo} and the residue was purified by filtration through a thick pad of silica using hexanes to collect residual acetylene, followed by 1:1 hexanes:methylene chloride to collect the acene diol.

The acene diol intermediate was dissolved in 20 mL of tetrahydrofuran and 5 mL of 10\% HCl to which 0.26 g of tin(II)chloride dihydrate (1.14 mmol) was added in one portion. The solution was stirred at room temperature for 1 hour, after which the solution was extracted with methylene chloride (3x 10 mL). The combined organics were washed with water (3x 10 mL), dried with MgSO$_4$ and the solvent removed \textit{in vacuo}. The residue was filtered through a pad of silica using 9:1 hexanes:methylene chloride as eluent to collect 0.04 g of dark green solid. Absorption characteristics likely from dimers were seen by UV-vis even in fresh solutions.

5.8 References


6 Summary

Acenes and their analogues are a versatile series of frameworks for organic semiconductors. The optical and electronic properties of these materials are tunable to a large degree by variation of the length of the acene and can be further tuned using substituents. Increasing the number of linearly fused aromatic rings increases the energy of the highest occupied molecular orbital (HOMO) and decreases the energy of the lowest occupied molecular orbital (LUMO), leading to decreasing optical and electronic gaps. The use of substituents affords the ability to further tune the electronics of the chromophore in addition to the ability to target packing motifs in the solid state.

These properties were explored in Chapter 2, leading the observation that electron withdrawing groups lower the energy of the LUMO energy while having little to no effect on the HOMO of the molecule. The use of bulky alkylsilylenyl groups was used to change the crystal packing of the molecules to target “sandwich herringbone” packing motifs. Though this motif was observed for one of the tetracene nitrile derivatives, the LUMO of these molecules was too high in energy to make an appropriate acceptor for poly(3-hexylthiophene) (P3HT) in organic photovoltaic (OPV) devices. The energy offset between the LUMOs of these two materials is too small to facilitate effective charge transfer between them. The dicyanovinyl derivatives of both pentacene and tetracene did possess appropriate LUMO energies to use as electron acceptors for use with P3HT, but the sandwich herringbone packing motif proved elusive, and devices fabricated using these materials performed poorly with power conversion efficiencies (PCE) on the order of $10^{-2}$% and lower.
The use of anthrathiophene and benzo[1,2-b:4,5-b’]dithioephene (BDT) molecular electron acceptors containing benzothiadiazole with strong electron acceptors were likewise ill-suited for use in organic photovoltaic devices in conjunction with P3HT. These devices had efficiencies like those of the electron deficient acenes described previously. A new substitution pattern for BDT is described further into Chapter 3 where one substituent was added to the central ring of BDT instead of the standard symmetrical substitution of two substituents. This allowed for the synthesis of linear analogues of bend molecular electron donors described in the literature.

The use of BDT instead of dithiophenesilole (DTS) allowed for exploration of the effect of molecular geometry on device performance. Bent molecular geometry has been attributed to the effectiveness of large molecular donors in OPV devices. Linearizing these molecules is then expected to decrease OPV efficiencies. The linearized molecule did exhibit lower PCE (2.9%) than the bent molecule (7.2%), due to a 60% decrease in current density for devices employing the linear molecule. The decrease in current density may be attributed to the lack of bend in the molecule, reducing the tendency for inter-stack communication often observed in crystal structures of bent molecules. It was not possible to observe this disruption of intermolecular interactions directly, since x-ray quality single crystals could not be grown for the linear molecule, and could only be inferred. It was also expected that the symmetrical substitution of the BDT group would further disrupt molecular interactions, and as a confirmation, no photovoltaic response was observed in devices fabricated with this material.
The use of non-traditional heteroaromatic units in acene-like molecules was explored in Chapters 4 and 5 of this report. Indolizine is the most basic form of this structural motif, and the placement of the nitrogen atom at the bridgehead of the bicyclic unit fully incorporates the nitrogen lone pair into the $\pi$-conjugation, resulting in a naphthalene analogue. Incorporating indolizine into a larger aromatic framework resulted in molecules that possess similar optical and electronic properties of their linear acene counterparts.

The first example of acene-like bent molecules was the benzo[2,3-b:5,6-b']diindolizine (BDI) chromophore, which closely mimics the optical properties of pentacene. Despite the zig-zag shape of the BDI molecule, the $\pi$-electron system appears fully conjugated around the whole of the chromophore, leading to the pentacene-like absorption and emission profiles in the visible region of the electromagnetic spectrum. The bridgehead placement of the nitrogen atoms in the chromophore allows for this conjugation, which is absent in similarly shaped chromophores such as benzo[2,3-b:5,6-b']bisbenzothiophene BBBT. The BBBT molecules exhibit properties of their longest linear region, anthracene in this case.

To target molecules suitable for transistor studies, derivatives that exhibit 2-D “brick-work” packing motifs were targeted. Triethyldisilylethynyl (TES), propyldiethyldisilylethynyl (PDES) and allyldiethyldisilylethynyl (ADES) substituents all exhibited the brick-work packing motif, while groups larger or smaller lead to 1-D “slip-stack” packing motifs. Transfer integrals between molecules with 2-D motifs were comparable to those calculated for TIPS-pentacene, with TES having the highest and transfer integrals decreasing with increasing size of the alkylsilyl group. Solution processed devices fabricated from these
materials had maximum mobility of 0.1 mA/cm² and could not be improved further due to limited solubility of the BDI molecules.

To increase the utility of the indolizine unit, 1,2-diformyl (2.2.2) cyclazine was synthesized for incorporation into acene-like frameworks. The cyclazine unit is a tricyclic moiety with a nitrogen atom at the central bridgehead position between all three rings. Access to the ortho-dialdehyde derivatives allows for use of aldol condensations to produce acene quinones with indolizine end-caps. Fully conjugated indolizine capped acenes, much like BDI, have significant bathochromic shifts in the absorption and emission profiles as compared to the linear portion of the molecule chromophore. This observation suggests that the bridgehead positioning of nitrogen atoms has a general effect of expanding ring currents around bends or non-linearity in aromatic frameworks.

The stability of the indolizine capped acenes decreases significantly with increase in chromophore length. The indolizine capped anthracene molecule was stable and could be isolated and studied, but the indolizine capped tetracene and the diindolizine capped anthracene were very difficult to isolate. These larger molecules were obtained in very small quantities as their degradation products. The use of electron withdrawing substituents to decrease the LUMO energies of these molecules or the use of bulky substituents to prevent contact of the chromophores may improve stability, and these strategies should be pursued in further investigations of these molecules.
APPENDIX: LIST OF ABBREVIATIONS

\(^1\text{H} \text{NMR}\)  proton nuclear magnetic resonance  
\(^{13}\text{C} \text{NMR}\)  carbon-13 nuclear magnetic resonance  
1-D  one dimensional  
2-D  two dimensional  
Å  angstrom  
A  acceptor  
A  amps  
Ac\(_2\text{O}\)  acetic anhydride  
AcCl  acetyl chloride  
ACN  acetonitrile  
ADES  allyl diethylsilyl  
ADES-BDI  1,4-bisallyl diethylsilyl ethynyl benzo[2,3-b:5,6-b’]diindolizine  
ADT  anthradithiophene  
Ag/AgCl  silver/silver(I) chloride  
AIA  anthra[2,3-cd]indolizine  
AIBN  azobisisobutyronitrile  
AlCl\(_3\)  aluminum chloride  
AM1.5  air mass 1.5 solar spectral irradiance  
Ar  aryl group  
BBr\(_3\)  boron tribromide  
BBBT  benzobisbenzothiophene  
BDI  benzo[2,3-b:5,6-b’]diindolizine  
BDT  benzo[1,2-b:4,5-b’]dithiophene  
BDT-Qn  benzo[1,2-b:4,5-b’]dithiophene 4,8-quinone  
BHJ  bulk heterojunction  
Bu\(_4\text{NPF}_6\)  tetrabutylammonium hexafluorophosphate  
CHCl\(_3\)  chloroform  
Ci  capacitance of dielectric  
cm  centimeter  
CN-Pn  cyano pentacene  
CN-TCPS-Pn  2-cyano-6,13-bistri(cyclo-pentyl)silyl ethynyl pentacene  
CN-TCPS-Tt  2-cyano-6,11-bistri(cyclo-pentyl)silyl ethynyl tetracene  
CN-TIBS-Tt  2-cyano-6,11-bistri(iso-butyl)silyl ethynyl tetracene  
CN-Tt  cyano tetracene  
CO\(_2\)  carbon dioxide  
Cu(NO\(_3\))\(_2\) 3H\(_2\)O  cupric nitrate trihydrate  
CuI  copper(I) iodide  
D  donor  
D-A  donor-acceptor  
DABCO  1,4-diazabicyclo[2.2.2]octane  
DCE  1,2-dichloroethane  
DCM  dichloromethane/methylene chloride
DCV  dicyanovinyl
DCV-Pn dicyanovinyl pentacene
DCV-TCPS-Pn 2-dicyanovinyl-6,13-bistri(cyclo-pentyl)silylthyl pentacene
DCV-TIPS-Pn 2-dicyanovinyl-6,13-bistri(iso-propyl)silylthyl pentacene
DCV-TCPS-Tt 2-dicyanovinyl-6-11-bistri(cyclo-pentyl)silylthyl tetracene
DCV-Tt dicyanovinyl tetracene
DEHOB 1,3-di(2-ethylhexyloxy)benzene
DEHOB-BDT 4-[3,5-di(2-ethylhexyloxy) benzene] benzo[1,2-b:4,5-b’]dithiophene
DEHOB-BDT-BT-ID 6’-indanedione-2,3’-benzothiadiazole-7-[3,5-di(2-ethylhexyloxy) benzene] benzo[1,2-b:4,5-b’]dithiophene
DEHOB-TIPS-BDT 4-[3,5-di(2-ethylhexyloxy) benzene] 2,6-bistri(iso-propyl)silyl benzo[1,2-b:4,5-b’]dithiophene
DEHOB-Bpin 3,5-di(2-ethylhexyloxy) benzene pinacolatoboron
DEMS diethylmethylsilyl
DEMS-BDI 1,4-bisdiethylmethylsilylthyl pentacene benzo[2,3-b:5,6-b’]diindolizine
DFT density functional theory
DHB 2,5-dihydroxybenzoic acid
DIBAL-H di(iso-butyl)aluminum hydride
DIO 1,8-diiodooctane
DMF N,N-dimethyl formamide
DMSO dimethyl sulf oxide
DSC differential scanning calorimetry
DTS dithieno[2,3-b:2’,3’-b]silole
ΔE difference in energy
e elemental charge of an electron
e– an electron
EA-FBT-bTh ethyl 3-acrylo-4-fluoro-6-(5’-hexyl-2,2’-bithiophene) benzothiadiazole
Et3N triethylamine
EtOH ethanol
eV electron volt
EWG electron withdrawing group
Fc/Fc+ ferrocene/ferrocenium
FF fill factor
FI fluorescence
FMO frontier molecular orbital
g grams
GC-MS gas chromatography-mass spectroscopy
H2SO4 sulfuric acid
HBr hydrobromic acid
HCl hydrochloric acid
HOMO highest occupied molecular orbital
hv incident light
(1D)1/2 square root of drain current
IC internal conversion
1D drain current
1IMP current at maximum power
1SC short circuit current
ISC intersystem crossing
ITO: indium tin oxide
I-V: current-voltage
J_{SC}: short circuit current density
K_2CO_3: potassium carbonate
KAUST: King Abdullah University of Science and Technology
KCN: potassium cyanide
KHMD: potassium hexamethyldisilazide
KOAc: potassium acetate
kT: Boltzmann constant times temperature/thermal energy
kWh: kilowatt hours
L: length of conductance channel
LiHMDS: lithium hexamethyldisilazide
LUMO: lowest unoccupied molecular orbital
µ: mobility
M: molarity
mA: milliamps
MALDI-TOF: matrix assisted LASER desorption ionization-time of flight
Me_3SnCl: trimethyltin chloride
MeOH: methanol
meV: millielectron volt
mg: milligrams
MgSO_4: magnesium sulfate
MHz: megahertz
mL: milliliter
mmol: millimoles
MnO_2: manganese dioxide
N (N-substituted): nitrogen
H: power conversion efficiency
n-BuLi: n-butyllithium
NaOH: sodium hydroxide
NBS: N-bromosuccinimide
NIR: near infrared
NIS: N-iodosuccinimide
nm: nanometer
NO_2-BDT: 4-nitro benzo[1,2-b:4,5-b’]dithiophene
ns: nanosecond
OFET: organic field effect transistor
OPV: organic photovoltaic
P3HT: poly(3-hexylthiophene)
PC60BM: phenyl-C_{61}-butyric acid methyl ester
PCE: power conversion efficiency
Pd_2dba_3: tris(dibenzylidineacetone)dipalladium(0)
Pdc_{3}(PPh_3)_2: bis(triphenylphosphine)palladium(II) dichloride
PDES: propyldiethylysilyl
PDES-BDI: 1,4-bispropyldiethylysilylethylene benzo[2,3-b:5,6-b’]diindolizine
PDI: polydispersity index/molecular weight distribution
Pd(PPh_3)_4: tetrakistriphenylphosphine palladium(0)
PEDOT:PSS: poly(3,4-ethylenedioxythiophene) polystyrene sulfonate
PESA  photo electron spectroscopy in air
PFBT  2,3,4,5,6-pentafluorobenzenethiol
Ph   phosphorescence
P_{in}  incident power
PPh_{3}  triphenylphosphine
ps   picosecond
PV   photovoltaic
RCCLi  various substituted lithium acetylides
R_{p}  shunt resistance
R_{s}  series resistance
S_{0}  ground singlet state
S_{1}  first excited singlet state
SF   singlet fission
SnCl_{2}  tin(II) chloride
t-BuLi  tert-butyl lithium
T_{1}  first excited triplet state
TA   anthra[2,3-b]thiophene
TBAF  tetrabutylammonium fluoride
tBu   tert-butyl
tBu-BDI  1,4-bis(tert-butyl)ethynyl benzo[2,3-b:5,6-b']diindolizine
TCPS tri(cyclo-pentyl)silyl
TES   triethylsilyl
TES-BDI  1,4-bistriethylsilyl ethynyl benzo[2,3-b:5,6-b']diindolizine
TFA   trfluoroacetic acid
THF   tetrahydrofuran
TIBS-DAIA  9,10-bistri(iso-butyl)silyl ethynyl anthra[2,3-cd: 6,7-cd]diindolizine
TIBS-TA-BT-DCV  2,3'-(6'-dicyanovinylbenzothiadiazole)-5,10-bistri(iso-butyl)silyl ethynyl anthrathiophene
TIBSCCLI  tri(iso-butyl)silyl lithium acetylide
TIPS   tri(iso-propyl)silyl
TIPS-AIA  9,10-bistri(iso-propyl)silyl ethynyl anthra[2,3-cd]indolizine
TIPS-AIT  5,12-bistri(iso-propyl)silyl ethynyl tetraceno[2,3-cd]indolizine
TIPS-BDI  1,4-bistri(iso-propyl)silyl ethynyl benzo[2,3-b:5,6-b']diindolizine
TIPS-BDT  2,6-bistri(iso-propyl)silyl benzo[1,2-b:4,5-b']dithiophene
TIPSCCLI  tri(iso-propyl)silyl lithium acetylide
TLC   thin layer chromatography
TMEDA N,N,N',N'-tetramethyl ethylenediamine
TMS   trimethylsilyl
TMS-BDI  1,4-bistrtrimethylsilyl ethynyl benzo[2,3-b:5,6-b']diindolizine
TMS-BDT  2,6-bistrtrimethylsilyl benzo[1,2-b:4,5-b']dithiophene
TMSA   trimethylsilyl acetylene
TMSCI trimethylsilyl chloride
UV-vis ultraviolet-visible
V   volts
V_{D}  drain voltage
V_{G}  gate voltage
V_{MP}  voltage at maximum power
V_{OC}  open circuit voltage
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<td>$V_{TH}$</td>
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<td>$W$</td>
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<td>$\text{Zn(CN)}_2$</td>
<td>zinc(II) cyanide</td>
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<tr>
<td>$\Omega$</td>
<td>ohms (unit of electrical resistance)</td>
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