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CHEMICAL STABILITY AND PERFORMANCE INFLUENCE OF CHOICE SUBSTITUENTS AND CORE CONJUGATION OF ORGANIC SEMICONDUCTORS

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CHEMICAL STABILITY AND PERFORMANCE INFLUENCE OF CHOICE SUBSTITUENTS AND CORE CONJUGATION OF ORGANIC SEMICONDUCTORS

A Dissertation Presented
By
JACK THANH LY

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

DOCTOR OF PHILOSOPHY

February 2019

Polymer Science and Engineering
CHEMICAL STABILITY AND PERFORMANCE INFLUENCE OF CHOICE
SUBSTITUENTS AND CORE CONJUGATION OF ORGANIC SEMICONDUCTORS

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By

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ACKNOWLEDGEMENTS

First and foremost, I would like to thank the Briseno group members who was present during my time at the University of Massachusetts Amherst. The culture of critically analyzing data and questioning motive and results has developed me to be the scientist I am today. I came into the group with a strong knowledge and background in fundamental polymer science and chemistry but was rather ignorant in the niche field of organic semiconductors. The breadth of knowledge needed to carry out an impactful report of new and effective active organic materials in terms of electronic applications needed much collaboration between chemists, physicists, and engineers alike.

Dr. Lei Zhang, now at a Professor at the Beijing University of Chemical Technology, personally mentored and guided me in the labs to develop many synthesis techniques that will be invaluable to me for the rest of my career. Benjamin Cherniawski and Edmund Burnett, members of the entering PSE class of 2012, represented great examples of critical thought and designing certain experiments to ensure results that answer meaningful questions. Additionally, their criticism immensely humbled me and made me into an effective scientist.

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guidance of the PI. This quality is not often seen, giving me the relative unique, unanchored type of experience in scientific research.

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To my family and specifically my brother-in-law, Dr. William Brooks, I thank you for your everlasting support. Will, you introduced the world of polymers to me at a young age and convinced me to keep pursuing beyond my bachelor’s degree.
ABSTRACT

STABILITY AND PERFORMANCE INFLUENCE OF CHOICE SUBSTITUENTS AND
CORE CONJUGATION OF ORGANIC SEMICONDUCTORS

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Realizing organic based active materials for electronic devices, such as thin film transistors and photovoltaics, has been long sought after. Advancement in the field driven by chemists, engineers, and physicists alike have bolstered organic based semiconductor performance levels to rival those of traditional inorganic amorphous silicon-based devices. Within the field of organic semiconductors (OSC), two categories of active materials may be generalized: (1) polymer and (2) small molecule semiconductors. Each class of OSC inherently have their own advantages and disadvantages. Polymer semiconductors (PSC) allow a wide range in tunability via choice monomers and side chain engineering to illicit desirable energy levels and morphological arrangements in the thin film. However, due its polymeric nature, long range crystallinity is limited. Thus, its performance is heavily hindered compared to the much more crystalline small molecule adducts. Though small molecule semiconductors do indeed achieve high performance in the device, design rules for realizing such performance benchmarks render this class of materials to be susceptible to degradation in ambient conditions, namely, via photo-oxidation
In this dissertation, I address the issues of creating high performing polymer semiconductors in a thin film transistor device via tuning dihedral angles of the conjugated core. A bottom up synthetic approach utilizing planarizing torsion angle inducing moieties is exampled here between acceptor-donor and acceptor-acceptor designs. These findings may be further extended in realizing future high performing PSC. Regarding conjugated small molecules, I report the impact of employing a combination of different aryl and ethynyl substituents in tetra-substituted tetracenes upon photo-oxidative stability and the cycloreversion of oxidized chromophores to regenerate the parent molecule. Synthesis of target molecules presented in this dissertation is reviewed and presented. Techniques to gauge optoelectronic properties of formed OSC includes a combination of cyclic voltammetry, ultra-violet visible spectroscopy, ultra-violet photon electron spectroscopy, and time resolved spectral techniques. Collaborative efforts for forming functional devices and investigate underlying fundamental physics of device properties and photo-physics are also presented in this dissertation. Lessons learned from this work will help guide the design of future OSC for effective performance benchmarks and stability.
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CHAPTER 1

INTRODUCTION

1.1 Early History of Organic Semiconductors

Organic based semiconductors have a rather intriguing history that dates to the early mid-19th century. The first evidence of a partially conductive material was achieved by the anodic oxidation of aniline in sulfuric acid. Analytical chemist, Henry Letheby, described the oxidized form to be deep blue color – presumably the first example of acid doped poly(aniline) in which was thoroughly described over a half a century later by Alan MacDiarmid.2,3 In the mid-20th century, researchers formed semiconducting polycyclic aromatic small-molecule compounds when complexed with halide salts.4,5

Kallmann and Pope first discovered organic materials can become semiconducting when charge carriers are injected at the electrode in anthracene crystals.6,7 The electrode in their 1960 report comprised of an iodine containing electrolyte where the application of a positive bias formed a current. In fundamental solid-state physics, the minimum thermodynamic energy required to remove an electron from a solid to the solid’s surface in vacuum is referred to as the work function. Understanding the work function parameter of the electrode controls the injection of charges through the organic crystal, a metal solid with an appropriate work function may be employed rather than an electrolyte solution. This discovery of injecting charges from an electrode lead to the development of organic light-emitting when holes and electrons from opposite metal contacts radiatively recombined.8

In the early 1970s, it was found the inorganic polymer, poly(sulfur nitride) (SN)x, was super conductive at extremely low temperatures. Alan Heeger and Alan MacDiarmid
collaborated to study metallic properties (SN)$_x$, but soon shifted attention to polyacetylenes after MacDiarmid meeting Hideki Shirakawa in Tokyo. Their collaborative work upon poly(acetylenes) paved way to the understanding and development of conductive polymers. Shirakawa adapted Ziegler-Natta polymerization of acetylene to make well defined films of poly(acetylenes) never achieved before.\textsuperscript{9} His procedure allowed silvery all-trans-poly(acetylenes) with modest conductivity of $10^{-3}$-10$^{-2}$ S m$^{-1}$. With his experience from the (SN)$_x$ materials, MacDiarmid wanted to modify the poly(acetylene) by iodine treatment. Heeger lab measured iodide treated trans-poly(acetylene) conductivity of 3000 S m$^{-1}$, seven orders of magnitude increase.\textsuperscript{10-12} Many pioneering work followed yielded other polymers: poly(pyrrole), poly(thiophene), poly(phenylenevinylene), and poly(aniline), \textbf{Figure 1.1} Poly(acetylene) remains the most crystalline conductive polymer but is not the first to be commercialized due to ease of oxidation by air and sensitively to moisture. Polypyrrole and polythiophene differ from polyacetylene most notably in that they may be synthesized directly in doped form and very stable in air. Their collective pioneering work upon conductive polymers was rewarded with the 2000 Nobel Prize in Chemistry.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figures.png}
\caption{Early examples of polymer semiconductors}
\end{figure}
1.2 Fundamental Elements of Semiconductors

Semiconductor can fundamentally be described by its electronic band structure. In solid state physics, the electronic band structure of a solid describes the range of energies that an electron may or may not have. Allowed electron energies are referred to as energy bands and forbidden energy ranges are known as band gaps, $E_g$. The energy band that lies closest to the fermi level is referred to as the valence band and conduction band. Fermi level is the thermodynamic work required to add an electron into a system. Where these energy bands lie to one another determines a materials category and function of a conductor, semiconductor, or insulator (Figure 1.2).

![Figure 1.2. Band structure of conducting, semiconducting, and insulating materials](image)

Electron conductivity of a solid depends upon the capacity to flow electrons from the valence to conduction band. Distinction of energy bands of a conducting solid (such as metals) is meaningless due to the absence of the bandgap. This renders the material to be intrinsically conducting and requires negligible to no work to enable electrical conductivity. As the nomenclature hints, semiconductors are not inherently conductive. A small band gap describes the band structure of the material, typically within a of 0.1 to 4 eV. To enable current through a semiconductor, an electron must overcome this energetic
barrier to be promoted from the valence to conduction band. This process is enabled via an external energy, such as heat or magnetic field. However, if the $E_g$ is sufficiently large ($> 5$ eV), valence electrons are held tight, rendering a material to be an insulator.

### 1.3 Design of Organic Semiconductors

The three fundamental elements for designing an effective organic semiconductor consists of the (1) electronic structure, (2) molecular structure, and (3) morphology. Analogous to the discussion of the valence and conduction band, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) is used to describe an organic semiconductor’s electronic structure and band gap. These energy levels and relationship to each other reflects a material’s optoelectronic properties, such as range of light absorbed/emitted and ease of charges to be injected or extracted from the OSC active layer.

**Figure 1.3.** Electronic Parameters of a band structure.

HOMO and LUMO energy levels are commonly described as the ionization potential (IP) and electron affinity (EA), respectively. These values can be experimentally...
determined by electrochemical redox measurements where the onset of oxidation and reduction may yield the IP and EA through the following relationship:

\[
\text{IP}_{CV} = - (E_{\text{ox} \text{ onset}} - E_{\text{Fc/Fc}^+}^{1/2} + 4.8) \text{ eV}
\] (1.1)

\[
\text{EA}_{CV} = - (E_{\text{red} \text{ onset}} - E_{\text{Fc/Fc}^+}^{1/2} + 4.8) \text{ eV}
\] (1.2)

Where \( E_{\text{red} \text{ onset}} \) and \( E_{\text{ox} \text{ onset}} \) are the potential in which the onset of reduction and oxidation occurs and \( E_{\text{Fc/Fc}^+}^{1/2} \) is the half-oxidation potential of the external standard, ferrocene. If both values are obtained, the band gap may be determined from the difference of the two values. However, it is common to only observe one of these values, so employing other complimentary characterization techniques have are also been used to determine electronic structure.

Ultra-violet to visible light (UV-Vis) spectroscopy may also give rise to describing the optical bandgap of OSCs. Following the simple relationship of photonic energy to wavelength of light, \( E = (hc)/\lambda \), the optical \( E_g \) can be determined by

\[
E_g,\text{opt} \text{ (eV)} = 1240 \text{ (eV nm)/}\lambda_{\text{onset}} \text{ (nm)}
\] (1.3)

where \( \lambda_{\text{onset}} \) is the onset of light absorption. Though this gives no notion to LUMO and HOMO levels, an optically determined \( E_g \) may be used in combination of either IP or EA from cyclic voltammetry to give the missing electronic parameter by

\[
E_g = \text{IP} - \text{EA}
\] (1.4)

Advanced spectroscopy techniques may also be employed to directly measure the IP and EA energy levels of solid surfaces. Ultra-violet photoelectron spectroscopy (UPS) measures the binding energy of an electron ejected from the HOMO. Electrons from the high lying molecular orbital, otherwise known as valance region, is excited via a known high energy light source (>10 eV) in ultra-vacuum conditions. Secondary cutoff region
spectra can be drawn using the kinetic energy scale so the material work function (WF) can be identified directly. Onset of electron collection from the HOMO on the binding energy scale can then be combine with WF to yield the IP as expressed below.

\[
\text{IP} = \text{WF} + \text{HOMO}
\]

Inverse photoemission spectroscopy (IPES) is a complementary technique that emits a concentrated beam of electrons at a well-defined energy (< 20 eV) to a sample surface. The beamed electrons are coupled to a high lying unoccupied molecular orbit which subsequently relaxes to the LUMO, then radiatively emits. Difference between emission energies and source electron energy yields energy of lower unoccupied states. Thus, the onset of emission collected can be considered the LUMO. The EA is then calculated as

\[
\text{EA} = \text{WF} - \text{LUMO}
\]

Where the work function is obtained from the UPS measurements, as previously mentioned.

The HOMO and LUMO levels described thus far are completely dependent upon the molecular framework and conjugation of organic semiconductors. As the number and density of \(\pi\)-electrons increases, electrons fill discrete HOMO and create accompanying LUMO levels that trends towards convergence, resulting in a smaller bandgap. To tune these discrete levels, manipulation of electron density of conjugated core may be afforded with either electron rich or electron poor building blocks/motifs.

1.3.1 N-type vs P-type Building Blocks

Within the field organic semiconductors, the molecular design may fall into either of the two categories depending upon the electron density: P-type or N-type molecules. P-type materials are described to having a high electron density, thus an energetically low
lying HOMO and ionization potential relative to vacuum level (0 eV), Figure 1.3. To the opposite end, N-type material are defined to be electron poor with high lying LUMO and electron affinity energies relative to vacuum level. Referring to examples in Figure 1.4 below, it is immediately apparent that what enables a N-type material over P-type characteristics is the presence of electron withdrawing moieties within or flanking the conjugated structure. Electron withdrawing groups typically include, but not limited to, imides, amides, fluorides, and cyano groups.

Figure 1.4. Examples of organic p-type and n-type semiconductors

Though we may identify the HOMO and LUMO of OSCs, their preferable transport behavior of either holes or electrons identifies the organic species to be either P-type or N-
type materials, respectively. This does have a direct correlation to the electron structure as the frontier molecular orbital closest to the fermi level of the electrode in the device determines the mode of generating current and what kind of charge carrier is transported. If the HOMO/IP energy level is closest to the fermi level of the contact electrodes, such as gold, the OSC will prefer to transport holes thus being a P-type material. The same can be said for N-type materials with LUMO level being closest to the contact electrode, Figure 1.5.

![Figure 1.5. Electronic structure example for p-type (pentacene) and n-type (F16CuPc) OSCs.](image)

It should be noted that the offset of the frontier orbital energy level to the metal contact, otherwise known as the charge injection barrier, needs to be minimalized to afford efficient charge collection in a device. If this offset is too large, efficiency and performance of a device can diminish or completely not function.

Synthetic efforts may also enable the combination of P-type and N-type response via a bottom up approach utilizing both design rules. Below in Figure 1.6 is a hybrid, ambipolar dithenonaphthalene diimde example by combining the molecular designs of P-
type dithienonapthalene and N-type naphthalene diimde. This formed hybridized contains both attributes of P-type and N-type electronic structure with low lying IP and high lying EA energies, thus also affording a smaller bandgap. Combination of electron dense and deficient moieties is one of the common approaches to tuning and adapting the energetic bandgap.

**Figure 1.6** Band structure engineering of OSCs via molecular design to form hybrid materials.

1.3.2 Factors in OSC Bandgap Engineering

Thus far, the concept of tuning the frontier molecular orbital energy, and ultimately the bandgap, have been described via electron density of the conjugate core. The increase or decrease of electron density of a molecular core may also be enabled by the side group electronic inductive or mesomeric effect. This is one of many contributions that may affect the energetic bandgap. Considering a typical OSC molecular design adopts a linear conjugated form, the following variables in terms of energy should be considered that cumulatively impact the \( E_g \): (1) bond length alternation, (2) deviation from planarity, (3) resonance structures of \( \pi \)-electrons, (4) inductive/mesomeric effect of side groups, and (5) intermolecular electronic coupling in the solid state. Their sum contribution may be figuratively expressed below:

\[
E_g = E^{Sr} + E^0 + E^{Res} + E^{Sub} + E^{int}
\]  

(1.7)
The inductive or mesomeric effect of side groups is denoted in the form of \( E_{\text{Sub}} \). A classic example of this effect is often shown in the choice side group of C3 position of polythiophenes. If there is a propensity of having an electron donating or electron withdrawing group, the P-type or N-type characteristic of electronic structure is enhanced via upshift or downshift of the HOMO and LUMO, respectively.

![Figure 1.7. Side group contribution \((E_{\text{Sub}})\) to perturbing HOMO and LUMO energy levels.](image)

Of course, the expansion of the aromatic group orthogonal to the conjugated backbone may also play a large role in effecting the OSC \( E_g \).

First, the existence of alternating bond lengths of single and double bonds along the polymer chain have the largest contribution to a finite \( E_g \). The energy relating to bond length alternation \( (E_\delta r) \) is a consequence of Peierls distortion theorem that states perfect 1D lattice is unstable, thus favorable distortion along a linear OSC localizes \( \pi \)-electron coupling and creates an inherent limitation to the effective conjugation length. Additionally, mesomeric (aromatic or quinoidal) forms of polyaromatic polymers differs in their respective ground state energy forms, also attributing to the energy associated with bond length alternation.

Although \( E_\delta r \) is the largest contribution to a finite bandgap, the single bonds that connects aromatic/conjugated moieties to one another allows the occurrence of interannular rotations. Because of the delocalization of \( \pi \) orbitals heavily depends upon
torsional angles linking the discreet aromatic structures, any departure from coplanarity ($E^\theta$) will contribute to an increase in $E_g$. From a synthetic chemist perspective, design of an OSC should be in heavy consideration of creating coplanar moieties/repeat structures to maximize an effective conjugation length.

Previous work within the Briseno research group studied the conjugation limit of increasing oligomeric size of quarter thiophenes as compared to poly(quarter thiophene). Identification of effective conjugation length was determined to be 22 thiophene repeat units through the identification of UV-Vis absorption saturation limits that reflect the polymeric optical properties. The contribution of both $E^{6r}$ and $E^\theta$ in this study was the limiting factors for effective conjugation length. Theoretically, enabling more planar conformations may extend the conjugation length, thus lowering the $E_g$ for even more red-shifted absorption.

An important difference between polyacetylenes and polyaromatics lies in the aromatic resonance of the latter’s discreet units. If the aromatic resonance energy is sufficiently strong in stabilizing the cycle, $\pi$ electrons within these units may be confined within the individual rings and be in direct competition with $\pi$ electron delocalization along OSC backbone. This aromatic energy contribution ($E^{Res}$) should also be considered for impacting the final $E_g$ value.

The four parameters discussed thus far have considered the intrinsic properties of a linear OSC to impact the HOMO-LUMO energy offset. However, when these types of materials are used in a device, their applied form is almost always in the solid state where intermolecular interactions may allow hybridized, extended electron delocalization. This is evident when comparing the UV-Vis absorption of solution against films of OSCs as
they typically redshift. Aggregate forms may allow some degree of orbital overlap and thus the condensed phase can represent an important contribution to the bandgap ($E^{\text{int}}$).

1.3.3 Organic Semiconductor in Devices

Organic semiconductors have emerged as an attractive alternative to amorphous silicon as the active transport material in electronic applications. Attributes such as solution processability and enabling stretchable, flexible devices not found in the traditional brittle inorganic semiconductors have driven the field to develop OSCs with device performance competitive to amorphous Si. Most notably, the promise of forming fully functional devices via a large-scale solution base process enables cheaper and less demanding conditions (deposition of Si typically ranges >400 °C). To evaluate the performance of synthesized OSCs highlighted in this dissertation, simple thin film transistor and organic photovoltaic devices are constructed, measured, and presented.

![Diagram of basic architecture and operation of bottom gate, bottom contact thin film transistors.](image)

**Figure 1.8.** Basic architecture and operation of bottom gate, bottom contact thin film transistors.

Operation and architecture of a simple thin film transistor is shown above, **Figure 1.8.** Transistor shown in this array is simplified to its essentials. (1) Electrodes are in direct contact with (2) the OSC layer and the bottom of the (3) dielectric; these contacts are identified as source-drain electrodes and gate electrodes, respectively. Between the source and drain exists a constant voltage bias across the semiconductor, but collection of charges/current is never observed until a certain amount of bias is set at the gate electrode.
(V_g). When enough bias is applied at the gate, oppositely formed charges are created at the dielectric-semiconductor interface and then collected at the source-drain contacts. Analogy to easily describe this operation can be made with a simple water faucet: positive pressure of water is always placed across the water source but current is not observed until the gate/valve is opened. For transistors, a material can illicit N-type or P-type response as electrons or holes are generated and collected via electrodes with applied positive or negative bias, respectively. An example of data generated from P-type transistor operation is displayed below, Figure 1.9.

Figure 1.9. Representative source drain current vs gate bias data output for p-type semiconductors.

The generated source-drain current (I_DS) vs gate bias (V_G) plot is described as the transport characteristics. From this plot, important parameters of the organic field effect transistor (OFET) are collected: the threshold voltage (V_{Th}) describes at which the minimal V_G needs to be applied to observe a current, current on/off ratio (I_{ON}/I_{OFF}) identifies saturated current normalized by the current with no V_G applied, and charge carrier mobility
(\(\mu_e\)) describes how well the active transport material can move generated charges. For N-type and P-type response, the charge carrier mobility may be more specified as electron (\(\mu_e\)) and hole (\(\mu_h\)) mobilities, respectively. The charge carrier mobility may be calculated from the slope in the following Shockley relationship with known transistor dimensions such as width (W) and length (L) between contacts and capacitance of choice dielectric.

\[
I_{DS} = \mu \frac{W C_l}{2L} (V_G - V_{Th})^2
\]  (1.8)

Organic photovoltaic (OPV) device architecture differs from thin film transistors in that they contain both N-type and P-type materials that may be mixed, creating the active bulk heterojunction that facilitates the photoconversion process for solar cells. For simplicity, an OPV bilayer device is shown below (Figure 1.10). Only two electrodes are present in such devices where the cathode and anode are ideally interfaced with the N-type and P-type material, respectively. Four key processes occur in the photoconversion mechanism: (1) light is absorbed, typically by the P-type material, which creates an exciton, (2) exciton diffuses to the donor/acceptor interface to (3) dissociate into geminate electron and holes, and (4) hole/electron charges are collected at the anode/cathode, respectively.

![Figure 1.10. Simple architecture of OSC based OPV bilayer device.](image)
Type of active transport material used in OPV or OFET has thus far been categorized in terms of electron density: P-type (donor) or N-type (acceptor). Within the field of OSCs, we may further categorize these molecules on terms of size, namely, discreet, monodisperse small molecules or polydisperse, long aspect ratio molecules – polymers. Inherently, each subcategory of materials has their own respective advantages and disadvantages.

1.4 Small Molecule Semiconductors

Small molecules may be much more crystalline in the solid state and thus achieve overall higher performance in the device when compared to the more amorphous polymer type. Highly crystalline but relatively small π-surface area, this class of OSC heavily rely upon intimate intermolecular orbital overlap in the solid state. One of the major issues arises upon molecule-molecule interactions is the presence of polymorphs where crystalline habit, thus molecule-molecule distances, may vary. Shown below is a calculated result from of tetracene dimer offset relationship to electronic transfer integral values, \( t \) (meV), of hole and electron carriers.\(^{14,15}\)
Figure 1.12. Electronic transfer integrals of tetramer dimers as a function of longitudinal displacement set at 3.74 angstroms (left) and short axis (right). Figure adapted from Chemical Review 2007 publication.\textsuperscript{15}

However, isolating a certain polymorph may be achieved through a thermally annealing, templated growth, or via method of deposition and crystal growth.

A subclass of small conjugated materials, acenes, has been aggressively investigated in the science community for the development and application in organic semiconductors. They are the most extended class of fused polycyclic aromatic hydrocarbons (PAH), typically described by the fewest localized Clar resonance sextets per number of aromatic rings. Acenes offer an attractive structural platform in OSC applications with a planar backbone. Many important electronic properties such as decrease in reorganization energy and increase carrier mobility and bandwidth scale with the size of the acene. Unfortunately, dramatic decrease in stability trends rapidly with further benzannulation due to loss of benzenoid like character to stabilize the entire acene core.
Figure 1.13. Decrease in HOMO-LUMO offset with increasing size of oligoacene.

Light induced oxidation and dimerization are the major degradation pathways of linear acenes. It is well known that, based on nucleus-independent chemical shifts (NICS) calculations, the central ring of linear polyacenes are more reactive. Tetracene readily dimerizes in the presence of light but has been reportedly reversible with heat. Pentacene dimer on the other hand cannot be easily thermo-reversed. This thermodynamically favorable cycloaddition is theorized to spontaneously occur with even larger acenes.
However, incorporation of large, sterically demanding substituents on the most reactive rings has been the solution of negating dimerization reactions.

**Scheme 1.1.** Photo-induced butterfly dimers of pentacene and tetracenes.

Amending the molecular motif and electronic structure has been the main focal approach to enhancing the sustainability of this class of molecules. Namely, substitution at the periposition with large bulky substituents have offered a steric barrier to dimer and endoperoxide formation. Extension of conjugation along the short axis with relatively small substituents has shown promising results in spreading the electron density, hindering reactivity of the most central benzene rings. Choice of bulky substituents must be carefully approached in this strategy as sterically congesting the acene disrupts pi-stacking motif, inhibiting charge transport. Oxidative stability of large PAH may also be enhanced by increasing the number of Clar structures in the molecular design. Following the Clar sextet model, molecules with more benzenoid sextets increase the overall aromatic stabilization energy. This can be afforded by adopting unconventional modes of ring annulation such as triangular and zig-zag geometries.

In the second chapter of this dissertation, we will review the reversible binding of singlet oxygen within one of the highest performing substituted acene to date, rubrene. We
also investigate the substituent effect of tetra-substituted tetracenes (rubrene derivatives) upon photooxidation and challenge the common notion that lowering LUMO levels of acenes to be the most optimal method for increasing acene resistance towards photooxidation in chapter 3. Expansion of increasing stability from redesigning the core of acenes to afford additional Clar structures are also briefly explored.

1.5 N-type Polymer Semiconductors

In contrast to small molecule adducts, polymer semiconductors are typically polydisperse in size and length because of typical condensation polymerization synthetic methods (i.e., Suzuki, Stille, Sonagashira, and Heck coupling). Maximizing the molecular weight of PSCs is highly desired. From a morphological position, if the bulk phase of a PSC has rather low molecular weight, higher density of chain ends will result thus creating more void space and free volume that effectively acts as a plasticizer and increase the amorphous content. Increasing order via affording higher molecular weights of PSCs is key. Polymers heavily rely upon in-chain charge carrier mobilities, thus having a macromolecule with large molecular weight and long-range order in the microstructure is a standard design approach for boosting performance.
Figure 1.14. Narrowing of HOMO-LUMO gap with extended conjugation from monomers, oligomers, and polymers.

The promise of low-cost, scalable electronic devices has helped drive the development of polymer semiconductors.\textsuperscript{16–19} Applications of mixed-type PSCs with respective unipolar carrier mobilities includes fully complementary organic integrated circuits, photovoltaics, and thermoelectric generators. It remains important to synthesize high-performance PSCs for the advancement and implementation of organic p-n junctions with complementary hole and electron mobilities. Over the last decade, impressive progress has been made with regard to charge-carrier mobility, mostly in terms of p-type (hole conducting) materials.\textsuperscript{20–32} Comparatively, high mobility n-type (electron conducting) PSCs have achieved less progress, since such materials generally do not exhibit appropriate electronic structural parameters.\textsuperscript{33–37} The small number of high-performance n-type PSCs has largely been attributed to a lack of monomers with appropriate electron affinities in combination with co-monomers for stable, unipolar device characteristics.
Rylene diimide-based units are attractive building blocks for the design of stable n-channel OSCs. The presence of two imides increases the electron affinity, and offers a molecular handle for substituent engineering to control solubility and thin film morphology. Naphthalene diimide (NDI) is among the most thoroughly studied of monomer units for the synthesis of n-type PSCs. In combination with an appropriate co-monomer, an n-type PSC with a large electron affinity (i.e., low lying LUMO energy level) for unipolar transport and ambient device stability may be afforded. The first report of a stable electron-transporting NDI-based copolymer exhibited a high electron mobility of 0.85 cm$^2$ V$^{-1}$ s$^{-1}$; further optimization has produced state-of-the art NDI-based polymers with mobilities up to 6.5 cm$^2$ V$^{-1}$ s$^{-1}$ through modification of N-substituents and donor repeat units.

In the chapters 5 and 6, we review our efforts in increasing planarity of NDI based PSCs. Through modification of acceptor-donor repeat structure via vinylene moiety, we investigate the torsional angle tuning/planarization impact upon transport characteristics in thin film transistors. Additionally, design of an unconventional all-acceptor type PSC is studied with the rational design of also increasing polymer backbone planarity. Both chapters is compared and measured against the industry benchmark n-type polymer, P(NDI2OD-T2) or commonly referred to as N2200.

1.6 Dissertation Organization

The concept and design of conjugated small molecules and polymers have thus far been introduced. Characterization techniques assessing the energetic levels of OSCs discussed will be the primary method for describing synthesized materials in this dissertation. This dissertation will overview the photo-oxidative instability for a class of
small molecules, oligoacenes, design of stable oligoacene materials for OPV applications through bottom up, band level engineering, and torsional angle tuning of n-type naphthalene diimide based polymers.

In chapter 2, we investigate the photo-oxidation of one of the highest performing small molecule p-type materials - Rubrene. Reversibility and formed oxidized product is exampled in forming fully functional transistors. This section exhibits the regeneration of oxidized acnes from the endoperoxide. During the course of this work, we identify a second stage oxidized form as catalyzed by acidic impurities. These findings offer strong consideration and implication of impurities in batch solutions when forming organic based devices.

In chapter 3, we review the photo-stabilization effect of various side groups among a rubrene-based library. To our surprise, we did not see photo-stability trend with experimentally determined LUMO levels as suggested by previous reports. Time-resolved spectroscopy techniques reveal the direct relation of photo-kinetics with resistance to photo-oxidation. Overall shorter excited state lifetimes kinetically outcompete with sensitization of reactive oxygen species. These findings offer new design criteria for oligoacenes for realizing longer, higher performing derivatives.

In chapter 4, anthanthrene based molecules are developed for use in OPV applications. Anthanthrene is known as a two-dimensional oligoacene, a design motif that has shown to be much more resistance towards degradation pathways. Choice conjugation through both short and long axis displays the tunability of this large pi-surface molecule, with examples of photo-voltaic response in all small molecule solar cells. Flanking the short axis through ethynyl linkages with rylene diimides also result in low energetic band
gap materials. Perylene diimide based materials lie in highly twisted conformations, offering potential for non-fullerene acceptors.

In chapter 5, vinylene bridged naphthalene diimide based polymers are synthesized and measured against benchmark polymer, N220 (otherwise known as P(NDI2OD-T2). Vinylene bridging naphthalene diimide and bithiophene comonomer enables ambipolar response in thin film transistors. Overall, synthesized polymers overall out performs N2200. Results are rationalized through quantum calculations of polaron orbital distributions. Findings in this chapter may guide the development of higher performing polymer semiconductors with more delocalized orbitals as enabled by more planar conformations.

In chapter 6, an all acceptor naphthalene diimide-bithiazole polymer is synthesized and investigated for temperature induced ordering. 5,5’-bithiazole is employed as an alternative comonomer to bithiophene with the duality of protons absent at the 4,4’ C position and increase n-type characteristics of formed polymer. Torsional angle potential energy profile is calculated where complete planar conformations are possible above a certain thermal energy threshold. GIXD reveal annealing films above 200 °C drastically increases ordering and promotes device performance. Similar conjugated zwitterionic polymer is also shown to increase device performance through electrode energy modification.

Chapter 7 concludes with lessons learned form this thesis. Additional future work is presented to further build upon these findings. While findings of this thesis has advanced the rational design of more stable oligoacenes and increase the performance of conjugated polymers, there is still much more to investigate in this field.
CHAPTER 2

REVERSIBLE BINDING OF OXYGEN. IMPLICATIONS OF DEVICE

2.1 Introduction and Overview

Organic semiconductors (OSCs) have attracted interest in large-area devices due to their mechanical flexibility, solution processability, and performance that rivals that of amorphous silicon.\textsuperscript{50–54} Although these materials appear as attractive candidates for next-generation semiconductor materials, their propensity to degrade under ambient conditions has hindered their commercial use. Even the benchmark organic semiconductor, rubrene, one of the best performing materials,\textsuperscript{55–58} has been shown to readily oxidize in both solution and amorphous thin films.\textsuperscript{59–65} The photo-oxidation of rubrene has been well documented,\textsuperscript{65,66} involving the photosensitized formation of singlet oxygen and subsequent formation of the endo-peroxide Diels-Alder adduct.\textsuperscript{67}

In our efforts to monitor and clarify the photo-oxidation of rubrene\textsuperscript{60,66,68,69} and its thermal cycloreversion,\textsuperscript{70} we observed an irreversible second stage oxidation product, \textbf{rubrene-Ox2}. In addition, we describe an acid-catalyzed process that irreversibly destroys the active transport layer and leads to permanent degradation of device performance. Here, \textsuperscript{1}H NMR and UV-Vis were utilized to monitor the thermal cycloreversion process of the oxidized species. The fidelity of this cycloreversion process to restore the intrinsic properties of rubrene was demonstrated via the fabrication of high mobility devices from previously oxidized rubrene. Prolonged photo-oxidation in CHCl\textsubscript{3} solution converts the endo-peroxide irreversibly to \textbf{rubrene-Ox2}. It should be noted that this secondary degradation product had been reported in 1955\textsuperscript{23} through an acid treatment of \textbf{rubrene-Ox1}, to form the same product we report here.\textsuperscript{71–73} However, in that report, neither the
mechanism of product formation nor the crystal structure were reported. Herein, we report the first crystal structure of rubrene-Ox2, and through quantum mechanical computations, propose an acid catalyzed endo-peroxide rearrangement mechanism for the generation of rubrene-Ox2.

**Figure 2.1.** A) Molecular structure of rubrene, rubrene-Ox1, rubrene-Ox2. B) $^1$H NMR oxidation process of rubrene and pure rubrene-Ox1.

2.2. Stage 1 Oxidation of Rubrene

Rubrene-Ox1 can be easily accessed in high yield (97%) by stirring a rubrene solution in chlorinated solvents under ambient laboratory conditions. All solution concentrations for this study were $2 \times 10^{-5}$ M in chloroform. The formation of rubrene-Ox1
was monitored using $^1$H NMR (Figure 1) through the appearance of a new triplet and doublet peak at 6.86 and 6.75 ppm, respectively. After 120 minutes, full conversion to **rubrene-Ox1** was determined. The nmr spectrum matched that of separately purified **rubrene-Ox1**, shown in the bottom spectrum of Figure 2.1B. The characterization of rubrene-Ox1 is consistent with previously reported work.$^{74,75}$

**Scheme 2.1.** Stage 1 Oxidation of Rubrene.

![Scheme 2.1](image)

Stage 1 oxidation detail: A solution of rubrene was prepared by dissolving 100 mg ($1.87 \times 10^{-4}$ moles) of rubrene in 100 mL of CHCl$_3$ and allowed to stir in ambient laboratory conditions. Solution was exposed to both air and light for 24 hours and was dried under vacuo. The residue was purified via silica-gel column chromatography in hexanes. Product collected as a white solid in nearly quantitative yield (97%, 103 mg, $1.82 \times 10^{-4}$ moles). $^1$HNMR (CDCl$_3$, 400MHz): $\sigma$ 7.40 - 7.34(b, 6H), 7.22 – 7.17(b, 6H), 7.16 – 6.98(m, 12H), 6.86(t, 2H), 6.74(d, 2H).
Figure 2.2. A) UV-vis spectra of rubrene in CHCl$_3$ recorded at regular interval (10 mins) during exposure to light, B) The absorbance intensity vs exposure time.

Figure 2.3. A) UV-Vis spectra of thin films of rubrene-Ox1 heating at 150 °C for 30 mins (red), rubrene-Ox1 (black), and rubrene (blue), and B) $^1$H NMR spectra for pristine rubrene, heat treated rubrene-Ox1, and rubrene-Ox1.

The degradation profile of rubrene in solution was also investigated through UV-Vis absorption to complement $^1$H NMR experiments. In solution and amorphous films, pristine rubrene has three signature absorption peaks at 529, 494, and 464 nm while rubrene-Ox1 has no distinct peaks in the visible spectra range. UV-Vis measurements were carried out on both solution state and thin films of pristine rubrene and rubrene-Ox1. A rubrene half-life value of 26 minutes in solution was determined through the careful
monitoring and depletion of the three distinct rubrene peaks under laboratory conditions (Figure 2.2). **Rubrene-Ox1** thin films were annealed to give cycloreversion to reform the parent rubrene. Upon heating the thin films of **rubrene-Ox1** at 150 °C, distinct absorption peaks of rubrene emerged within minutes. After 30 minutes of heating, the thin film spectrum of the thermally treated **rubrene-Ox1** sample matches that of pristine rubrene, displaying the efficiency of the thermolysis. Additionally, **1H NMR spectra** (Figure 2.3B) were collected for the thermolysis of **rubrene-Ox1** powder at the same temperature under a nitrogen atmosphere; cycloreversion approached full conversion in the first 10 minutes with the disappearance of the peroxide adduct peaks around 6.75 ppm. The bulk, white powder converted to a vibrant red color during this heating process.

### 2.3 Stage 2 Oxidation of Rubrene

#### 2.3.1 Analysis of Stage 2 Product

The oxidation of rubrene can be monitored visually as the solution color changes from red to colorless. Stirring for four days results in a yellow solution, indicating that a subsequent reaction in chlorinated solvents occurred. A previous report observed similar results when treating a rubrene solution with CF$_3$COOH, yielding a yellow product, identified as indenonaphthacene.$^{76}$ That product, however, is a different structure from the compound observed here, and was not a product observed in our studies. The structure of the purified **rubrene-Ox2** was confirmed to be the structure shown via single crystal analysis and **1H NMR** (Figure 2.4). The crystal structure of **rubrene-Ox2** in Figure 3B shows that the molecular structure is related to indenonaphthacene with the exception of a ketone at the C-1 position in place of a phenyl substituent. This secondary rearrangement product also lost the elements of phenol.
Figure 2.4. Crystal structures of, A) *rubrene-Ox1*, B) *rubrene-Ox2*, and C) $^1$H NMR of *rubrene-Ox2*.

Prolonged photodegradation of rubrene was performed in a chloroform solution neutralized by Na$_2$CO$_3$. No observable yellow color was produced after 4 days; however, upon the addition of CH$_3$SO$_3$H, the solution immediately became yellow (Figure 2.5). The net loss of a phenol renders the process irreversible.
Figure 2.5. 5 mg of Rubrene-Ox1 were mixed dissolved in (1) chloroform, (2) toluene, (3) Na\textsubscript{2}CO\textsubscript{3} treated chloroform, and (4) Na\textsubscript{2}CO\textsubscript{3} treated chloroform with Methanesulfonic acid.

2.3.2 Calculated Acid-Catalyzed Mechanism

Figure 2.6 shows the proposed acid-catalyzed mechanism for rubrene *endo*-peroxide rearrangement to **rubrene-Ox2**. Chloroform is known to contain acidic impurities (HCl).\textsuperscript{77} The proposed mechanism was evaluated using M06-2X/6-311+G(d,p)-IEFPCM\textsubscript{CHCl}\textsubscript{3}/M06-2X/6-31G(d,p)-IEFPCM\textsubscript{CHCl}\textsubscript{3} and B3LYP-D3BJ/6-IEFPCM\textsubscript{CHCl}\textsubscript{3} calculations. Both methods predict the same mechanism, but the following discussion is based on the computed free energies relative to rubrene and \(^3\text{O}_2\) using M06-2X/6-311+G(d,p)-IEFPCM\textsubscript{CHCl}\textsubscript{3}/M06-2X/6-31G(d,p)-IEFPCM\textsubscript{CHCl}\textsubscript{3}. The protonation of *endo*-peroxide **rubrene-Ox1** by model acid, H\textsubscript{3}O\textsuperscript{+}, gives cation, **2**. The protonated *endo*-peroxide undergoes a ring opening to afford the stabilized carbocation **3**, which is 27.2 kcal mol\textsuperscript{-1} lower in energy than **2**. Attack of the cation at C-5 produces Wheland intermediate **4**, which is higher in energy than **3** by 5.4 kcal mol\textsuperscript{-1}. Subsequent deprotonation of **4** by H\textsubscript{2}O gives **5**, which rearranges via a [1,2]-Ph shift and dehydration to give **6**. Finally, **6** loses PhOH to afford the observed product, **rubrene-Ox2**.
Figure 2.6. A) Proposed acid-catalyzed rearrangement mechanism. B) Computed free energies of the proposed mechanism of **rubrene-Ox1** rearrangement to **rubrene-Ox2** using M06-2X/6-311+G(d,p)-IEFPCM$_{CHCl_3}$//M06-2X/6-31G(d,p)-IEFPCM$_{CHCl_3}$. 
2.4 Transistors of Pristine and Oxidized Rubrene

2.4.1. Thin Film Transistors

Having established the structures of the rubrene oxidation products and the means and mechanisms of interconversions, we turned to exploration of device characteristics under different conditions. Although rubrene-Ox2 is formed irreversibly, rubrene-Ox1 could be a potential precursor to functional transistors. Known examples of acene precursors often employ light and or heat-sensitive sufinylacetamide and monoketone moieties to yield active semiconductors. \(^{78–86}\) To evaluate the semiconductor properties of thermally recovered rubrene, we fabricated thin-films via spin casting from solution. Pristine rubrene and reduced rubrene from the endo-peroxide are annealed to form the orthorhombic crystals. \(^{87}\) As shown in Figure 2.7a-c, pristine rubrene and reduced rubrene-Ox1 show interfacing crystallites with different colors corresponding to the desired crystalline phase \(^{88–91}\) while rubrene-Ox1 instead exhibits an amorphous, featureless film. Transfer characteristics of each film are shown in Figure 5d. Pristine and reduced rubrene-Ox1 showed hole mobility of 0.037 and 0.009 cm\(^2\) V\(^{-1}\) s\(^{-1}\), \(V_{th}\) of 16 and 13 V, and routine current on/off ratio of \(\sim 10^4\) and \(\sim 10^3\), respectively. While the mobilities are rather low, we produced the first example of additive-free solution-processed rubrene. \(^{92,93}\) The lower mobility of reduced rubrene-Ox1 may result from the presence of a rubrene-Ox1 impurity post-thermolysis or structural disorder at the dielectric-semiconductor interface.

2.4.2 Single Crystal Transistors of Cycloreversed Rubrene-Ox1

Finally, to demonstrate the reversibility of rubrene-Ox1 oxidation, we carried out physical vapor transport experiments with bulk oxidized rubrene as the source material. This experiment was carried out at 300 °C in which two events occur: (1) the cycloreversion
process, and (2) the sublimation of the reformed rubrene. It is interesting to note that the
cycloreversion and sublimation occur in one step to produce large, ultrathin rubrene
crystals with high purity. We fabricated single crystal transistors from these crystals and
measured carrier mobilities approaching 1.5 cm² V⁻¹ S⁻¹, with V_threshold of 3 V, and current on/off
ratios of ~10⁶. Figure 2.7E shows the transfer characteristics of the single crystal rubrene
device. Output characteristics for the same device exhibits excellent current modulation
when scanned from 0 to -40 V (see supporting information). These characteristics
demonstrate that rubrene crystals grown from a **rubrene-Ox1** source can reproduce the
fully conjugated form to yield high mobility transistors. This experiment clearly shows the
reversibility of **rubrene-Ox1** to rubrene to form fully functional devices.

![Figure 2.7](image)

**Figure 2.7.** Polarized optical images of A) pristine rubrene, B) **rubrene-Ox1**, and C) reduced **rubrene-Ox1** crystalline thin films. Transfer characteristics of D) pristine rubrene,
rubrene-Ox1, reduced rubrene-Ox1 thin film transistors, and E) single crystal rubrene crystal transistor (grown from rubrene-Ox1 source via PVT).

2.5 Conclusions

In the course of studying the formation and thermally activated cycloreversion of rubrene-Ox1 to pristine rubrene, we observed an irreversible, second stage oxidized product - rubrene-Ox2. It was found that acid impurities in chlorinated solvents lead to a pyramidalized ketone derivative, which is inactive in organic transistors. Using DFT, we identify the lowest energy pathway to the acid catalyzed formation of this irreversible product. Such impurities present in solution processed rubrene devices will detrimentally impact device performance and cannot be remediated through the application of heat to reform the parent acene. Devices from pure, thermally treated rubrene-Ox1 did in fact yield high carrier mobilities in both thin films and single crystal transistors. Understanding the formation of the irreversible adduct will help us design more chemically robust rubrene derivatives.

2.6 Acknowledgements

This work was funded by the National Science Foundation (DMR-1508627) and Office of Naval Research (N000147-14-1-0053). We thank Dr. Sean Parkin at the University of Kentucky for providing crystal structure analysis. Also, I would like to personally thank Steven Lopez (former Houk Group Member at UCLA, now professor at Northeastern Univ.) whom performed the quantum calculations and for insightful discussions upon stage 1 and stage 2 oxidation mechanism.
CHAPTER 3

ENABLING SHORT EXCITED STATE LIFE-TIMES FOR PHOTO-OXIDATIVELY STABLE RUBRENE DERIVATIVES

3.1 Introduction and Overview

Oligoacenes with linearly annellated benzene units have received much attention in both experimental and theoretical studies because of their high performance properties. For example, pentacene and its derivatives have proven to be one of the most successful organic semiconductors for organic thin film transistors due to their high charge-carrier mobilities. As oligoacenes increases with size, so do their electronic properties: absorption of light red shifts, hence a lower energy band gap, larger $\pi$-surface area may increase intermolecular electronic coupling, and larger conjugated cores trend with smaller reorganization energies. Unfortunately with increasing oligoacene size, insolubility and rapid degradation pathways, such as photo-oxidation and dimerization, also emerge. We have previously reported the adoption of an unconventional “angular” mode of annulation to afford more stable oligoacenes. However, one of the most common strategies to increase solubility and stability to this class of small molecules is the addition of bulky substituents, such as phenyl, arylthio, or ethynyl moieties, at peri-positions of oligoacene framework. The enhanced stability of oligoacenes via substituents have been attributed to the combination of steric resistance and electronic effects. Inclusion of bulky substituents at the peri-positions have proven to be a successful approach to negating dimerization while improving solubility. However, even solubilized oligoacenes still suffer from photo-oxidation in both solution and the solid state.
There is still ongoing discussion about the substituent-effect regarding photo-oxidative stability in oligoacenes. For example, Miller et al have shown that silylethynyl-substituted pentacenes, TIPS-pentacene, are not the longest-lived species under photo-oxidative conditions, but alkylthio- and arylthio-substituted pentacenes are most resistant to photo-oxidation, contrary to popular perception that ethynyl-type side groups are the best choice substituent.\textsuperscript{109} Maliakal \textit{et al} explained the increased photo-stability of alkynyl-pentacenes by low lying LUMO energy relative to pentacene.\textsuperscript{110} However, Linker and coworkers have determined that fast competitive physical quenching of $^{1}\text{O}_2$ by ethynyl-substituted pentacenes also is key to their persistence.\textsuperscript{113}

Similar to pentacene, tetracene is another model compound with high reactivity to oxygen to investigate chemical stability. Several derivatives of substituted tetracenes have been reported, such as diethynyltetracenes, tetraalkyltetracenes, dialkoxytetracenes, and rubrene derivatives.\textsuperscript{112,114–116} Notably, rubrene has been extensively studied for many years because of its extremely high carrier mobilities.\textsuperscript{117–124} Indeed, it is well-known that rubrene undergoes a fast oxidation process if exposed to air, and this process is strongly enhanced in the presence of light. Despite that few rubrene derivatives have been reported, the effect of the substituents on the photo-oxidation has not been fully understood, which would provide some clarity on the photo-stability of oligoacenes.

A library of six rubrene derivatives were synthesized and investigated for photo-oxidative stability ranking against commercially available benchmark rubrene (\textbf{Rub-1}) via a facile solution state photo-oxidation experiment. Here, the synergistic photo-stabilization effect of aryl, ethynyl, and combinations of side groups for tetra-substituted tetracenes, otherwise called rubrene derivatives are studied. To our surprise, there was not observe an
overall trend of increased ambient stability with deeper electron affinity energy levels, commonly referred to as the LUMO\textsuperscript{125}. Excited state lifetimes of rubrene derivatives were also determined via advanced temporal spectroscopy techniques, time resolved photoluminescence and transient absorption spectroscopy. This report reveals for the first time that oligoacenes with the shorter lived excited states, rather than deeper electron affinity energies, reflect longer lived and photo-oxidatively more stable compounds. Presumably, a shorter lived excited state returning to ground state kinetically out competes the photo-sensitization and generation of reactive oxygen species O$_2^{-}$ and $^{1}$O$_2$ (Scheme 2.2), thus enabling longer lived species. From our small molecule library study, thiophene analogues enabled the shorter lived excited states and ultimately more stable rubrene derivatives.

3.2 Synthesis, Molecular Characterization and Electronic Structure

3.2.1 Synthetic Approach and Characterization

![Figure 3.1](image)

**Figure 3.1.** All aryl, mixed aryl and ethynyl, and all ethynl Rubrene derivatives studied in this chapter.

General: $^1$H NMR and $^{13}$C NMR spectra were recorded in deuterated solvent on a Bruker ADVANCE 400 NMR. $^1$H NMR chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) reference using the residual protonated solvent as an internal standard. MALDI-TOF-MS were determined on a Bruker BIFLEXII Mass spectrometer
with trithiophenes as matrix. All chemicals were purchased from commercial suppliers and used without further purification unless otherwise specified. THF was freshly distilled from sodium prior to use. Quinones were prepared as specified from previous reports.126,127

Procedures for Rub-2 and Rub-3

In a flame dried, nitrogen purged 250 mL round bottom flask, 2-bromothiophene (8.76 mmol) was dissolved in 100 mL dry THF. Mixture was cooled to -78 °C and 2.5 M of n-BuLi (8.76 mmol) was added via syringe over 30 minutes. Reaction was allowed to stir at -78 °C for 1 hour followed by 30 minutes at room temperature. Appropriate quinone solid (2.92 mmol) was quickly added and allowed to continue to stir at room temperature overnight. Water was added to quench reaction, organic layer was extracted, washed with brine, dried over Na₂SO₄, filtered and dried. Crude product was purified via silica chromatography (1:1 hexanes/dichloromethane). Intermediate product was collected and dried in a 50 mL round bottom flask. Solid was dissolved in 30 mL of dry dichloromethane with ZnI₂ (3 eq.) and purged with N₂ for 30 minutes. NaBH₃CN (10 eq.) was added and allowed to reflux for 6 hours. Red color observed for both formed products. Reaction cooled to room temperature, extracted, washed, and dried over NaSO₄. Crude product was purified via traditional silica chromatography with dichloromethane/hexane mixture of 1:4. Red product collected, dried, and recrystallized from slow evaporation of dichloromethane/methanol solution.

Rub-2. Yield: 47%. ¹H NMR (400 MHz, CDCl₃): δ = 7.57 (dd, 2H), 7.43 (d, 2H), 7.18 (m, 14H), 6.94 (b, 2H), 6.74 (s, 2H), 6.45 (s, 2H). ¹³C NMR(400 MHz, CDCl₃): δ = 141.50, 136.95, 131.91, 131.59, 130.65, 130.61, 130.32, 129.54, 127.31, 126.67, 125.70, 125.66,
125.21. NMR assignments agree with previous report. Chemical formula: C_{38}H_{24}S_{2}. Calculated Mass: 544.73 g/mol. MALDI-ToF: 543.78 m/z.

**Rub-3.** Yield: 4.6%. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.63 (d, 4H), 7.29 (d, 4H), 7.24 (d, 4H), 6.89 (t, 4H), 6.68 (b, 4H). NMR assignments agree with previous report. Chemical formula: C$_{34}$H$_{20}$S$_{4}$. Calculated Mass: 556.77 g/mol MALDI-ToF: 555.91 m/z.

**Procedures for Rub-4, Rub-5, Rub-6, and Rub-7**

In a flame dried, nitrogen purged 100 mL round bottom flask, choice ethynyl reagent (4.38 mmol) was dissolved in 30 mL dry THF. Mixture was cooled to -78 °C and 2.5 M of n-BuLi (4.38 mmol) was added via syringe over 30 minutes. Reaction was allowed to stir at -78 °C for 1 hour followed by 30 minutes at room temperature. Appropriate quinone solid (1.46 mmol) was quickly added and allowed to continue to stir at room temperature overnight. 2M HCl (aq) solution of SnCl (4.38 mmol) was added and allowed to stir for 3 hours. Reaction significantly changed colors upon addition of solution. Organic layer was extracted, washed with brine, dried over Na$_2$SO$_4$, filtered and dried. Crude product was purified via silica chromatography (1:1 hexanes/dichloromethane). Product was collected, dried, and recrystallized from slow evaporation of dichloromethane/methanol solution.

**Rub-4.** Yield: 70%. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.53 (d, 2H), 7.62 (dd, 2H), 7.57 (d, 2H), 7.5 (m, 10H), 7.26 (dd, 2H), 0.17 (s, 18H). $^{13}$C NMR(400 MHz, CDCl$_3$): $\delta$ = 141.8, 132.7, 130.5, 127.8, 127.7, 127.3, 126.9, 126.7, 125.4, 116.7, 114.5, 102.4. Chemical formula: C$_{40}$H$_{36}$Si$_2$. Calculated Mass: 572.90 g/mol MALDI-ToF: 572.28 m/z.

**Rub-5.** Yield: 44%. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.59 (dd, 2H), 7.90 (dd, 2H), 7.68 (d, 2H), 7.51 (dd, 2H), 7.36 (dd, 2H), 7.28 (dd, 2H), 7.20 (d, 2H), 0.25 (s, 18H). $^{13}$C
NMR (400 MHz, CDCl₃): δ = 141.29, 131.27, 127.64, 127.27, 127.03, 126.92, 126.27, 125.98, 118.49, 113.20, 101.22. Chemical formula: C₃₆H₃₂S₂Si₂. Calculated Mass: 584.94 g/mol MALDI-ToF: 584.32 m/z.

**Rub-6.** Yield: 53%. ¹H NMR (400 MHz, CDCl₃): δ = 8.62 (dd, 2H), 7.59 (m, 6H), 7.49 (m, 6H), 7.33 (m, 12H), 7.26 (dd, 2H). ¹³C NMR (400 MHz, CDCl₃): δ = 141.12, 137.75, 134.13, 132.57, 131.53, 131.03, 128.38, 128.09, 127.95, 127.91, 127.87, 127.48, 127.00, 126.94, 125.58, 124.07, 118.94, 108.70, 89.52. NMR assignments agree with previous report.¹¹⁴ Chemical formula: C₄₆H₂₈. Calculated Mass: 580.73 g/mol MALDI-ToF: 580.41 m/z.

**Rub-7.** Yield: 44%. ¹H NMR (400 MHz, CDCl₃): δ = 8.87 (dd, 4H), 7.65 (dd, 4H), 7.54 (d, 8H), 7.27 (m, 4H), 7.21 (m, 8H). ¹³C NMR (400 MHz, CDCl₃): δ = 134.08, 131.53, 129.92, 128.29, 128.14, 127.58, 123.87, 118.90, 108.41, 89.50. Chemical formula: C₅₀H₂₈. Calculated Mass: 628.77 g/mol MALDI-ToF: 628.58 m/z.

**Scheme 3.1.** The two step synthesis pathway from known quinones to afford rubrene derivatives.
Rubrene derivatives studied in this chapter are shown in Figure 3.1. Here, we modify the rubrene structure with varying combination of phenyl, thienyl, trimethylsilyl ethynyl, and phenyl ethynyl groups. The synthetic pathway to these analogues were carried out in a two-step process: appropriate, previously reported quinones were added to a THF solution of lithiated substituents followed by a reductive aromatization step with either SnCl₂ or ZnI₂ for the addition of ethynyl and thiophene motifs, respectively (Scheme 3.1). Target molecules were obtained in moderate yields apart from Rub-3 with very low yields.
3.2.2 Optoelectronic Properties

**Figure 3.2.** A) UV-vis-spectra of rubrene derivatives in chloroform, and B) energy level diagram of the derivatives determined from cyclic voltammetry.

Light absorption spectra of rubrene derivatives were obtained via UV-Vis spectroscopy, **Figure 3.2A**. We immediately note that derivatives containing only aryl substituents, **Rub-1**, **Rub-2**, and **Rub-3**, have the most blueshift absorption spectra. Compared to the **Rub-1** peak absorption of 531 nm, the **Rub-2** and **Rub-3** spectra is slightly redshifted by 3 and 7 nm, respectively. This small redshift in absorption is a result of thiophene increased electron donating inductive effect as compared to phenyl substituent. This is supported by a deeper shift in the ionization potential and electron affinity displayed in **Figure 3.2B**.

A similar modest redshift of 2 nm in peak absorption can also be observed in **Rub-5** as compared to **Rub-4**, again due to stronger inductive effect of thiophene. Among the mixed aryl and ethynyl derivatives, **Rub-6** exhibits the most red-shifted peak absorption of 578 nm, an 11 nm red-shift/decrease of 0.04 eV as compared to **Rub-4**. Extended conjugation of phenyl acetylene was attributed to this redshift. Overall, increasing ethynyl
content resulted in higher absorption wavelength of light. This effect is most dramatically observed in Rub-7 with the most red-shifted peak absorption of 638 nm.

Cyclic voltammetry (CV) studies were performed in dichloromethane with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte to estimate the ionization potentials (IP) and electron affinity (EA) energy of the derivatives (Figure 3.2B and supporting information). Overall, there is a disproportionate shift in the EA among the target molecules compared to the relatively unperturbed IP. This result suggests the HOMO of these molecules to be stabilized by the tetracene core. In agreement with results observed in the UV-Vis spectra, thienyl substituents only had modest effect, lowering the electrochemical bandgap (E_g) in Rub-2 and Rub-3 as compared to Rub-1 by 0.05 and 0.11 eV, respectively. All ethynyl-type substituent had the most profound effect upon the bandgap with Rub-7 having the highest EA energy of 3.6 eV. Following previous reports of increased resistance to photo-oxidation, we would expect materials with the lowest lying EA energy to be the most stable material.110,111

3.3 Kinetics of Photo-oxidation

To rank the substitution effect upon photo-oxidative stability, chloroform solutions (2.0 × 10^{-5} M) were prepared for each analyte and exposed to ambient light and air at room temperature. UV-Vis measurements were taken at various times to track the photo-oxidation process. Example of this experiment is shown in Figure 3.3B for benchmark Rub-1. Affirming the spectra shape did not change in any of our measurement over time, we plotted normalized max wavelength peak absorption-time profiles for each of our rubrene derivatives, Figure 3.3C and 3.3D. In our reactions, these rubrene derivatives were treated to identical conditions such that the measured half-lives could be directly
compared. Normalized peak absorbance-time profiles were determined for each derivative and the order of decreasing resistance to photo-oxidation follows: Rub-3 > Rub-2 > Rub-5 > Rub-7 > Rub-6 > Rub-4 > Rub-1.

Figure 3.3. A) Photo-oxidation of 2.5 x 10^{-5} M CHCl₃ solution in ambient conditions, B) absorption degradation profile spectra of Rub-1, C) and D) normalized peak absorption-time profiles of rubrene analogues in short and extended time ranges, respectively.

To our surprise, a negligible increase in photo-oxidative stability was observed in Rub-4 and Rub-6 as compared to the commercially available Rub-1. Previous reports consistently remark acetylene-type substituents enhances stability of pentacene compared to 6,13-bisphenyl pentacene analogues via lowering of the LUMO, and thus lower triplet energy to retard ^{1}O₂ sensitization. Others have regarded the bis-ethynyl functionality
to also enable the physical quenching of $^1\text{O}_2$, however, we see this effect is negligible and non-operative. Tetracene has a shorter conjugation length than that of pentacene, thus the bandgap is appreciably larger. Use of two ethynyl substituents may not effectively lower the electron affinity level to lower the excited state and thus slow the $^1\text{O}_2$ sensitization. Noticeable decrease of the EA energy was observed with Rub-7, which did result in an order of magnitude increase in observed half-life. This result is consistent with the notion of lowering the LUMO levels increases the oxidative stability of oligoacenes.

Thiophene containing species (Rub-2, Rub-3, Rub-5) showed the most profound effect upon observed resistance to photo-oxidation. To our surprise, the optoelectronic properties, summarized in Table 3.1, did not show any significant overall trend in the stability among these materials. Thiienyl and ethynyl containing Rub-5 has very similar characteristics to Rub-4 and Rub-6 yet is nearly 40 times more stable. An even more drastic comparison is noted between the strictly aryl containing species; phenyl and thiienyl containing Rub-2 is at least three orders more stable than Rub-1 while Rub-3 is completely stable. These results are reminiscent of work by Kaur et al. that report alkylthio- and arylthio-substituted pentacenes were far more stable ethynyl analogue.\textsuperscript{109} The work hints the possibility of sulfur containing side groups participate in the physical quenching of $^1\text{O}_2$. Thus, the narrative of electronic contribution of choice side groups must be challenged and reconsidered from these experimental results; they do not have an apparent trend upon photo-oxidative stability of tetra-substituted tetracenes.
Table 3.1. Optical, electrochemical, and half-life properties of rubrene derivatives

<table>
<thead>
<tr>
<th>Compound</th>
<th>Optical</th>
<th>Electrochemical</th>
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<tbody>
<tr>
<td></td>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td>$E_g$ (eV)</td>
</tr>
<tr>
<td>Rub-1</td>
<td>531</td>
<td>2.19</td>
</tr>
<tr>
<td>Rub-2</td>
<td>534</td>
<td>2.15</td>
</tr>
<tr>
<td>Rub-3</td>
<td>538</td>
<td>2.08</td>
</tr>
<tr>
<td>Rub-4</td>
<td>567</td>
<td>2.04</td>
</tr>
<tr>
<td>Rub-5</td>
<td>569</td>
<td>2.02</td>
</tr>
<tr>
<td>Rub-6</td>
<td>578</td>
<td>1.98</td>
</tr>
<tr>
<td>Rub-7</td>
<td>638</td>
<td>1.79</td>
</tr>
</tbody>
</table>

3.4 Molecular Structures and Crystal Geometries

Figure 3.4. The torsion angle along the backbone ($\Phi$) was determined by the C–C double bonds at either end of the tetracene backbone (labeled as C1, C2, C3, C4). Lifetimes are shown in parenthesis.
To understand how molecular design affects steric hinderance and its impact on upon photooxidative stability, we consider the backbone torsion caused by the peri-positioned side groups. Solution-borne crystals were analyzed via single crystal x-ray crystallography. Individual molecules shown in Figure 3.4. Here, we define the degree of backbone twist via the terminal sp² carbons C₁ and C₂ orientation to C₃ and C₄.

Although compounds Rub-1 and Rub-7 showed planar conformation of the tetracenes, Rub-2 and Rub-3 have twisted core conformations. It is likely that the interactions between the side substituents strongly contribute to the planarization of the tetracene cores. All the phenyl and thienyl substituents rotated away from a coplanar conformation with the tetracene backbone and lead to less conjugation, affirming the little electronic effect these groups have on the tetracene core previously mentioned. Rub-2 and Rub-3 with at least two thienyl substituents have larger twisted tetracene cores with torsions of 29.4° and 39.5°, respectively.

![Figure 3.5](image.png)

**Figure 3.5.** High and low yielding endoperoxides of rubrene derivatives. Single crystal analysis of obtained endoperoxides reveal regioselectivity.

Formed endoperoxides from the photo-oxidation of Rub-1, Rub-4, Rub-5, and Rub-6 were purified and isolated in high yields. Single crystal analysis showed formation
of the endoperoxide were stereoselective across the acetylene functionalized ring, where applicable. We believe steric congestion by the adjacent aryl group drives the stereoselectivity towards the acetylene functionalized rings. Additionally, cycloreversion to reform the parent acene was proven possible through application of heat (see supporting information). This cycloreversion process is consistent with results from previous reports of similar tetracenes and anthracenes.\textsuperscript{111,114,130} Endoperoxide forms of Rub-2, Rub-3, and Rub-7 were not detected due to low yield, suggesting these species may undergo other degradation pathways in CHCl\textsubscript{3} or the endoperoxide form was not stable either.

3.5 Quantum Calculations – Transition State Energies

Quantum calculations using Domain Based Local Pair-Neutral Orbit Coupled-Cluster (DLPNO-CCSD(T)) method at the PCM-M06-2X/6-311+G**//PCM-M06-2X/6-31G level was utilized to further corroborate the experimental results, Table 3.2. Results unanimously shows a preferred concerted oxidation mechanism for all derivatives (see supporting information). Resulting calculated transition state energies ($\Delta G^\ddagger$) generally trend well with measured half-life values. Transition state energies of multivariant substituted were evaluated on both core rings to gauge regioselectivity of endoperoxide formation. Lower $\Delta G^\ddagger$ energy resulted for endoperoxide formation across ethynyl substituted rings in Rub-4, Rub-5, and Rub-6. Free reaction energy also yields these products as thermodynamically favored further supporting earlier experimental results. For Rub-2, the site for endoperoxide formation were competitive.
Table 3.2. Measured half-life values and calculated transition state energies (Δ\(G^\ddagger\)) for all rubrene analogues. Energies were calculated using DLPNO-CCSD(T)+PCM-M06-2X/6-311+G**//PCM-M06-2X/6-31G* method. Highlighted energies reflect preferred endoperoxide formation.

<table>
<thead>
<tr>
<th></th>
<th>Rub-1</th>
<th>Rub-4</th>
<th>Rub-6</th>
<th>Rub-7</th>
<th>Rub-5</th>
<th>Rub-2</th>
<th>Rub-3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Half-life (mins)</strong></td>
<td>17</td>
<td>22</td>
<td>22.5</td>
<td>635</td>
<td>795</td>
<td>&gt;2400</td>
<td>Very Stable</td>
</tr>
<tr>
<td><strong>Δ(G^\ddagger) (kcal/mol)</strong></td>
<td>23.8</td>
<td>23.7</td>
<td>22.7</td>
<td>24.8</td>
<td>25.0</td>
<td>26.2</td>
<td>27.6</td>
</tr>
<tr>
<td></td>
<td>(26.3)</td>
<td>(26.1)</td>
<td>(26.2)</td>
<td>(26.3)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.6 Excited State Decay Kinetics

3.6.1 Photo-oxidation Mechanism

Although the quantum calculations trends well with the observed photo-oxidation half-lives, there is still a need to experimentally rationalize the discrepancy of photo-oxidative stability this series of rubrene analogues. Additionally, the measured IP and EA energies do not match the photo-oxidative stability order. The only conclusive result thus far is that thiophene moieties make the system more resistant to photooxidation. Since none of the normal trends apply (lower lying LUMO energy yields more stable oligoacenes), the photophysical characteristics of these derivatives are investigated as decay mechanisms are important in the oxidation process.
Scheme 3.2. Photo-mechanism of endoperoxide formation.

The mechanism to endoperoxide formation within our experiment is dependent upon the sensitization of O$_2^\cdot$ and ¹O$_2$ through either type 1 or type 2 photo-oxidation, shown in Scheme 3.2. First, light is absorbed to promote the acene to an excited singlet state followed by two possible processes: (1) relaxation of the excited state, either through radiative (fluorescence) or non-radiative decay, and (2) intersystem crossing of the singlet state to the triplet state which can decay through phosphorescence. However, in the presence of oxygen, electron or energy transfer can also occur from the (1) singlet or (2) triplet state of the acene to the triplet ground state of oxygen to produce O$_2^\cdot$ and ¹O$_2$, respectively. This excited state oxygen is a very reactive species that has been implicated as a primary culprit in photo bleaching of organic compounds. As oxidative degradation is an excited state phenomenon, understanding the photo-physical characteristics of the tetrasubstituted tetracenes may aid in understanding why certain derivatives with higher EA energies show higher oxidative stability.
3.6.2 Fluorescence Quantum Yield

Fluorescence quantum yield ($\Phi_x$) of rubrene derivatives were determined via slope of intergraded fluorescence vs peak absorbance plot and using the following relationship

$$\Phi_x = \frac{\Phi_{ST}}{\text{Grad}_{ST}} \frac{\eta_x^2}{\eta_{ST}}$$

Where $\text{Grad}_x$ is the slope of the analyte plot, $\eta_x$ is the refractive index of analyte solvent, $\text{Grad}_{ST}$ is the slope of external standard slope, $\eta_{ST}$ is the refractive index of standard solvent, and $\Phi_{ST}$ is known external quantum yield. Zinc phthalocyanine ($\Phi_{ST} = 30\%$) was used as the external standard in 1% pyridine in toluene ($\eta_{ST} = 1.497$) with a measured $\text{Grad}_{ST}$ of $1.19 \times 10^6$. Dichloromethane was used as the analyte solution ($\eta_x = 1.4125$).

Rub-3 showed very low fluorescence intensity that were not reliable for this measurement.

Figure 3.6. Integrated fluorescence vs peak absorption of a) Rub-1, b) Rub-2, c) Rub-4, d) Rub-5, e) Rub-6, and f) Rub-7.
Table 3.3. Half-life, Gradₓ, and Φₓ of rubrene derivatives in order of stability.

<table>
<thead>
<tr>
<th></th>
<th>Half-life (mins)</th>
<th>Gradₓ</th>
<th>Φₓ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rub-1</td>
<td>17</td>
<td>3.71 x 10⁶</td>
<td>84% (100%)¹³²</td>
</tr>
<tr>
<td>Rub-4</td>
<td>22</td>
<td>4.60 x 10⁶</td>
<td>104%</td>
</tr>
<tr>
<td>Rub-6</td>
<td>22.5</td>
<td>4.75 x 10⁶</td>
<td>107%</td>
</tr>
<tr>
<td>Rub-7</td>
<td>635</td>
<td>3.71 x 10⁵</td>
<td>8.37%</td>
</tr>
<tr>
<td>Rub-5</td>
<td>795</td>
<td>9.03 x 10⁴</td>
<td>2%</td>
</tr>
<tr>
<td>Rub-2</td>
<td>&gt;2400</td>
<td>1.06 x 10⁴</td>
<td>0.24%</td>
</tr>
<tr>
<td>Rub-3</td>
<td>Stable</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Tetrasubstituted tetracenes described here heavily varied in fluorescence as described in quantum yields (Φₓ) results, Table 3.3. Derivatives with the highest Φₓ included Rub-1, Rub-4, and Rub-6 all above 80% compared to drastically lower values of Rub-7, Rub-5, and Rub-2 at or below 8%. This evidence supported the hypothesis of more stable derivatives may have dominate non-radiative decays. However, these results do not describe our material temporal characteristics upon these decays. We note Φₓ for Rub-3 was not reported here as low fluorescence signal from photoluminescence did not yield reliable data.
3.6.3 Ultra-Fast Time Resolved Spectroscopy

![Normalized absorption and fluorescence spectra](image)

**Figure 3.7.** Normalized absorption and fluorescence spectra of a) **Rub-1**, b) **Rub-2**, c) **Rub-3**, d) **Rub-4**, e) **Rub-5**, f) **Rub-6**, g) **Rub-7**, and h) complied normalized fluorescence spectra.

Femtosecond and nanosecond transient absorption (TA) and time resolved photoluminescence (trPL) were conducted to observe excited-state decay rates of radiative and non-radiative pathways for all rubrene derivatives. The similar spectral shape of the absorbance spectra (**Figure 3.2A**) and fluorescence data (**Figure 3.7**) shows the tetracene singlet excited state is independent of flanking substituents. With confidence, temporal spectral analysis may be measured and directly compared. TrPL is used to measure the singlet excited state radiative decay lifetimes across all rubrene derivatives, while TA gives
both radiative and non-radiative singlet excited state decay lifetimes for all rubrene
derivatives, as well as triplet decay in Rub-7 (Table 3.4).

TrPI emission data was collected across the entire visible spectrum in one kinetic
trace, with good reproducibility and signal to noise ratios. The data was collected form
chloroform solutions. For Rub-4, Rub-6, Rub-7, Rub-2, and Rub-3, one relevant lifetime
was extracted by fitting a mono-exponential function to the emission decay, while for Rub-
5, two relevant lifetimes were fitted to a bi-exponential emission decay function. The
lifetimes generated through TrPI are denoted by the superscript r in Table 3.4. Rub-6 and
Rub-4 have the longest radiative lifetime decays ($\tau_F$) from the singlet state, around 11 ns
and 15 ns, respectively. These derivatives also have the highest quantum yields and
shortest half-lives. Rubene derivatives with longer half-lives, show shorter lived $\tau_F$ and
considerably smaller quantum yields, with Rub-3 having a $\tau_F$ of 0.35 ns and an
undetectable $\Phi_X$. While Rub-3 and derivatives with longer half-lives do have quantifiable
$\tau_F$ values, they also have considerably low quantum yields, indicating singlet decay
happens through a more dominate non-radiative pathway.

Both femtosecond (fs-TA) and nanosecond TA (ns-TA) experiments were run in
chloroform with good reproducibility and no photodegradation of the rubrene derivatives,
which was monitored by UV/Vis measurements taken before and after laser exposure.
Rubrene derivatives were excited using 470 nm or 560 nm depending on the singlet
absorption band maximum to prevent excitation light from obscuring the spectral window
of the TA measurement. The excited singlet state of Rub-2, Rub-3, and Rub-5, studied
with fs-TA, evolves as a broad absorption band ~ 440 nm over the first few picoseconds,
which maintains with no significant spectral changes over hundreds of picoseconds for
Rub-2 and Rub-3 and over several nanoseconds for Rub-5. The absorption is concurrent with a ground state bleach, though in Rub-2, Rub-3, and Rub-5 this is somewhat concealed by the excitation wavelength. Single-wavelength fittings at ~440 nm show that the singlet excited states of Rub-3 and Rub-5 exhibit decays that can be fit to tri-exponential functions (Table 3.4). Radiative lifetimes can be identified by comparing the lifetimes determined through TrPl to the lifetimes fit through single-wavelength fittings of the singlet excited-state absorption band, indicated by an r superscript in Table 3.4. Additional lifetimes are understood to be associated with non-radiative decay pathways from this singlet state. The dominate decay pathway for Rub-5 is radiative with a lifetime of ~0.4 ns. Non-radiative decay comprises 10% of singlet excited state decay pathways of Rub-5 with a lifetime of ~40 ps. Rub-3 shows a dominate non-radiative decay lifetime of ~25 ps with minimal contribution from radiative pathways. Additionally, Rub-2 single-wavelength analysis shows decay fitted to a bi-exponential function, with the dominant decay pathway being non-radiative (~50 ps).

Rub-7 was analyzed using both fs-TA and ns-TA. This derivative has a broad singlet absorption band evolving ~540 nm concurrent with a ground state bleach. While the singlet state decays over several nanoseconds, the bleach is never fully recovered and the evolution of a triplet state is observed ~450 nm. The triplet state decays over several microseconds, as detailed through ns-TA.

Rub-1, Rub-4, and Rub-6 were also analyzed using both fs- and ns-TA. The singlet excited states for these derivatives evolve over several picoseconds ~430 nm, 440 nm, and ~470 nm, respectively, with concurrent ground state bleaches. The decays of these broad singlet states are long-lived and therefore, unresolved on a fs timescale. ns-TA was
employed to determine the lifetimes associated with full decay to the ground state. All three derivatives decayed through radiative pathways that could be fit to a mono-exponential function. As shown through TrPl, these three derivatives had significantly longer lifetimes than Rub-7, Rub-2, Rub-3, and Rub-5. The singlet states for all derivatives show nearly identical absorption profiles, showing the side groups do not affect the rubrene core excited state properties.

The lifetimes of the dominate decay pathways for the seven derivatives trends with the oxidative degradation half-lives, showing more stable derivatives decay through faster, non-radiative mechanisms, with non-stable derivatives decaying through slower, radiative mechanisms. While no information on the mechanism of degradation can be detailed as triplet formation was only exhibited for one derivative, it is clear that singlet decay lifetime directly corresponds to oxidative stability. It can be theorized that derivatives with long-lived singlet states allow for energy or electron transfer to more readily occur over decay to the ground state, while derivatives with short-lived singlet states decay faster than they can transfer energy or electrons.
Figure 3.8. Transient absorption spectra of a) Rub-1, b) Rub-2, c) Rub-3, d) Rub-4, e) Rub-5, f) Rub-6, g) Rub-7, and h) compiled decay fit of TA measurement.

Singlet state lifetimes were analyzed via blue highlighted wavelength. For Rub-7, triplet state lifetimes were obtained via fitting of 450 nm. The ultrafast lifetimes of <50 ps appears to completely retard both O$_2^-$ and $^1$O$_2$ production, thus leading little to no yield of the endoperoxide. Understanding the relationship between long lived singlets and singlet oxygen production, the synthesis of stable oligoacenes through varying side groups needs to be accessed via advanced trPL and TA techniques, not energy structure analysis alone. This observed relationship between photo-oxidatively resistant species and average singlet/excited state of rubrene derivatives can be observed in Figure 3.9 where half-lives
are plotted against the average singlet state lifetimes, \( <\tau> \). Average lifetime is calculated by the equation: 

\[
<\tau> = \frac{\left(\sum f_n \tau_n^2\right)}{\left(\sum f_n \tau_n\right)}.
\]

**Table 3.4.** Decay lifetimes extrapolated from singlet decay for rubrene derivatives compared to the oxidative half-life. The lifetimes in light yellow correspond to radiative lifetimes determined through trPL, while the lifetimes in blue are non-radiative decay pathways.

<table>
<thead>
<tr>
<th></th>
<th>( \tau_{1/2} ) (min)</th>
<th>( \tau_1 ) (ps)</th>
<th>( f_1 )</th>
<th>( \tau_2 ) (ps)</th>
<th>( f_2 )</th>
<th>( \tau_3 ) (ps)</th>
<th>( f_3 )</th>
<th>Triplet (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rub-1</td>
<td>17</td>
<td>12510 ± 2740\text{f}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rub-4</td>
<td>22</td>
<td>15307 ± 1168\text{f}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rub-6</td>
<td>22.5</td>
<td>11767 ± 742\text{f}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rub-7</td>
<td>635</td>
<td>871.1 ± 20.6\text{f}</td>
<td>82.5%</td>
<td>411.8 ± 10.2</td>
<td>17.5%</td>
<td></td>
<td></td>
<td>25.5 ± 1.5</td>
</tr>
<tr>
<td>Rub-5</td>
<td>795</td>
<td>357.4 ± 58.6\text{f}</td>
<td>74.7%</td>
<td>2631.3 ± 67.6\text{f}</td>
<td>14.8%</td>
<td>42.9 ± 24.7\text{f}</td>
<td>10.5%</td>
<td></td>
</tr>
<tr>
<td>Rub-2</td>
<td>&gt;2400</td>
<td>48.2 ± 0.15\text{f}</td>
<td>73.1%</td>
<td>125.2 ± 5.3\text{f}</td>
<td>26.9%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rub-3</td>
<td>(stable)</td>
<td>24.7 ± 1.6</td>
<td>89.3%</td>
<td>53.2 ± 4.6</td>
<td>8.1%</td>
<td>210.8 ± 4.6\text{f}</td>
<td>2.6%</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 3.9.** Determined half-life (\( \tau_{1/2} \)) plotted against average excited/singlet state lifetime (\( <\tau> \)) of rubrene derivatives. Average lifetime is calculated by the equation: 

\[
<\tau> = \frac{\left(\sum f_n \tau_n^2\right)}{\left(\sum f_n \tau_n\right)}.
\]
3.8 Conclusion

We synthesized and ranked the photo-oxidative stability of seven rubrene derivatives to study the stabilization effect of aryl, ethynyl, and combinations thereof side groups. Surprisingly, stability did not trend with electron affinity energies as previously reported for substituted oligoacenes. Using transient absorption and time resolved photoluminescence, we reveal that increased stability is directly coupled with short lived excited states. Thiophene containing molecules (Rub-2, Rub-3, and Rub-5) displayed the shortest lived excited states where all aryl type thiophene-containing analogues reflect dominate non-radiative decay to the ground state. This ultra-fast decay back to the ground state kinetically out competes the triplet formation, thus immensely suppressing $^1\text{O}_2$ formation that ultimately photo-oxidizes the chromophore. For the first time, we highlight the importance of photophysic kinetics parameter for the realization and rational design of stable linear oligoacenes.

3.9 Characterization and Experimental Spectra

3.9.1 $^1\text{H}$ and $^{13}\text{NMR}$ of the Rubrene Derivatives

Figure 3.10. $^1\text{H}$ NMR of Rub-2.
Figure 3.11. $^{13}$C NMR of Rub-2.

Figure 3.12. $^1$H NMR of Rub-3.

Figure 3.13. $^1$H NMR of Rub-4.
Figure 3.14. $^{13}$C NMR of Rub-4.

Figure 3.15. $^1$H NMR of Rub-5.

Figure 3.16. $^{13}$C NMR of Rub-5.
Figure 3.17. $^1$H NMR of Rub-6.

Figure 3.18. $^{13}$C NMR of Rub-6.

Figure 3.19. $^1$H NMR of Rub-7.
Figure 3.20. $^{13}$C NMR of Rub-7.

3.9.2. CV Spectra of rubrene derivatives

Cyclic voltammograms (CVs) were recorded on a 1000B model electrochemical workstation using a platinum button as the working electrode, Ag wire as the counter electrode, Ag/Ag+ electrode as the reference electrode, and ferrocene/ferrocenium as an internal potential marker. 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF6) dissolved in dichloromethane was employed as the supporting electrolyte. Onset of oxidation ($E_{\text{ox \text{onset}}}$) and reduction ($E_{\text{red \text{onset}}}$) was used to determine the ionization potential ($IP_{CV}$) and electron affinity ($EA_{CV}$) of rubrene derivatives.
Figure 3.21. Cyclic voltammogram for a) ferrocene, b) Rub-1, c) Rub-2, d) Rub-3, e) Rub-4, f) Rub-5, g) Rub-6, and h) Rub-7.
3.9.3 Time resolved photoluminescence

Figure 3.22. Time resolved photoluminescence time profiles, model, and residual plots of a) Rub-1, b) Rub-2, c) Rub-3, d) Rub-4, e) Rub-5, f) Rub-6, and g) Rub-7.
3.10 Acknowledgements

This work was done with the support of the Office of Naval Research (Awards N00014-16-1-2612 and N000147-14-1-0053 at Penn State and Award N00014-17-1-2208 at Georgia Tech). I would like to thank Kara Martin and Prof. Elizabeth young for the helpful discussions upon photo kinetics and time-resolved spectroscopy techniques. Calculations were performed by Dr. Simil Thomas of Prof. Jean-Luc Bredas’ group at GA Tech. Single crystal crystallography was performed by Prof. Seam Parkin at the University of Kentucky.
CHAPTER 4

ETHYNYL BRIDGED ANTHANTHRENES FOR ALL-SMALL SMALL MOLECULE OPVS

4.1 Introduction and Overview

Development and application of linear polycyclic aromatic hydrocarbons are of great interest due to the attractive properties for organic electronic devices. As larger linear oligoacenes persists, a variety of electronic characteristics ensue, such as increase in carrier mobilities and increased range of light absorption. However, within the class of oligoacenes, we have demonstrated the unique mode of annulation from strictly linear to a two-dimensional PAH core results in more stable derivatives.\textsuperscript{106–108,133} Adopting an angular mode of annulation ensures increase resistance towards degradation pathways in ambient conditions (i.e., photo-oxidation) and reactivity towards other aromatics species (i.e., 4+4 cycloaddition towards fullerenes and other linear acenes). The increased stability of the two-dimensional oligoacene motif has been attributed to increased number of Clar sextet structure (thus, increase stability) and higher distortion energies required for Diels-Alder cycloaddition.\textsuperscript{106,107}

In addition of affording more persistent oligoacenes, the two-dimensional framework also increases the $\pi$-surface area for increased intermolecular overlap and charge transfer. Previously reported analogues of bistetracene can afford a brick-work like stacking, creating a two-dimensional crystal motif for charge mobilities as high as 6.1 cm$^2$ V$^{-1}$s$^{-1}$ in single crystal transistors.\textsuperscript{108,134} However, the aspect ratio of two-dimensionally annulated acenes heavily influences the crystalline packing that heavily influences device performance. Most low aspect ratio 2D acenes result in close-to-cofacial 1D $\pi$-$\pi$ stacking,
limiting charge transfer unidirectionally.\textsuperscript{102,133,135,136} Additionally, choice axis of extended conjugation plays a major role in the resulting optoelectronic values of 2D acenes. Dardenne \textit{et al.} predicted thiophene conjugation along the long axis of angular dibenzochrysene to enhance the absorption range into the visible region while others report ethynyl-type conjugation on the same aromatic core also resulted in stronger electronic communication along the short.\textsuperscript{137,138} Both lateral and longitudinal conjugation extension of anthanthrene core allows a platform for tuning both optoelectronic and solid state ordering.

For the design of non-fullerene acceptors, rylene diimide based moieties are attractive for its high conjugated pi-surface area with strong electron-withdrawing imides that allows solubility at the N-position. Dimer versions of perylene diimide paired at the N-position through a hydrazine linker that allowed intramolecular twist to disrupt cofacial stacking thus suppressing crystallinity. Though initial efforts achieved modest PCEs of 3.2\%, optimization of donor and acceptor molecules lead to a non-fullerene accepter/polymer donor OPV with PCEs of 5.6\%.\textsuperscript{139,140} Following this work, many researchers have expanded the library of perylene diimide based non-fullerene acceptors with the design rule having a large twist between chromophore dyes. Many dimer systems attached at the bay position, rather than the nitrogen head, emerged through either direct covalent bonds PDIs or bridging aromatic groups has led to impressive PCEs up to 8\%.\textsuperscript{141–145} As new rylene based acceptors emerge, it is immediately apparent the importance and impact of high intramolecular splay is present to facilitate multidirectional charge transfer, emulating electronic properties to that of fullerene materials.
In the first half of this chapter, we describe the one-pot synthesis of two new oligoacenes, TIPSThAA and TIPSThAA₂, through a tandem enhanced Stille/Hay-Glasser Coupling reaction. It was found the palladium catalyzed cross-coupling reaction of dibromo-bis(triisopropylsilyl ethynyl) anthanthrene with 2-stannyl-5-(2-ethylhexyl) thiophene in the presence of CuI and CsF resulted in a minor dimer product. Structure of purified minor product through ¹H NMR and MALDI-ToF spectroscopy confirmed the diethynyl bridged TIPSThAA₂. Optoelectronic of isolated products reveal the dimer species as a suitable small molecule donor for OPV applications. At room temperature fabricated OPV devices showed the best performance with exceptionally large $V_{OC}$ values of 0.9 eV with a PCE of ~2.0%. The more crystalline TIPSThAA were demonstrated in thin film transistors with hole mobility of $10^{-3}$ cm² V⁻¹ s⁻¹.

In the second half of this chapter, we briefly explore the optoelectronic properties of an anthanthrene core sandwiched between two rylene diimides, PDI-AA-PDI and NDI-AA-NDI. Results show an enhanced absorption around 500 nm for PDI derivative is indicative of a large torsion angle between the acceptor-donor-acceptor system as suggested from basic calculations allowing isolated anthanthrene molecule to heavily contribute to light absorption process. Following work optimizing alkyl chains and device fabrication is needed to access if these conjugated frameworks are suitable for OPV applications.

4.2 Synthesis and Characterization of Anthanthrene Donors

First, synthesis of 2-stannyl-5-ethylhexyl thiophene and 4,10-dibromo-6,12-bis(triisopropylsilyl ethynyl)anthanthrene were individually synthesized:
In a dry, nitrogen flushed round bottom flask, 3 g (35.7 mmol) of thiophene was dissolved in 100 mL of anhydrous THF. Solution was cooled to -78 degrees C for 10 minutes before adding 18.57 mL (29.2 mmol) of 1.6 M BuLi via syringe dropwise. Reaction was allowed to stir for 1 hr at -78 degrees C, warmed to room temperature and stirred for an additional hour. Solution became yellowish-honey colored. Reaction cooled to -78 degrees C again, and 4.59 g (23.8 mmol) of 2-ethylhexyl-1-bromide in 50 mL of anhydrous THF was added dropwise. Once dropwise addition was complete, solution was allowed to return to room temperature and heated overnight at 50 degrees C. Solution became a yellowish color overnight. Reaction was quenched via addition of HCl aqueous solution. THF solution was removed under pressure. Crude product was redissolved with ethyl ether, washed with aqueous HCl solution, and organic solution was dried over Na₂SO₄. Silica gel column chromatography was employed with hexanes. First elution collected colorless oil as purified product. 3.2 g (70%) yield. ¹H NMR (CDCl₃, 500MHz): σ 7.12 (d, 1H), 6.92 (t, 1H), 6.76 (d, 2H), 2.77 (t, 2H). ¹³C NMR (CDCl₃, 500MHz): σ 144.52, 126.68, 125.09, 123.05, 41.62, 33.98, 32.49, 29.00, 23.15, 14.27, 10.96.

Figure 4.1. ¹H NMR spectra of 2-(2-ethylhexyl) thiophene.
Figure 4.2. $^{13}$C NMR spectra of 2-(2-ethylhexyl) thiophene.

Stannylation of 2-ethylhexyl thiophene was facilitated in a dry, nitrogen flushed round bottom flask. 2.86 g (14.6 mmol) of 2-(2-ethylhexyl)thiophene was dissolved in 50 mL of anhydrous THF. Solution was cooled to -78 degrees C. Nitrogen gas was bubbled through solution for 30 minutes before syringe-dropwise addition of 9.56 mL (15.3 mmol) 1.6 M BuLi THF solution. Solution was allowed to stir for 1 hour at -78 degrees C for 10 minutes and warmed to room temperature to stir for an additional hour. Solution became a yellowish-honey colored. Reaction was cooled to -78 degrees C again before adding 16 mL (16 mmol) of 1 M trimethylstannyl chloride THF solution dropwise via syringe. Reaction allowed warm to room temperature and stir overnight. Reaction quenched via addition of water and THF solvent removed under pressure. Resulting oil was extracted with diethyl ether, washed with water three times, and organic layer dried over Na$_2$SO$_4$. Dried product yield a yellow oil. Product used in next step without further purification. 4 g (77%) yield. $^1$H NMR (CDCl$_3$, 500MHz): $\sigma$ 7.01 (s, 1H), 6.88 (s,1H), 2.80 (d, 2H). $^{13}$C NMR (CDCl$_3$, 500MHz): $\sigma$ 150.45, 134.99, 126.56, 124.47, 41.60, 33.93, 32.57, 29.05, 25.66, 23.17, 14.29, 10.97, 8.17.
Next, 4,10-dibromo-6,12-bis(triisopropylsilylethynyl)anthanthrene was synthesized in a dry, nitrogen flushed round bottom flask. 5.94 g triisopropylsilylacetylene was dissolved in 250 mL of anhydrous THF and cooled to 0 °C before 11.9 mL of 2.5M n-BuLi (29.7 mmol) at was added dropwise. The solution was allowed to stir for 1 h at 0°C before adding 1 g of 4,10-dibromo anthanthrene quinone. The mixture was warmed to room temperature and stirred over night. A solution of SnCl2·2H2O (3 g) in 3M HCl (15 ml) was added to the solution at room temperature, and it was then stirred for 3h and then poured into 500 mL of water, extracted with chloroform, and dried over Na2SO4. The crude product was purified by a short silica chromatographic column (Hexane/dichloromethane 10:1) to provide red, needle-like crystals. Yield: 82%. 1H NMR (CDCl3, 500MHz): σ
9.24(s, 2H), 9.20(d, 2H), 8.77 (d, 2H), 8.33(t, 2H), 1.32(m, 42H). $^{13}$C NMR (CDCl3, 500MHz): $\sigma$ 132.59, 130.87, 130.60, 130.08, 127.53, 127.14, 126.45, 125.67, 122.98, 120.91, 117.03, 105.75, 103.35, 19.13, 11.76; MALDI-ToF:

Figure 4.5. $^1$H NMR spectra of 4,10-dibromo-6,12-bis(triisopropylsilylethynyl)anthanthrene

Figure 4.6. $^{13}$C NMR spectra of 4,10-dibromo-6,12-bis(triisopropylsilylethynyl)anthanthrene.

The synthesis of both TIPSThAA and TIPSThAA$_2$ is described in Scheme 4.1. High yield of 2-(trimethylstannyl)-5-(ethylhexyl)thiophene was prepared in two steps from thiophene via n-butyllithium mediated nucleophilic aromatic substitution chemistries, as described above. Preparation of dibromo-bis(triisopropylsilyl ethynyl) anthanthrene was afforded according to previously reported procedures.$^{133}$ Our initial intention of using a
modified Stille coupling procedure was to boost the overall yield of **TIPSThAA**. Added CuI undergoes transmetallation with the organostanne to form the more reactive organo-copper halide while formed Bu₃SnI byproduct was removed by the formation Bu₃SnF through the presence of excess CsF. To our surprise, the enhanced Stille-Coupling conditions gave both **TIPSThAA** and a dimer species (**TIPSThAA₂**) in good and low yields, respectively. The formation of **TIPSThAA₂** was due to the presence of both additives, allowing deprotection of the triisopropylsilyl groups and appropriate copper oxidation of exposed alkynes for a tandem Hay-Glasser coupling to occur. Conventional silica gel chromatography techniques were employed to isolate pure **TIPSThAA** and **TIPSThAA₂**, as confirmed via ¹H NMR and MALDI-ToF (Figure 4.7-4.10).

**Scheme 4.1.** Synthetic route for **TIPSThAA** and **TIPSThAA₂**. i. nBuLi, -78 °C to RT 1 hr, 2-ethylhexyl bromide, -78 °C to RT 12 hrs in THF; ii. nBuLi, -78 °C to RT 1 hr, Me₃SnCl, -78 °C to RT 12 hrs in THF; iii. LiCCTIPS, -78 °C to RT 12 hrs, SnCl₂ (2M HCl aq.) RT, 2 hrs in THF; iv. PdCl₂, P(t-butyl)₃, CuI, and CsF, 110 °C 12 hrs in toluene/DMF. **TIPSThAA**: ¹H NMR (CDCl₃, 500MHz): σ 9.19 (d, 2H), 8.96 (s, 1H), 8.84 (d, 2H), 8.25 (t, 2H), 7.40 (d, 2H). ¹³C NMR (CDCl₃, 500MHz): σ 145.45, 139.52, 134.59, 132.37, 131.53, 130.55, 128.14, 127.73, 126.90, 126.07, 125.82, 124.57, 123.04, 117.38,
MALDI-ToF: 1024.3.

Figure 4.7. $^1$H NMR spectra of TIPSThAA.

Figure 4.8. $^{13}$C NMR spectra of TIPSThAA.

TIPSThAA$_2$: $^1$H NMR (CDCl$_3$, 500MHz): $\sigma$ 9.26 (d, 2H), 9.19 (d, 2H), 9.01 (s, 2H), 8.94 (s, 2H), 8.81 (d, 4H), 8.26 (t, 4H), 7.44 (m, 4H), 6.95 (m, 4H). MALDI-ToF: 1734.9.

Figure 4.9. $^1$H NMR spectra of TIPSThAA$_2$. 

104.82, 104.24, 41.80, 34.45, 32.65, 29.11, 25.77, 23.23, 19.19, 14.35, 11.76, 11.06.
Figure 4.10. MALDI-ToF spectra of TIPSThAA and TIPSThAA$_2$.

4.3 Electronic structure of TIPSThAA and TIPSThAA$_2$.

Optoelectronic characteristics of both products were investigated via UV-Vis, ultraviolet photoelectron spectroscopy (UPS), and cyclic voltammetry (CV), summarized in Table 4.1. UV-Vis spectra of TIPSThAA and TIPSThAA$_2$ were measured in chloroform solution and from a spin-coated thin film on glass (Figure 4.11a). A small redshift of 8 nm and broadening absorption of was observed for both molecules in the solid state relative to the solution spectra, partially due to multiple intermolecular interactions in the solid state. Notably, the absorption shape of the TIPSThAA$_2$ in solution depict aggregate formation with an absorption shoulder around 600 nm and overall less defined, broad peaks in contrast to the monomeric species. Ionization potentials (IP) and electron affinity (EA) energies determined by CV were virtually the same with both electrochemical bandgaps of approximately 2 eV. Ionization potential determined via UPS, however,
revealed the largest discrepancy between TIPSThAA and TIPSThAA₂ values: 5.52 and 5.02 eV, respectively. These results corroborate with the 0.53 eV difference in the optical bandgaps, indicating the conjugation extension along the short axis of the anthanthrene chromophore via bisalkyne bridge destabilizes the HOMO while the LUMO is relatively unchanged. Additionally, the determined energy levels of TIPSThAA₂ showed suitable for donor materials in BHJ solar cells.

**Figure 4.11.** (a) UV-Vis, (b) secondary electron cutoff and (c) magnified HOMO region spectra from UPS, and (d) energy diagram from combined UV-Vis and UPS data.

**Table 4.1.** Summary of Optoelectronic Properties of TIPSThAA and TIPSThAA₂.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Max λ (nm)</th>
<th>E&lt;sub&gt;g&lt;/sub&gt;&lt;sup&gt;opt&lt;/sup&gt; (eV)</th>
<th>IP&lt;sub&gt;UPS&lt;/sub&gt; (eV)</th>
<th>IP&lt;sub&gt;CV&lt;/sub&gt; (eV)</th>
<th>E&lt;sub&gt;A&lt;/sub&gt;&lt;sup&gt;CV&lt;/sup&gt; (eV)</th>
<th>E&lt;sub&gt;g&lt;/sub&gt;&lt;sup&gt;CV&lt;/sup&gt; (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TIPSThAA</td>
<td>500/508</td>
<td>2.40/2.33</td>
<td>5.52</td>
<td>-5.53</td>
<td>-3.53</td>
<td>2.00</td>
</tr>
<tr>
<td>TIPSThAA₂</td>
<td>530/538</td>
<td>1.99/1.80</td>
<td>5.02</td>
<td>-5.49</td>
<td>-3.51</td>
<td>1.98</td>
</tr>
</tbody>
</table>

4.4 Photovoltaic Devices of Anthanthrene Donors.

The photovoltaic properties of TIPSThAA₂ were measured in BHJ solar cells with TIPSThAA₂ as the donor and [6,6]-phenyl-C71-butyric acid methyl ester (PC<sub>71</sub>BM) as the acceptor. The device structure is ITO/PEDOT:PSS/TIPSThAA₂:PC<sub>71</sub>BM/Ca/Ag. The current density-voltage (J-V) characteristics of the solar cells under AM 1.5 solar simulator
at 100 mW/cm² light intensity as can be seen Figure 4.12a. The BHJ solar cells were fabricated by spin coating a solution of TIPSThAA₂ and PC₇₁BM in chloroform with different PC₇₁BM concentration. The TIPSThAA₂:PC₇₁BM weight ratios were tested 2:1, 1:1, 1:2. Blends in a 1:1 weight ratio resulting in an active layer with a thickness about 90 nm showed best device performance such as an open circuit voltage ($V_{OC}$) of 900 mV, a short circuit current density ($J_{SC}$) 4.8 mA cm⁻², a fill factor 0.48, and a power conversion efficiency (PCE) of 2.05 %. In contrast, different amount of PC₇₁BM in blend solution showed lower current density and efficiency. The solar cell parameters are summarized in Table 4.2. These device results are very attractive considering no solvent or thermal annealing were applied and solar cell were fabricated under ambient conditions.

The External quantum efficiency (EQE) spectra of all blends as a function of incident light wavelength were shown in Figure 4.12b. EQE spectra of 1:1 blend and other devices followed the optical absorption spectra and exhibit noticeable response in the 400-650 nm wavelength range, with a maximum of 66% from 465-525 nm. The $V_{OC}$ for all device remained almost constant from 870 mV to 900 mV and these values are among the highest open circuit voltages obtained from small molecule based devices.¹³³,¹⁴⁸,¹⁴⁹ On the other hand, $J_{SC}$ and FF of devices changed strongly with various PC₇₁BM loadings in blends because of the BHJ morphology.

The BHJ thin film surface morphologies were examined via Atomic Force Microscopy (AFM). Analysis of the AFM images clearly informs the drop off the device performance of different blends. For the 1:1 blends which had the highest $J_{SC}$ and FF, a relatively uniform film with small sized domains was observed (Figure 4.12c). For the 2:1 blend which had the lowest $J_{SC}$ and FF, the films were non-uniform and the surface had
large domains on the order of hundred nanometers (Figure 4.13). For the blend 1:2 based device yielded a PCE of 1.71\%, with similar Voc and FF but lower Jsc than the blend 1:1. For 1:2 blend, aggregation of PC$_{71}$BM occurred which is critical that charge collection. On the other hand, rough surfaces favor the light harvesting, in our case, 1 nm for 1:2 blend film is smoother than 3 nm for 1:1 blend, that can be the reason of decreased Jsc.$^{150}$ Thermal annealing effect on the surface of 1:1 blend film has been investigated. The film was annealed at 120 °C in ambient condition and decreased device performance is observed. The reason of this can be attributed by suppression of PC$_{71}$BM diffusion and aggregation during annealing time which cause to degradation of nanoscale BHJ morphology.

Figure 4.12 (a) Current voltage characteristics BHJ solar cells based on the blend of TIPSThAA$_2$:PC$_{71}$BM with different weight ratios. (b) IPCE spectra of the devices fabricated from TIPSThAA$_2$:PC$_{71}$BM blend. (c) AFM images of TIPSThAA$_2$:PC$_{71}$BM blend with 1:1 weight ratio.

Table 4.2. Solar cell parameters of from the TIPSThAA$_2$:PC$_{71}$BM blend devices extracted from J-V characteristics presented from Figure 4.12.
<table>
<thead>
<tr>
<th>TIPSThAA₂ :PC₇₁BM</th>
<th>Jsc (mA/cm²)</th>
<th>Voc (mV)</th>
<th>FF</th>
<th>PCE (%)</th>
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</thead>
<tbody>
<tr>
<td>2:1</td>
<td>2.3</td>
<td>870</td>
<td>0.38</td>
<td>0.75</td>
</tr>
<tr>
<td>1:1</td>
<td>4.8</td>
<td>900</td>
<td>0.48</td>
<td>2.05</td>
</tr>
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<td>1:2</td>
<td>4.0</td>
<td>900</td>
<td>0.47</td>
<td>1.71</td>
</tr>
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</table>

**Figure 4.13.** AFM images of TIPSThAA₂/PC₇₁BM thin film blends of 2:1 (left) and 1:2 (right) ratios.
**Figure 4.14.** Left: comparative J-V curves of 1:1 blend of PC$_{71}$BM acceptor with TIPSThAA (black) and TIPSThAA$_2$ (red) donors. Right: comparative J-V curves for as-cast vs annealed 1:1 TIPSThAA$_2$:PC$_{71}$BM BHJ OPVs.

**Table 4.3.** Solar cell parameters of from the donor:PC$_{71}$BM blend devices extracted from J-V characteristics presented from Figure 4.14.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Jsc (mA/cm$^2$)</th>
<th>V$_{oc}$ (mV)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TIPSThAA</td>
<td>0.23</td>
<td>80</td>
<td>0.28</td>
<td>0.01</td>
</tr>
<tr>
<td>TIPSThAA$_2$</td>
<td>4.5</td>
<td>910</td>
<td>0.44</td>
<td>1.82</td>
</tr>
<tr>
<td>(as-cast)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TIPSThAA$_2$</td>
<td>3.3</td>
<td>850</td>
<td>0.36</td>
<td>1.03</td>
</tr>
<tr>
<td>(annealed)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

BHJ devices formed from the monomeric species, TIPSThAA, showed very poor photovoltaic response compared to TIPSThAA$_2$. Single crystals of TIPSThAA were obtained by slow evaporation of a CH$_2$Cl$_2$/methanol solution whereas crystals were not obtainable for TIPSThAA$_2$. The inability of TIPSThAA$_2$ to form single crystals is attributed to the unhindered rotation of the diethynyl bridge, leading to a relatively amorphous conjugated small molecule. The alkyl chains coming off the thiophene creates an insulating barrier between the chromophore cores, as well as very limited $\pi$ overlap. However, we were able to obtain working transistors with mobilities $10^{-3}$ cm$^2$ V$^{-1}$s$^{-1}$ in field effect transistors (Figure 4.16).
Figure 4.15. X-Ray analysis of TIPSThAA single crystal. Protons and 2-ethylhexyl side chain is hidden for ease of view.

4.5 Thin Film Devices of Anthanthrene Donor Molecules

Figure 4.16. Field effect transistors I-V transport characteristic curves of TIPSThAA (left) and TIPSThAA$_2$ (right).

Table 4.4. Transistor parameters of TIPSThAA and TIPSThAA$_2$ from Figure 4.16.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\mu_h$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>$V_{Th}$ (V)</th>
<th>$I_{on}/I_{off}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TIPSThAA</td>
<td>$1 \times 10^{-3}$</td>
<td>-8.2</td>
<td>$3 \times 10^3$</td>
</tr>
<tr>
<td>TIPSThAA$_2$</td>
<td>$5 \times 10^{-5}$</td>
<td>-14.3</td>
<td>$5 \times 10^4$</td>
</tr>
</tbody>
</table>
4.6 Synthesis and Characterization of Rylene Flanked Anthanthrenes

The general approach to synthesizing the rylene-flanked anthanthrene molecules is carried out through the initial preparation of mono-brominated rylene diimides. Sequence of preparing mono-brominated 2-ethylhexyl rylene diimides are shown **Scheme 4.2**.

For the preparation of 5-bromo-N,N’-bis(2-ethylhexyl) perylene diimide, **Br-PDI**, perylene tetracarboxylic dianhydride (7.64 g, 20 mmol) was dissolved in 200 mL of dimethylformamide and 2-ethylhexyl amine (25.8 g, 200 mmol) in a 500 mL round bottom flask under inert conditions. Solution mixture was allowed to reflux at 185 °C for 8 hours in which the color changed from bright red to very dark red. After cooling to room temperature, solution was slowly poured into a 2M HCl aqueous (1L) solution and stirred overnight. Precipitate formed was collected via vacuum filtration, ashed with 200 mL of 5% NaOH (aq) solution, 500 mL of water, and 50 mL of ethanol. Formed 2-ethylhexyl perylene diimide intermediate product (1.5 g, 2.4 mmol) was then dissolved in dichloromethane (90 mL) under argon atmosphere. Excess amount of liquid bromine (9 mL, 72.5 mmol) was added dropwise to the solution and allowed to stir for 48 hours. Excess bromine was collected via bubbling inert gas though solution, trapping vapors into a bubble trap exhaust for 24 hours. Methylene dichloride solvent was removed under vacuum and crude product was purified via silica chromatography with chloroform as the eluent. Determined $^1$H NMR overall agrees with previous reports, **Figure 4.17**. Overall 2 step process had a 12% yield.

Synthesis of 4-bromo-N,N’-bis(2-ethylhexyl) naphthalene diimide, **Br-NDI**, slightly differed as bromination of the tetracarboxylic dianhydride occurred before
diimidation. Tetracarboxylic dianhydride naphthalene (2.68 g, 10 mmol) was stirred in 25 mL of sulfuric acid for 5 minutes to dissolve. Tribromoisocyanuric acid (1.83, 5 mmol) was added to the solution portion wise and allowed to stir overnight at room temperature. Solution became a yellow color overnight. Reaction mixture was then poured over ice, vacuum filtered, and washed with water followed by methanol wash to afford a crude yield of 2.72 g (79%) yield. Crude product (2.5 g, 7.2 mmol) was dissolved in 50 mL if acetic acid with 2-ethylhexyl amine (2.34 g, 18.1 mmol), yielding a yellow color solution. Air was removed from reaction mixture through three freeze-pump-thaw cycles and backfilled with nitrogen gas. Reaction was allowed to reflux at 130 °C for 2 hours. Solution became pink over this time. Solution was then poured over ~400 mL of ice, vacuum filtered, and washed with excess water. After drying in the oven overnight, crude product was purified via column chromatography with a 9:1 methylene chloride/hexane mixture to obtain a pink product. 1H NMR spectra collected for intermediate and final mono-bromo product agrees with previous report, Figure 4.18.154,155

Scheme 4.2. Synthetic pathways to form mono-bromo 2-ethylhexyl derivatives of perylene diimide (top) and naphthalene diimide starting from tetracarboxylic dianhydride forms of perylene and naphthalene, respectively.
N,N’-bis(2-ethylhexyl) perylene diimide: $^1$H NMR(400 MHz, CDCl$_3$): $\delta$ = 8.64 (d, 4H), 8.56 (d, 4H), 4.14 (m, 4H), 1.42-1.32 (m, 16H), 0.96 (t, 6H), 0.89 (m, 6H). In agreement with previous reports.$^{151-153}$

5-bromo-N,N’-bis(2-ethylhexyl) perylene diimide, Br-PDI: $^1$H NMR(400 MHz, CDCl$_3$): $\delta$ = 9.77 (d, 1H), 8.90 (s, 1H), 8.59 (d, 3H), 8.56 (d, 2H), 4.14 (m, 4H), 1.42-1.32 (m, 16H), 0.96 (t, 6H), 0.89 (m, 6H). In agreement with previous reports.$^{151-153}$

Figure 4.17. $^1$H NMR of N,N’-bis(2-ethylhexyl) perylene diimide (top) and 5-bromo-N,N’-bis(2-ethylhexyl) perylene diimide (bottom).
N,N'-bis(2-ethylhexyl) naphthalene diimide: $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.73$ (s, 4H), 4.13 (m, 4H), 1.42-1.32 (m, 16H), 0.96 (t, 6H), 0.89 (m, 6H). $^1$H NMR spectra collected for intermediate agrees with previous report.$^{154,155}$

4-bromo- N,N'-bis(2-ethylhexyl) perylene diimide, Br-NDI: $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.89$ (s, 1H), 8.78 (d, 1H), 8.72 (d, 1H), 4.12 (m, 4H), 1.42-1.32 (m, 16H), 0.96 (t, 6H), 0.89 (m, 6H). $^1$H NMR spectra collected for mono-bromo product agrees with previous report.$^{154,155}$

**Figure 4.18.** $^1$H NMR of N,N'-bis(2-ethylhexyl) naphthalene diimide (top) and 4-bromo-N,N'-bis(2-ethylhexyl) perylene diimide (bottom).
General procedure for the preparation of PDI-AA-PDI and NDI-AA-PDI was facilitated through a one pot sequential deprotection of 5,5’-bis(2-(2-ethylhexylthiophene)-6,12-bis(triisopropylsilyl acetylene) anthanthrene, 1, followed by Sonagashira coupling of appropriate mono-brominated rylene diimide, **Scheme 4.3**. Reagent 1 was first dissolved in toluene to produce a red colored solution followed by the addition of two molar equivalent1M solution of tetrabutylammonium fluoride and stirred for 5 minutes, removing triisopropyl silyl protecting groups. Solution became dark and fluoresces green. Mono-bromo rylene (2.1 eq.), diisopropyl amine (1 eq.), CuI (0.05 eq.), tri(o-tolyl)phosphine (0.1 eq.), and Tris(dibenzylideneacetone)dipalladium(0) (0.05 eq.) was added to the mixture and freeze pump thawed three times and backfilled with inert gas. Solution was allowed to reflux at 110 °C for 36 hours which yielded a green and purple color mixture for NDI-AA-NDI and PDI-AA-PDI, respectively. Reaction mixture was then dried under vacuum, extracted with chloroform, washed and dried over Na₂SO₄. Crude product collected was purified via silica column chromatography with 1:9 mixture of hexanes/methylene chloride to remove impurities followed by a tetrahydrofuran flush to collect final product. MALDI-ToF of THF eluent confirmed products with m/z values of 2028.17 and 2277.83 in agreement with calculated molecular weights of NDI-AA-NDI and PDI-AA-PDI, respectively (**Figure 4.19**). ^1^H NMR analysis of the two compounds did not yield reliable, and well resolved data for the two molecules.

**Scheme 4.3.** Synthesis of PDI-AA-PDI and NDI-AA-NDI through one pot sequential deprotection Sonagashira Coupling.
Figure 4.19. MALDI-ToF spectra and calculated molecular weights of NDI-AA-NDI (left) and PDI-AA-PDI (right).

4.7 Optoelectronic Properties of Rylene Flanked Anthanthrenes

Combination of UV-Vis spectroscopy and cyclic voltammetry measurements were performed to characterize optoelectronic properties of synthesized materials. UV-Vis measurements were done in both chloroform solution and solid state thin films in quartz cuvettes and glass substrates, respectively. In solution, PDI-AA-PDI peak absorptions were relatively more red-shifted than that of NDI-AA-NDI. Local peak maxima around ~500 nm of each molecule was attributed to the anthanthrene core, refer to Figure 4.11. Onset-edge absorption of both derivatives is shown in the near infra-red region,
corresponding to optical bandgaps of 1.51 eV and 1.36 eV for solutions and 1.31 eV and 1.27 eV, Table 4.5. A modest redshift of absorption on set and a peak shoulder around 850 nm of PDI-AA-PDI suggests an aggregated state already present in the CHCl₃ solution. Cyclic voltammetry results reveal perylene containing molecule to have a lower lying electron affinity level, 3.89 eV, than that of NDI-AA-NDI, 3.79 eV.

Figure 4.20 Optoelectronic properties of both NDI-AA-NDI (blue) and PDI-AA-PDI (red). UV-Vis-NIR spectroscopy shows absorption range from A) UV to NIR, B) zoomed-view of onset of absorption, and C) optical density vs concentration plot to obtain molar extinction coefficient. Cyclic voltammetry results shows D) quasi-reversible reduction peaks to calculate EA energies.

Table 4.5. Optoelectronic properties of NDI-AA-NDI and PDI-AA-PDI.

<table>
<thead>
<tr>
<th></th>
<th>Max λ₆₅₀/λ₇₅₀</th>
<th>E₅₀₂₆₅₀/E₅₀₂₇₅₀</th>
<th>εₘ₆₅₀ (x₁₀⁴)</th>
<th>IPcv (EAcv – E₅₀₂₇₅₀)</th>
<th>EAcv</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Wavelength (nm)</td>
<td>Energy (eV)</td>
<td>Absorption Coefficient (M⁻¹ cm⁻¹)</td>
<td>Energy Gap (eV)</td>
<td>Molar Extinction Coefficient (M⁻¹ cm⁻¹)</td>
</tr>
<tr>
<td>---------</td>
<td>----------------</td>
<td>-------------</td>
<td>-----------------------------------</td>
<td>----------------</td>
<td>---------------------------------------</td>
</tr>
<tr>
<td>NDI-AA-NDI</td>
<td>719/723</td>
<td>1.51/1.31</td>
<td>1.31</td>
<td>-5.10</td>
<td>-3.79</td>
</tr>
<tr>
<td>PDI-AA-PDI</td>
<td>731/N.A.</td>
<td>1.36/1.27</td>
<td>0.96</td>
<td>-5.16</td>
<td>-3.89</td>
</tr>
</tbody>
</table>

Noticeable higher peak ratio intensity of 500 nm was observed in PDI-AA-PDI, suggesting anthanthrene core was more active in absorbing light, possibly due to a high splay angle orientation between chromophore cores. This presumption is aligned with the determined molar extinction coefficient to be higher for NDI-AA-NDI (1.31 M⁻¹ cm⁻¹) than PDI-AA-PDI (0.96 M⁻¹ cm⁻¹) that would arise from being in a more planar conformation, Figure 4.20C. Molecular geometry of the small molecules were modeled using basic MMF94 minimalization methods via ChemBio3D software, Figure 4.21. Calculations were carried out through 500 iterations with a minimum of 0.1 RMS gradient. Saturated alkyl side chains are limited to methyl groups to simplify calculations. It is immediately apparent that based on these basic calculations, NDI base small molecule is much more planar oriented than PDI derivative. This may be attributed to the extended rylene core of PDI sterically congest anthanthrene interaction, heavily splaying the intramolecular orientation as enabled through alkyne linkage.
Figure 4.21. Optimized molecular geometries of small molecules viewed from face-on rylene orientation of A) NDI-AA-NDI and C) PDI-AA-PDI. Edge on orientations of B) NDI-AA-NDI and D) PDI-AA-PDI shows large discrepancy between rylene-anthanthrene orientation. Protons are hidden, and alkyl chains are omitted from calculations.

4.8 Conclusions

Anthanthrene molecules have show to be tunable through either the short or long axis for desired energy levels for applications in transistors and OPVs. Use of thiophene type derivatives were exampled to shift the absorption to lower energies. Cyclic voltammetry revealed the disproportionate shift in ionization energy while the LUMO is overall unperturbed. Use of an enhanced Stille coupling conditions developed by Baldwin and coworkers formed the unexpected dimer TIPSThAA$_2$. It was found that this material was suitable as small molecule donors in all small molecule solar cells with PCEs of
approximately 2% with exceptionally high VOCs – 900 meV. The crystalline TIPSThAA also show transistor response in the p-channel.

Band engineering of the electron affinity level, commonly referred to as the LUMO, were also shown possible with use of flanking rylene units. In the solid state, acceptor-donor-acceptors of anthanthrenes show very small band energy gaps. UV-Vis absorption spectra suggests anthanthrene absorption to be much stronger in the PDI derivative relative to NDI containing molecules. Basic optimized geometry calculations reveal PDI containing anthanthrene molecules to be highly twisted while NDI materials lie in a planar conformation. This molecular geometry offers great potential to realize anthanthrene based small molecule acceptors, an alternative to fullerene materials. Through the anthanthrene core, HOMO levels may be easily tuned through choice conjugation of the long axis.

4.9 Acknowledgements

I would like to thank Dr. Duygu Kara who worked upon the device work of this chapter. Her background on device physics and device fabrication expertise allowed me to assess the donor materials as OPV active materials. Dr. Leonardo Gonzalez also assisted with this chapter with measuring AFM images.
CHAPTER 5

VINYLENE BRIDGED NAPHTHALENE DIIMIDE COPOLYMERS

5.1 Introduction and Overview

Conjugated donor-acceptor copolymers (D-A) have proven to be one of the most successful high performance semiconductors in organic electronic devices.\textsuperscript{156–161} For example, copolymers based on diketopyrrolopyrrole (DPP), isoindigo, and rylene diimides as acceptors and thiophene derivatives as donors, have shown remarkably high carrier mobilities and efficiencies in organic transistors and solar cells.\textsuperscript{38,162–164} However, a number of challenges related to D-A copolymers remain to be tackled. For example, most semiconductors are one-type charge carrier transporting materials. Balanced ambipolar semiconductors, which transport both holes and electrons in one device, are highly desired due to their application in complementary-like circuits and in light emitting diodes.\textsuperscript{165,166} Additionally, in organic photovoltaics tuning the energy levels to maximize the open circuit voltage while maintaining a high short-circuit current, remains to be improved.\textsuperscript{167,168} These factors are strongly influenced by the ionization potential (IP) and electron affinity (EA) as well as the extent of electronic (de)localization of π-electrons, which can be tuned through molecular design.\textsuperscript{169,170} Although, these materials have been successfully modified to improve device performance via side chain engineering, the side chains usually affect the solubility and thin film morphology, but not electronic structure, such as IP, EA, and conjugation length, which have significant impact on transport properties.\textsuperscript{169–172}

In general, the electronic structure related to the conjugation backbone can be modified by careful combinations of donor and acceptor subunits, which allows a fine-tuning of energy levels for charge injection in D–A copolymers.\textsuperscript{157,160,169,170} Alternately, the
incorporation of π-spacers (e.g. vinylen linker or acetylenic linker) into the polymer backbone is another feasible option to tune their electronic properties.\textsuperscript{20,27,30,34,36,173–183} It has been verified that such π-spacers along the polymer backbone limit the rotational disorder between consecutive bulky aromatic units, leading to an extended conjugation and increased intermolecular interactions (Figure 5.1A).\textsuperscript{20,27,30,34,36,173–185} For example, the acetylenic linker has been extensively used to improve the electron transport in D-A copolymers by planarizing the molecular backbone.\textsuperscript{173} More recently, several reports have shown that incorporation of a vinylen linker along the backbone can strongly alter the electronic properties of materials and result in promising device performance (Figure 5.1B).\textsuperscript{20,27,30,34,36,176–183} The most popular approach to extend conjugation length of D-A copolymers is the incorporation of vinylen linkers within the donor segments only (Figure 5.1B).\textsuperscript{27,30,34,182–184} However, this raises a very intriguing question: How does the vinylen linker between donor and acceptor units affect the conjugation length and electron distribution of the D-A copolymers? Unfortunately, the conventional Heck coupling reaction, McMurry reaction, Horner–Wadsworth–Emmons reaction, which have been widely used for oligomers and homopolymers with double bonds in the backbones, are highly limited in their application for D-A copolymers due to monomers with suitable functional groups being unstable and unavailable.\textsuperscript{176,177,184,185}

Due to their chemical accessibility, high stability, and high electron affinity, naphthalenediimides (NDIs) have served as one of the most important building blocks to construct semiconductors for organic devices.\textsuperscript{186,187} In 2009, Facchetti and co-workers reported a novel n-type polymer based on NDI and bithiophene (P(NDI2OD-T2), Polyera ActivInk, NDI-2200), that showed a large electron field-effect mobility and much attention
has been paid to its physicochemical properties and thin film morphology.\textsuperscript{188–192} In particular, a range of NDI-thiophene copolymers were developed systematically by changing donor strength to investigate the structure-property relationships.\textsuperscript{39,42,193–195} Although some of the materials show ambipolar behavior, n-channel behavior is predominantly observed due to the high electron affinity of NDI.\textsuperscript{193–195} A few studies have investigated the effect of the donor units on the electronic properties of the NDI-containing copolymers, however, it is difficult to draw a conclusion on the influence of donor moieties on transport properties due to significant difference in molecular weight, thin film morphology, crystallinity, etc.\textsuperscript{193,195,196}

We demonstrated that incorporation of a vinylene linker between two NDI units can minimize steric effects and induce planarity, with such molecules showing promising performance as electron acceptors in organic transistors and solar cells.\textsuperscript{197} Herein, we report the synthesis and characterization of two new polymers based on NDI connected via a vinylene spacer to two thiophene donor units, instead of incorporation of vinylene linker into donor segments only (\textbf{Figure 5.1B}). To understand the optical and electronic properties of these polymers, theoretical calculations were performed to offer insights to NDI-V1, NDI-V2, and NDI-2200 (\textbf{Figure 5.1C}). We discovered that the vinylene linker between NDI and thiophene can minimize steric interactions, which leads to a smaller reorganization energy. Moreover, the vinylene linker significantly alters the transport behavior in NDI and thiophene copolymers, leading to hole mobilities as high as 0.43 cm\textsuperscript{2} V\textsuperscript{−1}s\textsuperscript{−1}. 
Figure 5.1. Typical design strategies for incorporating a vinylene linker into the backbone of conjugated polymers and representative polymers with vinylene linker in the backbones: A) vinylene linker in homopolymers, B) vinylene linker in donor moiety only, and C) vinylene linker between donor and acceptor moieties in this study, and chemical structure of NDI-2200.

5.2 Synthesis and characterization

Scheme 5.1. Synthetic approach to vinylene bridged naphthalene diimide copolymers.

From a synthetic chemistry viewpoint, it is difficult to synthesize and purify the electron-deficient building blocks (acceptors) with stannanes and boronates, due to chemical instabilities, which limits the versatility use of the acceptor building blocks. In 2012, The Marder and Iverson groups reported the synthesis of stannyl functionalized
naphthalene diimide derivatives, which are the key intermediate n-type building blocks for NDI-related semiconductor materials. In this chapter, we exhibit a new stannyl-functionalized NDI with vinylene linkers, via Stille coupling between dibromated NDI (compound 1) and bis(tributylstanny1)ethylene, as shown in Scheme 5.1. Surprisingly, the resulting 2, 6-ditributylstanny1 ethylene naphthalenediimide (compound 2), was very stable and can be successfully isolated by silica gel chromatography in moderate yield (~50%). Importantly, the stanny1ated NDI-vinyl building block can react with other aryl halides to broaden the reaction scope for NDI-based materials, particularly for the synthesis of conjugated molecules with vinylene linkers along the backbone. It should be noted that, in contrast to the single bond linker, the vinylene linker can minimize the steric effect from the oxygen atoms in NDI and hydrogen atoms in aryl rings and facilitate molecular orbital hybridization between adjacent conjugated units.

A (E)-1,2-di(thiophen-2-yl)ethane (2.0 g) was dissolved in chloroform (200 ml) at room temperature under nitrogen and NBS (4.1 g) was added subsequently. After allowing the solution to room temperature overnight, the reaction mixture was washed by water and extracted by dichloromethane. The organic layer was washed by brine, and dried by MgSO4, filtrated and evaporated. The crude material was purified by chromatography (hexane as eluent). Yield: 72%. 1H NMR (400 MHz, CDCl3): δ= 6.95 (d, J=4.0 Hz, 2H), 6.81 (s, 2H), 6.78 (d, J=4.0 Hz, 2H) MALDI-TOF (m/z): 350.20. Mass spec and 1H NMR data agrees with previous preparation.
Figure 5.2. $^1$H NMR spectrum of (E)-1,2-bis(5-bromothiophene-2-yl)ethane.

The preparation of 2,6- ditributylstannyl ethylene naphthalene diimides was synthesized in a long beck round bottom flask where NDI-Br$_2^{34}$ (0.7 g), bis(tributyltin)ethylene (1.3g), Pd(0) (0.040 g), and toluene (10 ml), the mixture was de-oxygen, and stirred overnight at 90 °C. The crude product was purified by chromatography. (eluent:Hexane/DCM=3:1). Yield : 50%. 1HNMR (400 MHz, CDCl3): $\sigma$= 8.95 (s, 2H), 8.39 (d, J=20.0 Hz, 2H), 8.38 (d, J=20.0 Hz, 2H), 4.16 (d, J=8.0 Hz, 4H), 2.01 (br, 2H), 1.68 (m,12H), 1.50-1.30 (m, 76H), 1.13 (m, 12H), 1.07 (t, J=8.0 Hz, 18H), 0.88 (t, J=8.0 Hz,12H); 13CNMR (CDCl3, 400) $\sigma$ 144.51, 142.13, 132.27, 44.78, 36.57, 32.10, 31.75,30.23, 29.66, 29.59, 29.36, 29.15, 27.40, 26.48, 22.69, 14.27, 13.75, 10.00. MALDI-TOF(m/z): 1458.15.
The desired polymers, NDI-V1 and NDI-V2, were synthesized by Stille polymerization with different thiophene derivatives. To a long neck round-bottomed flask were 2,6-ditributylstannyl ethylene naphthalene diimide (0.24 mmol), thiophene derivatives (0.24 mmol), Pd(dba)_3 (0.007 mmol), and P(o-tolyl)₃ (0.028 mmol), and chlorobenzene (8 ml), the mixture was de-oxygen, and refluxed at 115 °C for three days. The reaction mixture was precipitated into methanol. The precipitate was filtered and extracted (via Soxhlet) with methanol, acetone, hexane, and chloroform for 12 h each. Finally, the polymer was dissolved in chloroform and precipitated in methanol. These polymers were purified by successive Soxhlet extraction in methanol, acetone, and hexane to remove the catalyst and low molecular weight oligomers. The final polymers were dissolved in chloroform and then precipitated into methanol, which were characterized by $^1$H NMR spectroscopy and gel permeation chromatography (GPC). The number average molecular weight (Mn)/dispersity (D) is 35.0 kg.mol$^{-1}$/1.70 for NDI-V1 and 38.0 kg.mol$^{-1}$/1.52 for

**Figure 5.3.** $^1$H NMR of of 2,6- ditributylstannyl ethylene naphthalene diimide.
NDI-V2 determined by GPC. NDI-2200 was synthesized as described previously, with Mn of 40.0 Kg.mol\(^{-1}\), and D of 1.74.\(^{45,49}\)

5.3 Molecular Geometry

**Figure 5.4.** The torsional potential energy of NDI-thiophene derivatives as determined by tuned-\(\omega\)B97X-D/6-31+G(d) level of theory with the corresponding molecular structures shown on the right. Single point energies using spin component scaled MP2 with the cc-pVTZ basis set are included for comparison. See supporting information for computational details.

Density functional theory (DFT) calculations were carried out on a series of the subunits of NDI-2200, NDI-V1, and NDI-V2 to investigate the influence of vinylene linker on planarity of the conjugated backbones (**Figure 5.4**). The torsional potential of thio-NDI prefers a nearly perpendicular arrangement with an optimized dihedral angle of 68° with low energy access (less than ca. 1 kcal/mol) to torsions of 40-150° in the gas phase. Thus, the \(\pi\)-electron conjugation is strongly interrupted between the two units of thio-NDI. In contrast, the optimized dihedral angle which is strongly favored in vinylene-NDI is 145°,
or 35° away from planarity. The steric effects in thio-NDI between the sulfur/C-H of thiophene and oxygen atom in NDI promote a larger out of plane twist than the hydrogen atom in the vinylene linker and oxygen atom in vinylene-NDI. Thus, the inclusion of vinylene spacers between the NDI and thiophene is expected to increase the effective π-electron conjugation length in NDI-V1 and NDI-V2 as compared to NDI-2200.

5.4 Electronic Structure

![Graphical representation](image)

**Figure 5.5.** A) UV-vis of the polymers in the solid state, B) UPS spectra of the secondary electron cutoff region and the HOMO region, and C) The energy diagram for the three polymers (EA estimated from CV, and IP from UPS).

**Table 5.1.** Molecular weights, ionization potentials, electron affinities, and calculated molecular reorganization energies of the NDI-related polymers.

<table>
<thead>
<tr>
<th>polymer</th>
<th>$M_w/M_n$ (kg/mol)</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>IP (eV)</th>
<th>EA (eV)</th>
<th>$E_{\text{opt}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NDI-2200</td>
<td>40/23</td>
<td>394, 704</td>
<td>5.64</td>
<td>3.93</td>
<td>1.46</td>
</tr>
<tr>
<td>NDI-V1</td>
<td>35/20</td>
<td>456, 741</td>
<td>5.43</td>
<td>3.76</td>
<td>1.43</td>
</tr>
<tr>
<td>NDI-V2</td>
<td>38/25</td>
<td>469, 745</td>
<td>5.37</td>
<td>3.71</td>
<td>1.41</td>
</tr>
</tbody>
</table>

\textsuperscript{a}GPC molecular weights were determined with a polystyrene standard in trichlorobenzene.

\textsuperscript{b}UV-absorptions were measured in thin films on glass. \textsuperscript{c}IPs were determined by UPS (IP=WF+HOMO). \textsuperscript{d}EA were determined by thin film CV on a Pt electrode. The potentials
were determined with ferrocene (Fc) as standard by the formula: 
$\text{EA} = -(E_{\text{red onset}} - E_{\text{Fc/Fc}+}^{1/2} + 4.8) \text{ eV}$, wherein $E_{\text{Fc/Fc}+}^{1/2} = 0.60 \text{ eV}$. Estimated from thin-film absorption onset.

**Figure 5.5** shows the optical absorption properties of the polymers in the solid state. In films, NDI-2200, NDI-V1, and NDI-V2 exhibit absorption maxima of 704, 741, and 745 nm, respectively. There is a red shifting of the absorption spectra in the solid state with an increasing number of vinylene linkers in the backbones reinforcing the hypothesis of more planar conformations and more extended conjugation. Compared to NDI-V1, NDI-2200 displays a blue shift of $\lambda_{\text{max}}$ of 37 nm (0.088 eV), with NDI-V2 displaying a very small additional red shit of 4 nm (0.008 eV). This indicates that the vinylene linker between donor (thiophene) and acceptor (NDI) units play a more important role in enhancing internal charge transfer (ICT) transitions arising from the bonding of donor (thiophenes) and acceptor (NDI) building units along the polymer backbone than the vinylene linker between bithiophene (donor-donor). The $S_0 \rightarrow S_2$ band of NDI-2200 exhibits a maximum at 380 nm, while this band is shifted to longer wavelengths for NDI-V1 (to 479 nm) and NDI-V2 (to 489 nm). Interestingly, the vinylene linker does not significantly affect the absorption onset, with the optical gaps obtained from the absorption edge onsets only varying from 1.46 to 1.41 eV for the three polymers.

Cyclic voltammetry (CV) studies were performed in acetonitrile with 0.1 M TBAPF$_6$ as the supporting electrolyte at a scan rate of 100 mV/s and onset oxidation potentials were determined relative to Fc/Fc+ (4.8 eV). The three polymers exhibit two reversible reduction waves (**Figure 5.6**). According to their onset potentials, electron affinities (EAs) were estimated as 3.93, 3.76, and 3.71 eV for NDI-2200, NDI-V1, and NDI-V2, respectively.
The IPs were measured by ultraviolet photoelectron spectroscopy (UPS). From the secondary electron cutoff, the work function of UV-ozone treated Au measured to be 4.66 eV, while the work functions of the polymers were measured to be 4.56, 4.51 and 4.52 eV for NDI-N2200, NDI-V1 and NDI-V2 respectively. From the magnified HOMO region (Figure 5.2B), the HOMO onset of the polymers were 1.08, 0.92, and 0.85 eV. Therefore, the ionization energies (= WF + HOMO) of the polymers were determined to be 5.64, 5.43, and 5.37 eV for NDI-2200, NDI-V1 and NDI-V2, respectively. Typically, for NDI-based polymers, the IPs appear to be largely influenced by the donor strength, but with the EAs essentially unaffected. The vinylene linker between donor and acceptor can decrease both the IP and EA energies with a shift of about 0.21 eV as compared to the benchmark NDI-2200. However, NDI-V1 and NDI-V2 have very similar energy levels with a difference of ~0.06 eV. Similar to the optical absorption, the vinylene linker between donor and acceptor can increase the IP and EA energies more than the vinylene linker between the bithiophene donor unit (~ 0.21 eV versus ~ 0.06 eV). By combining thin film optical and electrochemical data, the IPs are estimated to be 5.39, 5.19, and 5.12 eV for NDI-2200, NDI-V1 and NDI-V2, respectively. Although these approximated values, which neglect the binding energy of the electron-hole pair, were found to be ~ 0.25 eV higher than those from UPS, this discrepancy is expected and in good agreement with the trend.

**Figure 5.6.** CV graph of thin film of A) N2200, B) NDI-V1, and NDI-V2
discussed above. This difference is not surprising since the solution-based CV measurements have counterions to stabilize the charged species while the UPS measurements do not. As the number of vinylene linkers increase, the ionization potential of the polymers decreases, which should facilitate hole injection from gold electrodes.

5.5 Quantum Chemical Calculation – Cation/Anion Radical Geometry

Figure 5.7. The cation radical geometry with the hole polaron plotted for NDI-2200 (A), NDI-V1 (C), and NDI-V2 (E). The anion radical geometry with the electron polaron plotted for NDI-2200 (B), NDI-V1 (D), and NDI-V2 (F). Orbitals plotted using an isovalue of 0.02 electrons/bohr$^3$. 
We next turn to studying the electronic and geometric structures of the tetramers computationally. We use the tuned-ωB97X method as the density functional approximation and the 6-31+G(d) basis set. When comparing the charged structures it is clear that the hole and or electron is more localized in NDI-2200 than in NDI-V1 and NDI-V2 for the cation and or anion (Figure 5.7). The hole polaron molecular orbital more localized for NDI-2200 with 82% being localized on one bithiophene unit while the largest contributing bithiophene-ethylene unit is 68% and 77% for NDI-V1 and NDI-V2 respectively. Interestingly, the additional ethylene linkers in NDI-V2 lead to a more localized hole polaron as compared to NDI-V1. Likewise for the negatively charged polaron the largest contributing NDI unit is 92%, 67%, and 65% for NDI-2200, NDI-V1 and NDI-V2. Thus, the negative polaron is much more delocalized upon adding vinylene bridges. The charges on each group were also explored and were found to be more pronounced in the more planar NDI-V1 and NDI-V2, a result of the resonant effects of the donor-acceptor motifs being allowed to play a larger role than in NDI-2200, where conjugation is less effective.

5.6 Thin Film Microstructure – GIXD

To further investigate the microstructure of the polymers, grazing incidence wide-angle X-ray scattering (GIWAXS) measurements were performed on thin film samples. Figure 5.8 presents the 2D GIWAXS scattering patterns of NDI-V1 and NDI-V2 on OTS-treated SiO$_2$ substrates. Table 5.2 summarizes the d-spacing and coherence lengths observed for the in-plane alkyl stacking and out-of-plane π-π stacking peaks. From the GIWAXS images it is apparent that both polymers exhibit a preferential face-on orientation of crystallites in as-cast films similar to that observed for NDI-2200. Key peaks are indexed on the 1-D in-plane and out-of-plane scattering profiles with the alkyl stacking peak located
at $q \sim 0.267$ Å corresponding to a lamellar stacking d-spacing of $\sim 2.34$ nm for both polymers, which is shorter than that of NDI-2200 ($\sim 2.54$ nm). A prominent $\pi-\pi$ stacking peak is observed at $q = 1.7$ Å corresponding to a $\pi-\pi$ stacking distance of $\sim 0.37$ nm for both polymers, slightly shorter than that of NDI-2200 (0.39 nm). Annealing leads to a significant increase in the coherence length of crystallites with the coherence length of the in-plane lamella stacking peak increasing from $\sim 8$ nm to $\sim 15$ nm with annealing. A similar increase in the coherence length of the $\pi-\pi$ stacking peak (out-of-plane) is observed increasing from $\sim 3$ nm to $4 - 5$ nm with annealing, corresponding to a $\pi-\pi$ stacking of $\sim 10$ chains. In addition to increased coherence length, the increased scattering intensity both in-plane and out-of-plane (Figure 5.8C and 5.8D) indicates that annealing leads to an increase in crystallinity and the growth of a significant population of crystallites scattering out of plane, indicating an edge-on orientation.

**Figure 5.8.** 2D GIWAXS scattering patterns of NDI-V1 and NDI-V2 spun on SiO$_2$OTS from chlorobenzene. A) NDI-V1, as cast, B) NDI-V2, as cast, C) NDI-V1, annealed at
200°C, D) NDI-V2, annealed at 200°C, E) In-plane (horizontal) and F) out-of-plane (vertical) scattering extracted from the 2D GIWAXS scattering patterns.

**Table 5.2.** Summary of crystallographic parameters from GIWAXS

<table>
<thead>
<tr>
<th>polymer</th>
<th>(100) d-spacing (nm)</th>
<th>(100) coherence length (nm)</th>
<th>(010) d-spacing (nm)</th>
<th>(010) coherence length (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NDI-V1 as-cast</td>
<td>2.34 ± 0.02</td>
<td>9.2 ± 0.2</td>
<td>0.370 ± 0.002</td>
<td>3.1 ± 0.6</td>
</tr>
<tr>
<td>NDI-V1 annealed</td>
<td>2.40 ± 0.02</td>
<td>15.3 ± 0.2</td>
<td>0.372 ± 0.002</td>
<td>4.2 ± 0.5</td>
</tr>
<tr>
<td>NDI-V2 as-cast</td>
<td>2.34 ± 0.02</td>
<td>8.0 ± 0.2</td>
<td>0.372 ± 0.002</td>
<td>2.7 ± 0.5</td>
</tr>
<tr>
<td>NDI-V2 annealed</td>
<td>2.34 ± 0.02</td>
<td>14.8 ± 0.2</td>
<td>0.370 ± 0.002</td>
<td>4.7 ± 0.5</td>
</tr>
</tbody>
</table>

5.7 Charge Transport Properties

Bottom gate bottom contact (BDBC) OFET devices were fabricated in a glove box and tested under air. The mobilities calculated in the saturated regime, threshold voltages and current on/off ratios are summarized in **Table 5.3**. Devices based on NDI-2200 exhibited electron transporting-dominant characteristics with a mobility of 0.007 cm$^2$V$^{-1}$s$^{-1}$ and no hole mobility was observed. However, the devices based on NDI-V1 showed typical ambipolar characteristics with average hole/electron mobilities of 0.43/0.15 cm$^2$V$^{-1}$s$^{-1}$ (**Figure 5.9**). Although NDI-V2 has stronger donor strength than NDI-V1, it also exhibited ambipolar characteristics but with slightly lower average mobilities for hole/electron of 0.12/0.08 cm$^2$V$^{-1}$s$^{-1}$. Compared to most of the electron dominant NDI-based polymers, NDI-V1 and NDI-V2 exhibit hole dominant characteristics, which were remarkably improved by the vinylene linkers.
Figure 5.9. Transfer characteristics in the saturated region of the BGBT thin film transistors: (A) NDI-V1 in air, (B) NDI-V1 under vacuum, (C) NDI-V2 in air, and (D) NDI-V2 under vacuum.

Table 5.3. Mobility, On/Off Ratio, and Threshold Voltage of the NDI-based polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Device geometry</th>
<th>P-channel</th>
<th>n-channel</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>μ&lt;sub&gt;h&lt;/sub&gt; (cm&lt;sup&gt;2&lt;/sup&gt;V&lt;sup&gt;-1&lt;/sup&gt;s&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>V&lt;sub&gt;th&lt;/sub&gt; (V)</td>
<td>I&lt;sub&gt;on&lt;/sub&gt;/I&lt;sub&gt;off&lt;/sub&gt;</td>
</tr>
<tr>
<td>NDI-V1</td>
<td>TGBC&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.02±0.01</td>
<td>~30</td>
</tr>
<tr>
<td></td>
<td>BGBC&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.43±0.02</td>
<td>~15</td>
</tr>
<tr>
<td></td>
<td>BGBC&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.005±0.001</td>
<td>~10</td>
</tr>
<tr>
<td>NDI-V2</td>
<td>TGBC&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.007±0.002</td>
<td>~30</td>
</tr>
<tr>
<td></td>
<td>BGBC\textsuperscript{b}</td>
<td>0.12±0.01</td>
<td>~15</td>
</tr>
<tr>
<td>-------------------</td>
<td>-----------------------</td>
<td>-----------</td>
<td>------</td>
</tr>
<tr>
<td>BGBC\textsuperscript{c}</td>
<td>0.004±0.001</td>
<td>~10</td>
<td>~10^2</td>
</tr>
<tr>
<td>NDI-2200</td>
<td>TGBC\textsuperscript{a}</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>BGBC\textsuperscript{b}</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>BGBC\textsuperscript{c}</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

\textsuperscript{a} TGBC: Top-Gate Bottom-Contact measured at ambient condition; \textsuperscript{b} BGBC: Bottom-Gate Bottom-Contact devices measured at ambient condition; \textsuperscript{c} BGBC: Bottom-Gate Bottom-Contact devices measured under vacuum; All the thin films were annealed at 200 °C for 20 mins in glovebox and performance tested for 6 devices.

5.8 Conclusions

In summary, we have developed an efficient and straightforward synthesis of 2, 6-ditributylstannyl ethylene NDIs. Two NDI copolymers connected via vinylene linkers to different donor strength units were synthesized. The vinylene linker minimizes steric interactions between the NDI and thiophene subunits, leading to an extended conjugation length with a smaller reorganization energy as revealed by density functional theory calculations (DFT). Although these two polymers exhibit electron dominant characteristics under vacuum, the devices under air flip the dominant polarity and yield hole mobilities up to 0.43 cm^2V^{-1}s^{-1}. This is the first report where a vinylene linker is incorporated between a donor and acceptor to tune the electronic properties. In addition, the building block can be used to produce vinylene-linked NDI-containing small molecules, oligomers, and polymers, which are promising semiconductor materials including but not limited, to organic transistors and organic solar cells.
5.9 Acknowledgements

I would like to thank the Office of Naval Research (N0001471410053) and the National Science Foundation (DMR-1508627) for support of this work. Dr Lei Zhang allowed the idea and guidance to making this work into a complete story. Dr. Yao Liu fabricated the transistor devices and optimization. Prof. Christopher McNeill measured the thin film microstructure to assess molecular orientation and ordering at the Australian Synchrotron. Calculations were performed by Dr. Bradley Rose of Prof. Jean-Luc Bredas’ group at KAUST.
CHAPTER 6
EFFICIENT ELECTRON MOBILITY IN AN ALL-ACCEPTOR
NAPTHALENEDIIMIDE-BITHIAZOLE POLYMER SEMICONDUCTOR

6.1 Introduction and Overview

Rylene diimide-based units are attractive building blocks for the design of stable n-channel OSCs.38 The presence of two imides but increases the electron affinity, and offers a molecular handle for substituent engineering to control solubility and thin film morphology. The bicyclic motif also allows potentially for efficient interchain charge transport due to its large π-surface area. Naphthalene diimide (NDI) is among the most thoroughly studied of monomer units for the synthesis of n-type PSCs.34,39–48 In combination with an appropriate co-monomer, an n-type PSC with a large electron affinity (i.e., low lying LUMO energy level) for unipolar transport and ambient device stability may be afforded. The first report of a stable electron-transporting NDI-based copolymer exhibited a high electron mobility of 0.85 cm² V⁻¹ s⁻¹; further optimization has produced state-of-the-art NDI-based polymers with mobilities up to 6.5 cm² V⁻¹ s⁻¹ through modification of N-substituents and donor repeat units.33,34,49

Although recent work has led to an increase in electron mobility, a large backbone torsion is still present in NDI polymers189,202–204, indicating that further molecular design modification could be employed to control and further enhance device performance. For instance, the incorporation of planarizing vinyl moieties between the donor and acceptor building blocks in NDI copolymers enables efficient hole transport in traditional n-type semiconductor polymers.41 While these efforts have indeed been successful in planarizing these systems, they often result in a more ambipolar response instead of true unipolar
transport. While intramolecular interactions also been contribute to planarizing molecular backbones for enhanced performance, recent studies by Marks, Guo, and coworkers show n-type polymers to have high electron mobilities despite their non-planar conformation when synthesized in combination with an electron deficient comonomer. Electronic structure of the non-planar, electron-deficient polymer yielded a wide bandgap with high ionization potential (i.e., low-lying HOMO). These results led our group to investigate an all-acceptor NDI-based polymer that might have intrinsically large torsion angles.

Here, we incorporate the electron-deficient bithiazole unit in NDI-based PSCs; this unit is particularly interesting due to its resemblance to the electron-rich thiophene analogue, offering optoelectronic tunability without significant molecular structure change. Although thiazole-based PSCs have struggled to outperform thiophene-based PSCs, improved oxidative stability and high electron affinities and ionization potentials (low-lying frontier energy levels) present attractive features to develop new, air-stable n-type materials. For example, electron conducting behavior has been reported for diketopyrrolopyrrole-bithiazole based polymers with long term device stability of up to 4 months. Thus, the combination of bithiazoles with electron deficient monomers can be considered as an alternative approach to traditional donor-acceptor polymers for air-stable high performance n-type materials.

In this work, we report the synthesis of an all-acceptor copolymer, poly{[N,N'-bis(2-octyldodecyl)-1,4,5,8-naphthalene diimide-2,6-diyl]-alt-2,2'-(5,5'-bithiazole)}, P(NDI2OD-BiTz). In comparison to the benchmark n-type polymer with bithiophene, P(NDI2ODT2), an imine is present at the 3,3’ position of the bis(pentacyclic) co-monomer. Density functional theory (DFT) calculations show the NDI-thiazole dihedral angles are
nearly perpendicular, presumably due to the repulsive lone pair interactions of imide and neighboring imine. Despite this large twist, we observe electron mobility on the order of 0.1 cm² V⁻¹ s⁻¹ with use of a polymer zwitterionic interlayer to improve charge injection. Vinyl containing derivative polymer, poly{[N,N'-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-ethene diyl]-alt-2,2 '-(5,5'-bithiazole)} (P(NDI2OD-V-BiTz), was also prepared but did not show any device response and thermal instability (T_d = 164 °C). Non-working devices of P(NDI2OD-V-BiTz) was presumably due to low molecular weight.

6.2 Synthesis and Characterization of Compounds

General: ¹H NMR and ¹³C NMR spectra were recorded in deuterated solvent on a Bruker ADVANCE 400 NMR. ¹H NMR chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) reference using the residual protonated solvent as an internal standard. MALDI-TOF-MS were determined on a Bruker BIFLEXII Mass spectrometer with trithiophenes as matrix. All chemicals were purchased from commercial suppliers and used without further purification unless otherwise specified. THF was freshly distilled from sodium prior to use.

2,2'-dibromo-5,5'-bithiazole was prepared in a flame dried, nitrogen purged 100 mL round bottom flash, 1.64 g (10 mmol) of 2-bromothiazole was dissolved in 40 mL of freshly distilled THF. Prepared 10.1 mL 0.5M solution of (tmp)²Zn·2 MgCl₂·2 LiCl was added drop wise via cannulation at room temperature over 30 minutes. Solution was allowed to stir at room temperature for 1 hour, reflecting a yellow/orange solution color. Reaction was then cooled to −40 °C, followed by portioned addition chloranil (2.71g, 11 mmol) over 30 mins. Solution was warmed up to 0 °C for 5 hours. Reaction was quenched
via 5 mL addition of saturated NH₄Cl (aq) solution. The organic layer was washed by brine, dried over MgSO₄, filtered and evaporated. The crude material was purified by chromatography (2:1 Hexane/dichloromethane) to rid of impurities, then flushed with dichloromethane. Collected red solution was reduced and recrystallized in acetonitrile to yield white solids. Yield: 80% (1.29 g). ¹H NMR (400 MHz, CDCl₃): δ = 7.61 (s, 1H). ¹H NMR peaks are in good agreement with previous reports.²¹¹,²¹²

Figure 6.1. ¹H NMR Spectra of 2,2’-dibromo-5,5’-bithiazole

N,N’-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-di(tributyltin) was prepared In a flame dried, nitrogen purged 50 mL round bottom flask. 0.5 g (0.51 mmol) N,N’-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-dibromide, 0.71 g (1.2 mmol) bis(tributyltin), 47 mg (0.051 mmol) Pd₂(dba)₃, and 62 mg (0.26 mmol) tri(o-tolyl)phosphine was dissolved in 20 mL of anhydrous toluene. The solution was heated to 110 °C and stirred overnight. Toluene was reduced under vacuum and the crude liquid was purified via chromatography (10:1 hexane/dichloromethane). The product was collected as a viscous yellow liquid. Yield: 80%. ¹H NMR (400 MHz, CDCl₃): δ = 8.95 (s, 2H), 4.14 (d, 4H), 1.97 (m, 2H), 1.57-1.51 (m, 12H), 1.41-1.18 (m, 86H), 0.89-0.83 (m, 32H). ¹H NMR peaks are in good agreement with previous reports.²¹³
Figure 6.2. $^1$H NMR of $N,N'$-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-di(tributyltin).

$N,N'$-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-di(tributyltin) was prepared via the following procedure. $N,N'$-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-dibromide (0.7 g), bis(tributyltin)ethylene (1.3 g), Pd(0) (0.040 g), and toluene (10 ml) was added in a long neck round bottom flask. The mixture was de-oxygen and stirred overnight at 90 °C. The crude product dried was purified by chromatography. (eluent: Hexane/DCM=3:1). Yield : 50%. $^1$H NMR (400 MHz, CDCl3): $\sigma=8.95$ (s, 2H), 8.39 (d, 2H), 7.36 (d, 2H), 4.13 (d, 4H), 2.01 (br, 2H), 1.68 (m, 12H), 1.50-1.30 (m, 76H), 1.13 (m, 12H), 1.07 (t, 18H), 0.88 (t, 12H). $^1$H NMR peaks were in good agreement with previous literature.41
Figure 6.3. $^1$H NMR of $N,N'$-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-di(vinyl-tributyltin).

Scheme 6.1. Stille cross-coupling polymerization to afford P(NDI2OD-BiTz) and P(NDI2OD-V-BiTz).

Poly{[N,N'-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-2,2'-(5,5'-bithiazole)} (P(NDI2OD-BiTz) was synthesized via Stille cross-coupling as depicted in Scheme 6.1. Through a bottom-up approach, monomers were appropriately functionalized with complementary trialkylstannyl and halogen groups for subsequent
polymerization. High-yield, one-pot synthesis of 2,2'-dibromo-5,5'-bithiazole was carried out as previously described by Paul and Heeney.\textsuperscript{211,214} N,N'-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-di(tributyltin) was prepared via Stille coupling of appropriate dibrominated naphthalene diimide precursor with hexabutylditin in high yields.\textsuperscript{41,198,214,215} P(NDI2OD-V-BiTz) was polymerized in a similar fashion with tris(dibenzyldeneacetone)dipalladium(0) and tritolyl phosphate catalyst/ligand.

The resultant polymer was purified via Soxhlet extraction using methanol, acetone, hexanes, and chloroform. The product collected from the chloroform fraction was precipitated in cold methanol and characterized via high temperature trichlorobenzene gel permeation chromatography (GPC). The number average molecular weight (Mn) and dispersity (D) for P(NDI2OD-BiTz) are 32.0 kg mol\textsuperscript{-1} and 1.95, respectively. P(NDI2OD-V-BiTz) number average molecular weight (Mn) and dispersity (D) was determined to be 15 kg mol\textsuperscript{-1} and 2.47, respectively.

It was determined that P(NDI2OD-V-BiTz) did not have any device response in the thin film transistor. This was attributed to low molecular weight of the polymer as measured via GPC. Annealing of thin films did not increase nor enable any device responsiveness. The degradation temperature of P(NDI2OD-V-BiTz) was measured via thermal gravitational analysis. The initial onset of degradation was set as this value, T\textsubscript{d} = 164 °C. Upon increasing temperature, a second degradation temperature was observed at 409 °C at 85% of sample weight. Molecular weight repeat unit analysis postulates this degradation reaction to be at the vinylene-thiazole junction as the release of bithiazole moiety is aligned with 15% loss of molecular weight.
Figure 6.4. Thermal degradation profile of P(NDI-V-Bitz).

Additionally, insoluble material was also observed after annealing the polymer above 170 °C. FTIR reflect a 988 cm\(^{-1}\) peak depression with annealing, indicative of vinyl proton bending. This gives evidence to possible thermal crosslinking of exposed vinylene functionalities. Due to the instability and unresponsive devices of this polymer, the rest of this chapter discussion will mainly concern P(NDI2OD-BiTz).
**Figure 6.5.** FTIR transmittance spectra of P(NDI-V-BiTz) unannealed and annealed thin films.

6.3 Molecular Geometry Calculations

To examine the potential energy landscape of the polymer building blocks, torsional energies of the dihedral angles between NDI and thiazole, and between two thiazole subunits were calculated both at the Spin-Component Scaled Second-Order Møller–Plesset Perturbation Theory (SCS-MP2) level and the density functional theory (DFT) tuned-ωB97XD level with the 6-31+G(d) basis set (Figure 6.3). There is excellent agreement between the results from the two methods, which point to a nearly perpendicular arrangement (~90°) between the thiazole and NDI units due to the repulsion between an oxygen in NDI and sulfur/nitrogen atoms in thiazole. It should be noted, however, that the torsion potential is very flat around the minimum, with easy fluctuations possible between
50° and 130° in the case of the isolated molecules. The optimized torsion potential between two thiazole units displays two minima, one around 150°, and the other around 50° (see Figure 6.3), while fluctuations of ca. ±20° possible. The flatness of the torsion potential curves may result in high torsional disorder along the conjugated polymer backbone and hence disturb the π-electron conjugation between monomer units.

![Illustration of the SCS-MP2 and DFT tuned-ωB97XD torsion potentials between the P(NDI2OD-BiTz) moieties.](image)

**Figure 6.6.** Illustration of the SCS-MP2 and DFT tuned-ωB97XD torsion potentials between the P(NDI2OD-BiTz) moieties.

Calculations of the geometric and electronic structures of P(NDI2OD-BiTz) oligomers were carried out at the tuned-ωB97XD/6-31G(d) level. The electronic properties essentially converge at the level of the tetramer, see Figure 6.4. Figure 6.5 illustrates that there occurs a strong localization of both the Highest Occupied Molecular Orbital (HOMO), which is distributed on bithiazole units, and the Lowest Unoccupied Molecular Orbital (LUMO), which is distributed on NDI units, as a consequence of the very large intramolecular torsions. Given the high values of the dihedral angles along the chain, the calculated reorganization energies are very significant, 0.99 eV for the cation and 0.66 eV.
for the anion, as the ion relaxes essentially into a single moiety, as illustrated for the anion in Figure 6.6.

**Figure 6.7.** Evolution of the TDDFT optical gap vs. oligomer size for P(NDI2OD-BiTz) as obtained at the tuned-ωB97X-D/6-31G(d,p) level of theory.

**Figure 6.8.** Illustration of the frontier molecular orbitals for the tetramer of P(NDI2OD-BiTz), as obtained at the tuned-ωB97XD/6-31G(d,p) level.
Figure 6.9. Illustration of the singly occupied molecular orbital (SOMO) in the anion of the P(NDI2OD-BiTz) tetramer as calculated at the ωB97X-D/6-31G(d,p) level of theory.

6.4 Experimental Electronic Structure Determination

Table 6.1. Molecular weights, absorptions, optical/transport band gap, ionization potential, and electron affinity of P(NDI2OD-BiTz).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Mw/Mn&lt;sup&gt;a&lt;/sup&gt; (kg/mol)</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt; (nm)</th>
<th>E&lt;sub&gt;opt&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt; (eV)</th>
<th>IP&lt;sub&gt;UPS&lt;/sub&gt;&lt;sup&gt;d&lt;/sup&gt; (eV)</th>
<th>EA&lt;sub&gt;CV&lt;/sub&gt;&lt;sup&gt;e&lt;/sup&gt; (eV)</th>
<th>EA&lt;sub&gt;PES&lt;/sub&gt;&lt;sup&gt;f&lt;/sup&gt; (eV)</th>
<th>E&lt;sub&gt;g&lt;/sub&gt;&lt;sup&gt;g&lt;/sup&gt; (transport gap)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(NDI2OD-BiTz)</td>
<td>63/32</td>
<td>389, 571</td>
<td>1.80</td>
<td>6.06</td>
<td>3.98</td>
<td>3.83</td>
<td>2.23</td>
</tr>
</tbody>
</table>

<sup>a</sup> GPC molecular weights were determined using polystyrene standards and trichlorobenzene mobile phase. <sup>b</sup> UV-absorptions were measured as thin films on glass. <sup>c</sup> Estimated from thin-film absorption onset. <sup>d</sup> The IP was determined from the SEC and UPS lowest-binding feature onset. <sup>e</sup> The EA was determined by thin film CV on a Pt electrode. The potentials were determined with ferrocene (Fc) as standard by the formula: EA = −E<sub>red</sub>.
\[ \text{onset} = E_{\text{Fc/Fc}^+}^{1/2} + 4.8 \text{ eV}, \] wherein \( E_{\text{Fc/Fc}^+}^{1/2} \) 0.53 eV. EAs were determined from SEC and IPES highest-binding feature onset. E\(_g\) was determined as \( \text{IP}_{\text{UPS}} - \text{EA}_{\text{IPES}} \).

**Figure 6.10.** (a) UV-Vis spectra of P(NDI2OD -BiTz) in chloroform and thin film on glass, (b) thin film cyclic voltammetry of P(NDI2OD -BiTz), UPS spectra of (c) the secondary electron cutoff region, (d) the HOMO region, and (e) the combined results of UPS and IPES showing the transport gap.

The optical absorption spectra of both the thin film and solution are shown in Figure 6.7a. In the thin film, P(NDI2OD-BiTz) exhibits a broad absorption peak with a maximum at 567 nm (2.19 eV), which is closely matched by the DFT calculations that gives an optical gap of 557 nm (2.23 eV, when taking account of a dielectric medium \( \varepsilon = 3.5 \)). Compared to the solution absorption, a large redshift of 55 nm (0.16 eV decrease) is observed in the thin film. The absorption onset is observed at 680 nm corresponding to an optical gap of 1.82 eV. The larger optical gap of P(NDI2OD-BiTz) with respect to P(NDI2OD-2T) (approximately 1.4 eV) is mainly the result of a larger ionization potential (deeper HOMO).
The polymer electron affinity (EA) and ionization potential (IP) were determined experimentally by the combination of cyclic voltammetry (CV), ultraviolet photoelectron spectroscopy (UPS), and inverse photoemission spectroscopy (IPES). CV measurements were performed in a 0.1 M tetra-n-butylammonium hexafluorophosphate acetonitrile solution at a scan rate of 100 mV/s. The first reversible reduction onset occurs at -0.29 eV. The electron affinity from this reduction is determined to be 3.98 eV, comparable to that in the bithiophene analogue. Figures 6.7c-e show the UPS and IPES spectra of a P(NDI2OD-BiTz) thin film on Au. These measurements probe the electronic structure in the solid state. In Figure 6.7c, the secondary electron cut-off (SEC) region spectra were drawn using the kinetic energy scale so the SEC indicates the work function (WF) directly. The WF of Au and P(NDI2OD-BiTz) films was measured to be 4.84 eV and 4.63 eV, respectively. The low-binding region spectra of Au and P(NDI2OD-BiTz) are shown in Figure 6.7d. Shirley-type background due to inelastic scattering was removed from the measured low-binding region spectrum to determine accurately the onset of the lowest-binding feature (i.e., IP). To assess the IP and EA values, the magnified low-binding UPS and high-binding IPES regions are shown in Figure 6.7e. The UPS onset is observed at 1.43 eV while the IPES onset is at -0.80 eV, which results in an IP value of 6.06 eV and an EA value of 3.83 eV, giving a transport gap of 2.23 eV (IP\textsubscript{UPS} – EA\textsubscript{IPES}). The hole and electron injection barriers from Au to P(NDI2OD-BiTz) are evaluated to be 1.43 eV and 0.80 eV. Comparing to the benchmark n-type polymer P(NDI2OD-T2), P(NDI2OD-BiTz) has a higher IP due to the bithiazole moiety while the electron affinity remains defined by the naphthalene diimide unit.\textsuperscript{41}
6.5 Annealing Morphology

![Figure 6.11. GIXD of P(NDI2OD-BiTz) before and after annealing at 200 °C for 30 mins on Si substrate.](image)

Table 6.2. GIXD data of as cast and annealed P(NDI2OD-BiTz).

<table>
<thead>
<tr>
<th>Sample</th>
<th>(100) Peak (Å⁻¹)</th>
<th>d-spacing (Å)</th>
<th>FWHM (Å⁻¹)</th>
<th>Coherence Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As Cast</td>
<td>0.292</td>
<td>21.5</td>
<td>0.101</td>
<td>62.1</td>
</tr>
<tr>
<td>Annealed</td>
<td>0.299</td>
<td>21.0</td>
<td>0.0385</td>
<td>163.2</td>
</tr>
</tbody>
</table>

The thin film microstructure of P(NDI2OD-BiTz) was characterized using grazing-incidence X-ray diffraction (GIWAXS). The diffraction pattern of the as-cast polymer, shown in Figure 6.8, exhibits a broad, weak maximum in the out-of-plane direction at \( q_z = 0.29 \, \text{Å}^{-1} \), corresponding to the lamellar spacing reflection (21.5 Å). This indicates that the polymer backbone is aligned in an edge-on orientation with respect to the substrate. Annealing the sample at 200 °C for 30 minutes greatly improves the structural ordering of the thin film microstructure as evident in the increased scattering intensity and the four reflections in the z-direction, i.e. normal to the surface of the film. The orientation of the polymer does not change upon annealing and still adopts an edge-on texture. Scherrer
equation analysis reveals a substantial coherence length increase of the lamellar stacks from unannealed (6.2 nm) to annealed film (16.3 nm). The thiazole unit has a profound effect on the morphology when compared to similar bithiophene containing derivatives, which adopts face-on molecular packing with an intense \( \pi \)-stacking peak present in the \( z \) direction, contrary to the P(NDI2OD-BiTz) with its edge-on packing and no peak associated with the \( \pi \)-stacking.\(^{41,190,191}\) Thus, the thiazole unit and large torsion angle has a large influence on the crystalline order between chains in the \( \pi \)-stacking direction, with the intrachain torsion frustrating the interchain packing, resulting in the lack of a \( \pi \)-stacking peak and also impacts the polymer orientation, which adopts in an edge on manner.

6.6 Optimization of Thin Film Transistors

![Graphs of Mobility and Threshold Voltage vs. Annealing Temperature](image)

**Figure 6.12.** Temperature annealing effects upon mobility and threshold voltages of P(NDI2OD-BiTz) BGBC devices with annealing time of 30 mins.

To evaluate the connection between the morphology and charge transport properties, bottom-gate, bottom-contact (BGBC) transistors were fabricated. Spin-coated films without any thermal annealing demonstrate low electron mobilities of \( 6.4 \times 10^{-4} \) cm\(^2\)/Vs with high threshold voltages (\( \sim 40 \) V), as shown in Figure 6.9. Upon annealing at 200 °C, or above, the mobility is observed to increase significantly, by a factor of about 15,
up to ~0.01 cm$^2$/Vs. This value is fully consistent with theoretical estimate of 0.008 cm$^2$/Vs, calculated on the basis of a polaron transport model, see SI for details; in spite of the strongly twisted character of the backbone, there still is a nonnegligible electronic coupling (transfer integral) of 14 meV between adjacent NDI units, which is sufficient to account for the observed mobility. The threshold voltage also sharply decreased upon annealing and exhibited a minimum of 1 V at 200 °C, then increasing at higher annealing temperatures.

To further optimize the mobility, we fabricated top-contact, bottom-gate (TCBG) devices and used a conjugated polymer zwitterion interlayer, P(T2NDISB), shown in Figure 6.10a. The zwitterionic interlayer was recently reported by Emrick and coworkers to boost the power conversion efficiencies of PBDTT-TT:PC71BM BHJ photovoltaic devices from 3.17% to 10.19%;$^{216,217}$ use of an n-type polymer backbone ensured efficient electron collection at the cathode while the zwitterionic functionality provided sufficient negative interface dipole to lower electrode work function. Here, we employ P(T2NDISB) similarly to decrease the charge injection barrier between semiconducting-transport layer and metal contacts of fabricated devices. These devices were all annealed at 200 °C. The TCBG device gave a mobility of 0.018 cm$^2$/Vs, and with the use of the NDI-interlayer (P(T2NDISB)), the mobility was improved to 0.11 cm$^2$/Vs.
Figure 6.13. a) BG-TC device architecture with the structure of P(T2NDISB) zwitterionic interlayer, b) transfer characteristics of devices with and without interlayer, c) output curves of devices without interlayer and d) with the interlayer.

6.7 Conclusion

An all-acceptor polymer, P(NDI2OD-BiTz), was synthesized via Stille polymerization and characterized in field-effect transistors to understand the interactions between these two electron deficient moieties. Density functional theory calculations
reveal repulsive interactions between the nitrogen of the thiazole imine and oxygen of the adjacent imide moiety, forcing an effectively perpendicular torsion angle. Despite this conjugated dihedral angle, annealed thin films transistor devices with high lamellar ordering yield electron mobilities of 0.1 cm²/Vs with current on/off ratios greater than 10⁵. GIXD reveals the profound effect of thiazole on morphology, as the annealed film of P(NDI2OD-BiTz) affords an edge on packing, opposite to that of similar bithiophene polymer analogues. Furthermore, we demonstrate the use of an NDI-polymer zwitterion interlayer effectively decreases the charge injection barrier of metal contact/semiconductor interface, thereby enhancing carrier mobilities by one order of magnitude. This work demonstrates the first report of thiazole containing NDI polymer with efficient electron mobilities.

6.8 Acknowledgements

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CHAPTER 7

CONCLUSIONS AND FUTURE OUTLOOK

7.1 Overview of Results

This dissertation reviewed the influence of stability and performance of small molecule and polymer semiconductors. In chapters 2, the oxidation of rubrene were studied which revealed the importance of having pure, acid free solvent that deter the acid-catalyzed irreversible second stage oxidation. Such irreversible impurities would severely impact device performance as creating a void/defect sight in solid state ordering. Later in chapter 3, designing rubrene derivatives through modification of short axis conjugated substituents were revealed an effective strategy of increasing resilience against photo-oxidation. Excited state photo-kinetics was identified as an important parameter to gauge in terms of photooxidation stability, rather than typical band energy structure analysis.

Chapter 4 overviewed the tunability of anthanthrene based small molecules for OPV applications. Ethynyl type conjugation along the short axis proved to immensely impact the molecule energetics as exampled with dimer and rylene diimide “sandwich” forms. The use of the two-dimensional oligoacenes core for creating small molecule OSCs ensured photo-stability and high surface areas for the potential of intimate intermolecular interactions.

Polymers presented in the later chapters studied the impact of planarizing NDI based designs. Vinylene linkers between the acceptor-donor repeat structure proved successful in increasing carrier mobilities through the planarization of the backbone in chapter 5. Surprisingly, this also enabled ambipolar response which was rationalized though quantum mechanical analysis of the ionic radical geometries. In chapter 6,
planarized forms of NDI based polymers were also studied in bithiazole based copolymers for all-acceptor PSC. Though initially calculated for relaxed geometries to adopt a completely perpendicular orientation between monomers, annealing at high temperatures induced dramatic increase in thin film microstructure ordering and device. It was presumed that higher thermal energies allowed intrannular rotation to adopt relatively more planar orientation.

7.2 Future work

From the viewpoint of oligoacenes, longer derivatives, namely pentacenes and hexacenes should be studied with varying substituents for increased stability. Findings from chapter 3 guides the design rule of using thiophene based side groups for effectively quenching excited state lifetimes in tetracenes. Future direction should address this effect within longer oligoacenes and be tested for only di-substituted tetracenes to investigate the consistency of results. Additionally, use of time resolved photoluminescence and transient absorption should also be measured for previously reported “stable” oligoacenes against unstable derivatives. The overall notion of using electronic structure to determine photo-stability of this class of molecules needs to be overall challenged so that the development of future high performing oligoacenes may be developed in a more accurate and rational approach.

Optimization of anthanthrene molecules from chapter 4 is needed to expand the small molecule application of this high π-surface oligoacene. As it has already been established within the Briseno Research Group, adopting a two-dimensionally annulated oligoacene can increase the stability of this class of molecules. However, limited reports have shown these types of materials to be competitive. Optimization of choice conjugation
via either the long axis and/or short axis needs to be further explored with appropriate side chains for solid state ordering.

Indeed, polymers exhibited in chapter 5 and 6 prove to be high performing and display high potential for further work. Following these established design rules, future directions these polymeric backbones can be expanded from both chemists and device engineer perspectives. Chemists shall optimize the side chain of NDI or adopt comonomers that enables both planar arrangements between and within donor monomers. Device engineers should investigate the use of these polymers in a variety of applications, such as OPVs.

7.3 Final Remarks

In this thesis, two areas of active research are covered: photo-oxidative stability of rubrene derivatives varying in short axis conjugation and performance influence of choice core conjugation among NDI based semiconductors. Although not directly related, we are able to make strong scientific advances in OSC design rules of both fields by careful investigation and collaboration with engineers and physicists alike. An important lesson learned from this work is that careful precise chemistries and emerging characterization techniques may allow the guidance of future materials for exciting breakthroughs. In conclusion, this thesis demonstrates importance of rational scientific approach to reveal new discoveries and materials for the advancement of OSCs.


