EVALUATING THE IMPACT OF CHEMICAL STRUCTURE ON THE INTERACTIONS AND OPTOELECTRONIC PERFORMANCE OF CONJUGATED SMALL MOLECULES

David John Dirkes III

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Approved by:

Wei You

Frank Leibfarth

Scott Warren

Joanna Atkins

Gerald Meyer

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ABSTRACT

David John Dirkes III: Evaluating the Impact of Chemical Structure on the Interactions and Optoelectronic Performance of Conjugated Small Molecules (Under the direction of Wei You)

Conjugated organic molecules have significant untapped potential in the field of organic electronics. The theoretical capabilities of many organic materials are excellent, but the real world results often fall short. Some areas of study, like organic field effect transistors (OFETs) and organic photovoltaics (OPVs), are in a state of regular advancement, yet many unanswered questions and unknown variables remain regarding the inherent structure-property relationship of organic components of these systems. We set out to study this crucial relation in our own way, targeting and synthesizing compounds we believe can give us some insight into what role the chemical structure plays in device performance. We hope that the lessons learned here can be used to create even better next generation materials and elucidate important design rules or which structural features to avoid. In Chapter 1, we outline the current state of the field and the reasoning that led us to pursue the work described in the subsequent Chapters.

The second Chapter of this dissertation details the synthesis of several new anthradithiophene (ADT) derivatives and evaluates the effect of heteroatom functional groups on the opto-electric properties, crystal packing, and OFET device performance they exhibit. One new ADT substituent greatly increased the photo-oxidative stability of the ADT core compared to other known stabilizing groups, offering a new means of solubilizing and stabilizing larger acene compounds. Two previously unreported linear acene crystal packing motifs were also

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discovered for two of the new ADT derivatives we synthesized. Thin film formation of the ADT derivatives showed some interesting differences between functional groups, and at least one derivative showed strong potential for future optimization and study in OFETs.

The third Chapter deals with the synthesis, characterization, and OPV results of a series of new A-D-A molecules functionalized with tricyano-furan acceptor units. We compared these new A-D-A compounds with similar molecules functionalized by the current top acceptor unit IC.

The fourth Chapter concludes the ADT and A-D-A projects while discussing what we have learned from the results. Future research directions are outlined that could further our understanding of the structure-property relationship that is key to OFET and OPV performance. Additionally, we describe our early work into the synthesis of a novel modified TCF analogue that hopefully will fix the flaws we observed in the TCF acceptors.

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LIST OF ABBREVIATIONS

A-D-A	Acceptor-Donor-Acceptor (usually representing covalently bound units)
ADT	Anthradithiophene
APPI-MS	atmospheric pressure photo-ionization-mass spectrometry
BAS	Bioanalytical Systems
BHJ	Bulk Heterojunction
BnDT	benzodithiophene
BnDT	benzo[1,2-b:4,5-b']dithiophene
BP	Benzopyran
BT	benzo[c][1,2,5]thiadiazole
BT-ADT	5,11-bis(butanethiol)-anthradithiophene
СВ	chlorobenzene
СТ	Charge Transfer
CV	Cyclic Voltammetry
CVD	Chemical Vapor Deposition
D-A copolymer	Donor-acceptor Copolymer
DCM	Dichloromethane
DMF	Dimethylformamide
Eox	oxidation potential
EQE	external quantum efficiency
EtOAc	Ethyl Acetate
FET	field-effect transistor
FF	fill factor

FTAZ	difluoro-benzotriazole or a polymer of BnDT and dithienyl difluoro- benzotriazole
HA-ADT	5,11-bis(hexanoate)-anthradithiophene
НОМО	Highest Occupied Molecular Orbitals
HT-ADT	5,11-bis(hexanethiol)-anthradithiophene
IDTor ID	indaceno-di(thiophene)
IDTT or IT	indaceno-di(thienothiophene)
INCN or IC	Indanone Malononitrile also called 2-(3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile
IQE	internal quantum efficiency
ITIC	5,5,11,11-tetrakis(4-hexylphenyl)- indaceno-di(thienothiophene)- bis(indanone malononitrile)
ΙΤΟ	indium doped tin oxide
Jsc	short Circuit current
K2CO3.	Potassium Carbonate
LDA	lithium diisopropylamide
LUMO	Lowest Unoccupied Molecular Orbitals
n-BuLi	n-butyllithium
NFAs	Non-Fullerene Acceptors
NLOs	non-linear optics
NMR	Nuclear Magnetic Resonance
OA-ADT	5,11-bis(octanoate)-anthradithiophene
o-DCB	ortho-dichlorobenzene
OFETs	Organic Field Effect Transistors
OLEDs	Organic Light Emitting Diodes

OO-ADT	5,11-bis(octyloxy)-anthradithiophene
OPV	Organic Photovoltaics
OT-ADT	5,11-bis(octanethiol)-anthradithiophene
РЗНТ	poly(3-hexylthiophene)
PC61BM	phenyl-C61-butyric acid methyl ester
PCE	Power Conversion Efficiency
PSC	Polymer Solar Cells
RBF	Round-bottom Flask
RM	Reaction Mixture
SF	Singlet Fission
Si	Silicon
SiO2	Silicon oxide
SM	Starting Material
TAZ	2-methyl-2H-benzo[d][1,2,3]triazole
ТСВ	1,2,4-trichlorobenzene
TCF	Tricyano-furan
THF	tetrahydrofuran
TLC	Thin Layer Chromatography
TT	thieno[3,4-b]thiophene
Voc	Open Circuit voltage
XRD	X-ray Diffraction

Chapter 1 INTRODUCTION TO ORGANIC ELECTRONICS

1.1 Traditional Semiconductors vs. Organic Semiconductors

The most common semiconducting materials are traditionally inorganic semiconductors like silicon. Modern technology is built on the back of silicon, which is the champion inorganic semiconductor used to make all the computer chips and processors that have improved our lives. Inorganic semiconductors have many positive qualities. They have extremely high charge mobilities and well-defined energy bands with low band-gaps. On top of that, they have been the subject of half a century of intense research and development that has created an incredible body of knowledge to work from. Organic (i.e., carbon-based) semiconductors cannot compete with silicon if transistor performance is the only focus. However, organic semiconductors do have advantages over their inorganic counterparts in that they allow for flexible electronics, are more light-weight, and could be produced at a fraction of the cost of inorganic materials.

1.2 Organic Semiconductors in Electronics

Organic π -conjugated molecules have seen use in all manner of electronic devices. They are used in field-effect transistors (OFETs), light-emitting diodes (OLEDs), optical switches, and solar cells (OPVs).^{1,2,3,4} OLEDs may be the most commonly recognized usage of organic electronics. OLEDs are now frequently used in phone screens, handheld electronics, and even TVs. Compared to OLEDs, most organic electronics fields are still in the very early stages of development and have yet to see the same level of success. However, the potential of organic electronics in these fields is very real and progress is being made each year toward more widespread applicability. Further advances in OFET research has the potential to make flexible

electronics a reality and could provide a much better understanding of how to control or guide the non-covalent intermolecular interactions that dictate the packing of organic molecules.

Advances in OPVs could lead to the more widespread utilization of solar energy and allow solar cells to be integrated into everyday objects like glass or used in places where traditional silicon solar cells cannot. Organic electronics also bear the promise of solution-processable fabrication methods, which could make their cost of production significantly lower than those of inorganic electronics.

Advances in organic semiconductor research could benefit many fields, but there are currently numerous challenges that will have to be overcome. In most organic optoelectronic applications, the effectiveness of the organic component greatly dependents on the how well the material can transport charges. How effectively an organic molecule can transport charges is fundamentally linked to its chemical structure and subsequent molecular packing. Lack of understanding regarding the factors controlling molecular packing and the interactions between conjugated molecules is one of the biggest reasons for lack of progress and one of the greatest challenges in optoelectronics research. There are no easy solutions to this problem; these interactions are complicated and often seem unpredictable. However, by evaluating highperformance molecules and performing studies or synthesizing new derivatives to elucidate the structure-property relationship in these materials, we can gain a better understanding of how to control these critical parameters.

1.2.1 Conjugated Small Molecules

Conjugated small molecules are primarily of interest for use as optoelectronic materials in OFETs. There has been an enormous amount of research devoted to this very broad field of organic semiconductors, and so this discussion will focus first on some of the properties of

organic semiconductors and then move on to address their role in their respective applications: OFETs and OPVs.

Charge transport through organic semiconductors occurs by charges hopping from molecule to molecule in the solid-state, facilitated by π -orbital overlap between molecules and interactions dictating the packing of those molecules.^{5,6,7} The many sp² hybridized carbon atoms that make up the conjugated organic backbone of these molecules come together to form the π -bonding molecular orbitals that define the HOMO and LUMO energy levels of the molecule, facilitate charge transport, and give these materials their optoelectronic properties. Organic semiconductor solids are formed by relatively weak Van der Waals interaction between molecules.

 π - π stacking interactions are one of the most significant charge transport pathways in both small molecules and conjugated polymers. Ideally, we want to incorporate functional groups that enhance π - π stacking between adjacent molecules and facilitate the creation of charge transport pathways. We know that the solid-state packing adopted by an organic semiconductor depends on the identity of the conjugated core, along with the substituents attached to the core. However, this has not made crystal structures easy to predict.⁸ There are several examples in the literature where the addition of a few hydrocarbons to a side chain of a molecule with the exact same core results in a wildly different crystal structure that changes the molecule's solid state charge transport properties by several orders of magnitude.^{910,11} This has complicated the study of crystal packing in organic semiconductors.

Three of the more common interactions that often control the crystal packing of conjugated materials are shown in **Figure 1.1** below.



Figure 1.1: Three types in interactions that often occur between conjugated organic molecules. The first two are forms of face-to-face interaction, while edge-to-face interactions are shown on the right and are driven by C-H --- π orbital interaction.

Acenes are among the most studied small molecule organic semiconductors.¹² Linearly fused aromatic and heteroaromatic rings are an extremely common core template that exhibit good intrinsic charge mobilities. The energy levels of these molecules can be changed by increasing the number of fused rings, and the packing of these acene derivatives can be changed by functionalizing them with substituent groups. The structures of some common acene cores are shown in **Figure 1.2** below.



Figure 1.2: A handful of linear acene molecules that have been thoroughly studied for use in OFETs.

Anthracene OFET single crystal devices have exhibited charge mobility at 0.02 cm²/V·s low temperature which is not particularly high, but charge mobility can increase drastically for acenes larger than anthracene.³ C₁₃-BTBT demonstrated an average mobility of 14.2 cm²/V·s in vapor-deposited OFETs, while solution-processed OFETs of this same material only provides a mobility of 2.75 cm²/V·s.¹³ Rubrene-based single crystal OFETs have achieved hole mobility values as high as 43 cm²/V·s, which is among the highest mobilities reported for conjugated organic materials.¹⁴

These results show that linear acenes have very good intrinsic charge mobility and a high maximum performance potential that they currently struggle to reach, as exemplified by the BTBT mobility disparity between vapor and solution deposited OFETs.

Acene molecules such as these typically exhibit solid state packing that follows one of the four packing motifs outline in **Figure 1.3**. As predicted by Gavezzotti et. al. in 1989, these four

patterns should be adopted by the vast majority of large conjugated molecules, dictated primarily by the shape of the molecule and the nature of the dominant interactions present in the molecule.¹⁵



Figure 1.3: The four most common solid state packing motifs seen in highly conjugated organic molecules.

Despite this helpful guide to acene packing motifs, it is still notoriously difficult to predict how a small molecule will pack, but this will be addressed further in chapter two of this work.

1.3 Organic Field Effect Transistors (OFETs)

A field-effect transistor (FET) is an electronic device that amplifies and switches electrical signals, using threshold voltages to block or permit the flow of charge across it. Transistors play a crucial role in all modern electronic devices. While traditional metal semiconductor FETs have been thoroughly researched and seen widespread use in computers of all kinds for well over 50 years, organic field-effect transistors (OFETs) are still finding their place.¹⁶

1.4 Organic Photovoltaics (OPVs)

Over the last several decades, advances in solar cell research have made solar energy an increasingly viable solution to our energy demands. Solar cell technology has come far enough

that it is seeing widespread use by the general public, and more people than ever are turning to solar power to meet their energy needs. These advances are primarily a result of high performing inorganic solar cells, usually silicon-based, that have been able to achieve excellent power conversion efficiencies, with single-junction crystalline silicon solar cells reaching 26.7% power conversion efficiency.¹⁷ However, there are downsides to inorganic solar cells as well. For example, silicon solar cells have a high cost of production, produce toxic waste byproducts, and are very susceptible to breaking due to their poor mechanical flexibility.

Despite these negatives, organic photovoltaics will only be able to thrive if they can achieve respectable power conversion efficiency for their prospective price point. To that end, development of new OPV materials that can enhance their efficiency is paramount.

To develop these materials, a solid fundamental understanding of the impact of chemical structure on photovoltaic properties is required. This has not been easy to study given the complexity of OPV bulk heterojunction solar cell blends and charge extraction in these systems. However, by designing a series of chemically distinct OPV molecules and evaluating their performance relative to one another, we can begin to learn what properties are truly important.

1.5 Electron Acceptors in Organic Photovoltaics

Differing from inorganic solar cells, where excitons are split with little energetic cost and charges easily drift apart, excitons in an organic solar cell are much more tightly bound. This is because excitons are highly localized in the molecular orbitals of organic molecules that absorb light and generate the exciton. Since positive and negative charges are drawn to one another and in organic molecules are spatially confined to a relatively small area, there is no room for them to drift apart and a large driving force is needed to separate the Coulombically-bound positive and negative charges. Additionally, because of their highly localized nature, organic excitons are not

able to diffuse very far from their point of origin within a solar cell before the exciton relaxes back to its ground state.

In organic photovoltaics, this requires blending a strong electron donor molecule, with a high HOMO energy that is desirable for the positively-charged holes, and a strong electron acceptor molecule, with a low LUMO energy that is desirable for electrons. The role of electron acceptor has long been dominated and defined by one class of material, fullerenes.

1.5.1 Fullerene

Phenyl-C₆₁-butyric acid-methyl ester (PC₆₁BM), a soluble variant of fullerene, has been the dominant electron acceptor used in polymer BHJ solar cells since its introduction in the mid-1990s.¹⁸ There are several reasons why fullerenes have seen widespread utilization. Fullerenes have a suitably low LUMO energy of -3.7 to -4.3 eV, which lets it pair well with the majority of donor polymers and facilitates photo-induced electron transfer from the polymer to fullerene. Fullerene also exhibits an extremely high electron mobility of up to $11 \text{ cm}^2/\text{V}\cdot\text{s.}^1$ Additionally, fullerenes are known to have several degenerate LUMO energy levels, allowing them to use the best suited of their multiple LUMOs to split excitons with the donor material.

On top of their high mobility, fullerenes are capable of transporting electrons in any direction due to their LUMO being delocalized over the entire surface of the molecule. This has also made it easier to incorporate them into BHJ blends with donor polymers, as fullerenes blend well with most donor polymers due to their favorable miscibility with conjugated polymers.

These favorable properties made them the champion electron acceptor material in OPVs for over fifteen years, and single-junction polymer solar cells have obtained PCEs over 10% using fullerenes as acceptors.¹⁹ However, they do have their limitations. Fullerenes unfortunately absorb very little light across the solar spectrum. Their light absorption becomes

minimal for any wavelength higher than ~550 nm.²⁰ Since a polymer solar cell's active layer is often a 50:50 blend of electron donor and electron acceptor, this means that any PSC using PCBM is absorbing sunlight almost exclusively with its donor. Only fifty percent of the active layer is actively absorbing. For a device specifically designed to absorb sunlight and convert it into energy, this limitation in fullerene is a problem. This limitation created a hunt for fullerene alternatives, and, while many failed to surpass fullerene, in recent years one class of materials has succeeded in surpassing fullerene.

1.5.2 Non-Fullerene Acceptors (NFAs)



Figure 1.4: Absorption spectra and structures for PCBM, ITIC, and a typical donor polymer FTAZ. The complimentary absorption of ITIC shows just how beneficial having your acceptor material absorb light can be to solar cell light absorption.

While many different Non-Fullerene Acceptors (NFAs) have been developed over the years, only one class of NFA molecules has truly surpassed fullerene thus far, Acceptor-Donor-Acceptor (A-D-A) structured low band-gap organic small molecules.²¹ These A-D-A molecules typically employ a fused ring, ladder-type donor core and utilize electron-deficient acceptor end groups to lower the HOMO/LUMO energy levels of the overall A-D-A molecule enough that it can act as an electron acceptor in an organic solar cell.²² This design strategy mimics the strategy used to great success in donor-acceptor (D-A) copolymers, which have become the

dominant electron donor material in OPVs, and A-D-A acceptors retain most all of the same benefits.²³

Mixing conjugated electron-rich and electron-deficient moieties on one molecule leads to molecular orbital hybridization over the whole system in a way that largely localizes the HOMO energy on the electron rich donor moieties and localizes the LUMO energy on the electron-deficient acceptor moieties, as shown in **Figure 1.5** below.



Figure 1.5: Molecular orbital hybridization diagram showing why D-A molecules end up with a significantly narrower band-gap than either of the separate donor or acceptor moieties

This enables easy tuning of the optical and electronic properties of the material by tuning the individual donor and acceptor components to create a material with appropriate energy levels or the exact absorption range needed. While their HOMO energy is largely localized on one part of the molecule and their LUMO energy is localized on another, A-D-A molecules still have significant wave-function overlap between their HOMO and LUMO energies, which gives them large extinction coefficients and results in strong light absorption.²²

1.5.2.1 ITIC (5,5,11,11-tetrakis(4-hexylphenyl)- indaceno-di(thienothiophene)-

bis(indanone malononitrile)



Figure 1.6: ITIC molecular structure. The donor IT section is colored blue and the acceptor IC end units are colored red.

ITIC was one of the very first NFAs to outperform fullerene and show the true potential of A-D-A molecules.^{24,25} ITIC is composed of one donor core with two acceptor end units on it. This section will step through the components of ITIC briefly and what properties they impart on the overall molecule.

The donor core is one indaceno-di(thienothiophene) (IT, or sometimes referred to as IDTT) molecule, which has five aromatic rings fused into place with four solubilizing chains total coming from two quaternary carbons on the IDTT backbone. The highly rigid nature of the IDTT backbone leaves the molecule almost exclusively planar and fully conjugated, which minimizes the number of vibrational or rotational conformations that can impact the optical and electrochemical properties of the molecule. IDTT is sufficiently electron-rich to be a good donor in a push-pull D-A molecule. While the planarity of the molecule is desirable, it is the four asymmetrically distributed alkyl chains that give this molecule its incredible solubility that is necessary to compensate for less insoluble acceptor units.

Indanone Malononitrile (INCN or IC) is a strong acceptor unit that stands as one of the only high-performance acceptor end units used in A-D-As that outperform PCBM. IC's strong electron withdrawing properties help shift the HOMO/LUMO energies of ITIC low enough for it to serve as an electron acceptor. Most of the crystallinity exhibited by ITIC is due to these IC end units, as the donor core is extremely soluble but largely insulated from direct π -orbital interaction with neighboring molecules by its side-chains. The planar nature of IC is also thought to facilitate charge transport through the A-D-A molecule, although direct evidence of this has been scarce. A-D-A molecules unfortunately do not crystallize to such an extent that their crystal structure can be determined through single crystal XRD like it can for linear acenes. As a result, direct evidence of how the A-D-A acceptors interact and arrange themselves in the solid state is quite limited.

Zhao et. al. demonstrated the potential of ITIC as an acceptor very well in a 2016 paper where they made solar cells using both ITIC and $PC_{71}BM$ as electron acceptors paired with the same donor polymer. PBDB-T:ITIC devices reached an average PCE of 10.68%, while PBDB-T:PC₇₁BM devices only reached 7.45% PCE.²⁶ This achievement was a result of both proper energy alignment allowing ITIC devices to obtain a higher V_{oc} than PCBM and very complimentary absorption between PBDB-T and ITIC. ITIC's ability to absorb light out to ~800 nm expanded the absorption window of the device by an additional 100 nm, significantly increasing amount of light the solar cell could catch and collect as energy. The expanded absorption of ITIC is really what made the difference and is the largest advantage that A-D-A molecules have over fullerene acceptors.

The electron mobility, another key parameter, of ITIC was also found to be comparable to that of fullerene, which is another key factor in its success. ITIC films exhibited electron

mobility of up to 3.0×10^{-4} cm²/V·s. This electron mobility is within range of those reported for fullerene derivatives (10^{-4} - 10^{-2} cm²/V·s).²⁴

Chapter 2 EFFECT OF HETEROATOM FUNCTIONALIZATION ON ANTHRADITHIOPHENE PROPERTIES, STABILITY, AND DEVICE PERFORMANCE

2.1 Introduction to Acenes

Linear acenes have proven to be an effective class of organic molecules that often exhibit high-hole mobility when deposited in a thin film.¹² In the solid state, charges move along the conjugated π -orbital acene backbone, transferring from acene to acene where their π -orbitals overlap.^{1,27} To maximize the effective mobility of small molecule acenes, one must maximize the degree of π -orbital overlap in the solid state.

Due to their high hole mobility and self-assembling properties, linear acenes such as anthradithiophene (ADT) have drawn a great deal of interest for use in organic field effect transistors.¹² While the inherent charge-transport properties of linear acenes like ADT are desirable, functional groups are required in order to render them soluble and lead them to adopt crystal packing that is favorable for charge transport.²⁸ Changing the chemical structure of the functional groups attached to the ADT core can dramatically change the material's electronic properties, photo-oxidative stability, solid-state molecular packing, and subsequent device performance. While a handful of alkyne-functionalized ADT derivatives have been thoroughly studied, there are few examples of other functional groups reported in the literature.^{29,30}

Despite evidence that functionalization of acenes can vastly improve their photooxidative stability and knowledge that acene substituents dictate the crystal packing, solubility, and resulting device performance, shockingly few functional groups have been investigated and characterized in the literature. Researchers have long stated that rational crystal engineering is

the end goal, but we have little understanding of what our tools (functional groups, heteroatoms) do. This lack of understanding is a serious issue that greatly limits the ability to engineer anything in these systems.

To further understand the structure-property relationship, from which these key properties are derived, we have designed and synthesized a series of ADT molecules bearing ether, thioether, and acetyl-oxy functional groups with alky chains of varying length. Specifically, five new and two known solution-processable anthradithiophene molecules were synthesized, characterized, and incorporated into organic field-effect transistors. Optical and electrochemical properties of the different functional groups were compared, showing a distinct optical band-gaps and a range of photo-oxidative stabilities that correlated well with their functional group. Through single-crystal XRD, the effect of heteroatom substitution and alkyl chain length on the molecular packing of these derivatives in the solid state was evaluated. We discovered unique packing motifs that have not been reported in the current literature. Thin films of these materials were also prepared using spin-coating or blade-coating and characterized by optical microscopy. OFETs were then prepared using these conditions to further understand the impact of such substitutions on charge carrier mobility of these functionalized ADT molecules.

2.2 The Road to Anthradithiophene

The initial goal of this project was to design a singlet fission-capable conjugated organic molecule that could be successfully incorporated into a donor-acceptor (D-A) copolymer and used as an active component in a polymer solar cell blend. We hoped to preserve and harness the singlet fission capability of the monomer in the D-A copolymer, allowing us to double the effective photocurrent of the solar cell by splitting high energy singlet excitons into two triplet

excitons with half the energy of the original singlet.³¹ In theory, using a singlet fission-capable polymer in a ternary blend polymer solar cell (i.e., a bulk heterojunction solar cell with two actively absorbing electron donor polymers and one electron acceptor molecule) would allow one to overcome the Shockley-Queisser limit that caps the performance of a singlet junction solar cell at 32% power conversion efficiency (PCE).^{32,33}

If the singlet fission-capable polymer splits the energy from high-energy photons (~2 eV) into two lower energy triplet excitons (~1 eV) that can both be harvested in the solar cell, while another lower band-gap material absorbs low energy photons (~1 eV) and generates singlet excitons in the traditional way, then one can increase the overall quantum efficiency without negatively impacting the V_{oc} of the solar cell, boosting the theoretical PCE limit from 32% to 45%.³¹

Unfortunately, the number of efficient singlet fission-capable molecules reported in the literature is quite small.^{34,35} Additionally, the choice of potential singlet fission chromophores was further limited by the strict energetic requirements (S_1 singlet = 2 eV and T_1 triplet = 1 eV) needed for SF to be effectively utilized in a solar cell.³¹

The most well-studied and efficient singlet fission chromophores are linear acenes such as tetracene and pentacene. Tetracene thin films have shown triplet yields of nearly 200%, where essentially every singlet exciton (2.36 eV) is converted into two triplets (1.2 eV).^{36,37} Baldo et al. was able to successfully incorporate tetracene into an organic solar cell and demonstrated that singlet fission can be employed effectively in these systems, obtaining a singlet fission efficiency of 71% when heated to 292 K.³⁷

Pentacene thin films have also shown triplet yields of nearly 200% where every singlet exciton (1.76 eV) is converted into two triplets (0.88 eV).³⁸ These energy levels are suitably

close to the ideal energy levels desired for use in SF-capable solar cells. Beyond that, Baldo et al. have been able to make organic solar cells utilizing pentacene as a singlet fission chromophore that obtain a peak external quantum efficiency (EQE) of 102%, something that would not be possible without active singlet fission in the solar cell.³⁹

While these early successes in the literature using tetracene and pentacene are interesting proof of concept systems, bare tetracene and pentacene cannot be easily incorporated into high-performance organic or polymer solar cells. Due to the extremely low solubility of these bare acene compounds, they can only be effectively deposited into a film using Chemical Vapor Deposition (CVD), a costly and time consuming technique that prevents them from being incorporated into a BHJ structure required for most organic and polymer solar cells. Even functionalized tetracene and pentacene derivatives, rendered solution processable by their side chains, could not be easily incorporated into a D-A copolymer due to their lack of attachment points that would allow for controlled polymerization. A different SF-capable compound would have to be found.

Anthradithiophene (ADT) stood out as a promising acene alternative that, due to its similarity to tetracene and pentacene, could potentially exhibit singlet fission and easily be incorporated into a D-A copolymer using chemistry that had already been well established for a smaller analogue of ADT, benzodithiophene (BnDT).⁴⁰

There was some precedence for incorporating ADT into a D-A copolymer in this way. Jiang et al. synthesized a series of (triisopropylsilylethynyl)-anthradithiophene (TIPS-ADT)cyclopentadithiophene conjugated copolymers and achieved BHJ device efficiencies close to 1%.⁴¹ Lim et. al. incorporated ADT into a terpolymer system with BnDT donors, but the low

solubility of ADT only seemed to limit their performance despite ADT copolymers exhibiting a higher hole mobility. ⁴²

None of these ADT D-A copolymers achieved a notably high PCE, but it was unclear if that was a result of a prohibitively low polymer solubility or low miscibility with the other BHJ materials. It appeared that none of the published ADT polymers used sufficiently solubilizing side chains that could overcome the inherent rigidity and immiscibility of the large ADT units. None of these ADT D-A copolymers were ever tested for singlet fission activity either.

Recognizing the singlet fission potential of ADT and limited exploration of its polymer solar cell application in the literature, we set out to develop a highly soluble ADT derivative that could be used to make high performance polymer solar cells.

Despite many attempts to make ADT derivatives with solubilizing chains large enough to render the polymers soluble, we were unable to ever make an ADT polymer soluble enough to reach a sufficient molecular weight for use in polymer solar cells. While we failed to make a suitable ADT D-A copolymer to produce high performing BHJ polymer solar cells, we were able to produce several ADT small molecule derivatives that have never before been reported in the literature. This provided us with the unique opportunity to study one of the most complicated and critical areas of organic electronics research: crystal engineering.

Crystal engineering in this context is the attempt to control the supra-molecular assembly of a conjugated organic material by incorporating functional groups or side chains designed to tune intermolecular interactions or guide the crystallization process with the end goal of enhancing the solid-state performance of the molecule.

It is well documented that the crystal packing motifs adopted and intermolecular interactions present have an enormous impact on the charge transport properties of conjugated

organic small molecules.^{3,43} Understanding the relationship between intermolecular interactions and the resulting crystal packing modes produced is crucial to the development of better organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and organic solar cells (OSCs).

Despite several decades of study, the structure-property relationship between chemical structure, molecular packing, and resulting device performance is still not well understood.⁴⁴ In order to improve our understanding of the structure-property relationship in organic semiconductors, we must study how different functional groups anchored at the same position on a conjugated core affect the solid-state packing of that material.

Linear acenes like pentacene and anthradithiophene are some of the most intensively studied organic semiconductors.^{45,1} Trialkylsilylacetylene functionalized pentacene and anthradithiophene molecules have become ubiquitous in the field of organic electronics. These functional groups made linear acenes that had once been completely insoluble into solution processable electronics with good performance. Beyond that, these functional groups actually helped control the crystal packing in ways that greatly improve their OFET performance.⁴⁶



Figure 2.1: ADT and Pentacene derivatives most frequently studied in the literature and the ADT derivatives featured in this work.
While the structure-property relationship of alkyne-functionalized ADT has been well studied, the effect of other functional groups on the properties of ADT or even pentacene is relatively unknown. There are very few reports of non-alkyne functionalized acenes. In the few cases where new ADT derivatives were synthesized in the literature, the solid-state crystal packing was often not reported. As a result, we have a great opportunity to expand our understanding of the structure-property relationship by studying the effect that heteroatom functionalization has on the properties and crystal packing of the ADT derivatives studied in this work.



2.3 Synthesis of Heteroatom Functionalized ADT Derivatives

Scheme 2.1: Synthesis route used to make ADT Derivatives

Scheme 2.1 shows the synthetic route used to prepare the ADT derivatives studied in this work. ADT quinone (5) was synthesized in four steps as previously reported in the literature.⁴²

Due to the fast nature of the Aldol condensation reaction used to form the ADT core (**5**), the ADT derivatives in this work are an inseparable mixture of syn/anti-ADT. While this mixture of isomers has been shown to influence device performance, its overall effect is minor compared to the impact that functionalization of the ADT core and processing conditions have on the device properties.³⁰

TES-ADT was also synthesized as previously reported by Anthony et al.⁹ Due to the ubiquitous nature of TES-ADT and the wide range of properties reported for it in the literature, TES-ADT was used as a reference compound for both photo-oxidative stability and device fabrication/performance to compare with the other derivatives synthesized in this work.

OO-ADT was also synthesized as previously reported by Lim et. al.⁴² From early experiments and reactions reported in the literature⁴², the quinone functional group on the central ring of ADT quinone exhibited a reactivity more akin to anthracene than benzodithiophene. Reactions that would proceed easily on BnDT quinone would either fail as a result of the lower solubility and reactivity of ADT quinone or destroy ADT quinone by reducing the ketones off entirely or reducing other sections of the core. All attempts to isolate ADT-diol after reduction of the quinone, which was done successfully for pentacene quinone⁴⁷ and BnDT quinone⁴⁸ failed. It appeared that even brief exposure to oxygen would quickly revert the diol back to the quinone, preventing any attempt at purification or product isolation.



Scheme 2.2: Reaction conditions for the acylation of ADT Quinone, along with suspected intermediates and unwanted side reactions.

Because of this, we explored the possibility of running an in-situ reaction of the ADTdiol with an electrophilic side chain. There is precedence in the literature for functionalizing smaller acenes like anthracene in this way⁴⁹ and Lim et al. used a similar approach to produce alkoxy functionalized ADT derivatives.⁴² In our hands, reductive acylation of ADT quinone using Zinc powder and alkyl anhydrides proceeded more slowly than reported for anthracene, but, with additional time and mild heating, acetoxy ADT derivatives could be obtained in good yield with simple purification.



Figure 2.2: Summary of the ADT acylation reactions explored in this work The relative success of each anhydride tested is shown, along with a picture of the crude or purified solid product obtained. The distinct color difference between the muddy yellow ADT Quinone and the orange acetylated ADT products can be clearly seen.

A series of acetoxy ADT derivatives were produced using this reductive acylation procedure with linear alkyl anhydrides of varying lengths. We observed that, if the acetyl alkyl chains were too short (2-4 carbons), the resulting ADT product was too insoluble to dissolve in common organic solvents like dichloromethane, complicating any attempts to separate it from the Zinc powder and potassium carbonate solids in the reaction mixture or remove unwanted acene biproducts. Increasing the alkyl chain length of the anhydride to six and eight carbons greatly improved the solubility of the ADT product. These two acetoxy ADT derivatives, 5,11bis(hexanoate)-anthradithiophene (HA-ADT) and 5,11-bis(octanoate)-anthradithiophene (OA-ADT) were successfully synthesized, purified, and characterized. We did not attempt to synthesize acetoxy ADT derivatives with longer alkyl chains, but would expect them to work just as well.

Despite these encouraging early results, the scope of the reductive acylation reaction on ADT quinone remained quite narrow. Attempts to synthesize ADT derivatives from α -carbon branched anhydrides failed. We believe steric hindrance from the α -carbon branched alkyl chains near the anhydride is preventing the bulky, reduced ADT Quinone intermediate from getting close enough to the anhydride carbonyl reaction site for the reaction to proceed. As a plausible support to our hypothesis on steric hindrance, reductive acylation of ADT Quinone using an anhydride of isovaleric acid, which is branched at the β -position, worked.

Attempts to overcome this limitation through substitution of the anhydride electrophile for similar, less sterically hindered electrophiles like acid chlorides or isocyanates also failed. The reduced ADT quinone is an extremely weak nucleophile as a result of extensive delocalization of the ADT quinone oxygen anion over the entire ADT backbone through resonance. Acylation was only successful when no stronger nucleophiles were present in the reaction mixture than the ADT-diol intermediate or produced during the acylation reaction. A failed acylation reaction would result in a mixture of the ADT quinone starting material and

several partially reduced ADT byproducts that could not be definitively identified by NMR or mass spectrometry, due to the poor solubility of the non-alkylated ADT compounds.

Having successfully synthesized a soluble acetoxy ADT derivative, we then attempted to replace the acetoxy groups with thioether substituents using a tricky acid-mediated, high heat, and water sensitive nucleophilic aromatic substitution reaction that had been successfully employed by Nerungsi et. al. to produce thioether functionalized anthracene derivatives in high yield.⁴⁹ By adapting this unusual nucleophilic aromatic substitution reaction, we could synthesize a new thioether functionalized ADT molecule, allowing us to further explore the effect of heteroatoms functional groups on ADT.

While we were able to eventually synthesize thioether-ADT derivatives, their synthesis was quite challenging. Even during our earliest attempts, it was clear that this reaction did work, but the reaction conditions required extensive optimization to get a sufficient amount of product. It was clear that ADT is much more sensitive to the extreme reaction conditions and additional nucleophilic aromatic substitution reactions than anthracene. Any water present in the reaction mixture will readily react with the acetoxy ADT starting material, undergoing an addition-elimination reaction at the side chain ester carbonyl. This reaction severs the ester side chains from the ADT core, converting them into carboxylic acids. The ADT core is left with two hydroxyl functional groups that rapidly oxidize back to ketones upon exposure to oxygen.

While the original procedure utilized toluene as a solvent and limited the amount of thiol reagent present, we found that the reaction proceeded best when run under a dry, inert atmosphere where the only solvent was the alkylthiol reagent of the desired alkyl chain length. When toluene was used as a solvent, a number of additional biproducts were produced. We are uncertain if this was due to reactions with water or impurities in the toluene, reactions between

toluene and the reagents, or if the lower concentration of alkylthiol reagent enabled competing side reactions to occur more frequently. However, it was clear that by running the reaction in straight alkylthiol the yield was greatly improved.

There were limitations to running the reaction neat in the alkylthiol reagent. The low boiling point of short alkylthiols (1 - 3 hydrocarbons) made them unfeasible; as the temperature required to initiate the reaction easily exceeded the boiling points of these short alkyl chain thiols. If the reaction mixture did not get hot enough (> 90 °C), then the solid *p*-toluenesulfonic acid catalyst did not dissolve and no reaction occurred. However, if the reaction got too hot (> 130 °C) or ran for too long (>3 hours), then a host of additional unwanted reactions would occur, destroying the desired thioether-ADT product. While there were often too many byproducts to count when this happened, APPI-MS (atmospheric pressure photo-ionization-mass spectrometry) did allow at least one ADT byproduct, with three thioether side chains attached to the core, to be identified.

By thoroughly drying the reagents and solvents, tuning the amount of acid catalyst used, changing the solvent system, and optimizing the reaction temperature, we were able to overcome most of these synthetic challenges and limit the number of biproducts produced.

We successfully synthesized and purified three thioether functionalized ADT derivatives: 5,11-bis(butanethiol)-anthradithiophene (BT-ADT), 5,11-bis(hexanethiol)-anthradithiophene (HT-ADT), and 5,11-bis(octanethiol)-anthradithiophene (OT-ADT).

2.4 Optical and Electrochemical Properties of ADT Derivatives

For organic semiconductors of all kinds, it is well documented that functionalization of a conjugated core with substituent groups can be used to tune the HOMO/LUMO energy levels of the molecule, impacting their resulting optical and electrochemical properties.³

Tuning the HOMO/LUMO energy levels of an organic semiconductor in this way can seriously alter the efficacy of charge carrier injection. HOMO/LUMO energy levels also determine whether the molecule will transport electrons (*n*-type), holes (*p*-type), or both (ambipolar) based on how the HOMO/LUMO energy levels align with the energy levels of other molecules in the system and the work function of the electrodes.⁵⁰ In order to obtain good charge injection between our ADT molecules and the other components of the device, we need to understand how to tune the HOMO/LUMO energy levels of ADT. Changes in HOMO/LUMO energy levels are particularly pronounced when heteroatoms are used as the substituent groups, and some of the functional groups we synthesized in this work have not been characterized in the literature for longer acenes.

The impact of the four ADT functional groups: acetoxy, ether, thioether, and trialkylsilylacetylene were evaluated by UV/Visible absorption spectroscopy, fluorescence spectroscopy, and cyclic voltammetry. **Figure 2.3**, shown below, summarizes the optical experimental results.



Figure 2.3: a) Normalized UV-Vis. spectra of ADT derivatives in $\sim 2*10^{-4}$ M CHCl₃ solution. **b)** Normalized fluorescence spectra of ADT derivatives in very dilute CHCl₃ solution

As seen in **Figure 2.3** a, the ADT derivatives all have similar overall band shapes in their spectra. This is because they all share the same conjugated ADT core, which is responsible for the series of sharp absorption bands. These sharp bands are the result of vibronic transitions across the ADT core and are a defining feature seen in all linear acenes. Since all of the molecules studied here have the same core, we do not expect that changing the substituents will change the shape of the spectra obtained. However, the substituent groups may change the Stokes shift -the wavelength difference between the maxima of the absorption and fluorescence spectra for the same electronic transition- of the ADT spectra. The rigidity of linear acenes, like ADT, usually results in a small Stokes shift, but substituent groups can affect the size of the Stokes shift.⁵¹

While the functional groups on ADT do not significantly affect the overall shape of the absorption or fluorescence spectra, they do shift the ADT absorption and fluorescence window. This shift results from the different electro-negativities and electron-donating or withdrawing properties of the functional groups changing the HOMO-LUMO band gap of the ADT core.



Figure 2.4: Normalized and overlaid absorption and fluorescence spectra of HA-ADT and OA-ADT in dilute CHCl₃ solution.

The acetoxy ADT derivatives, HA-ADT and OA-ADT, have a band-gap of 2.30 eV, the largest of the four ADT derivatives, with an absorption λ_{max} at 509 nm and mirrored fluorescence pattern with a small Stokes shift of 7 nm.



Figure 2.5: Normalized absorption and fluorescence spectra of OO-ADT in dilute CHCl₃ solution.

The ether functionalized derivative OO-ADT has a band-gap of 2.24 eV, the second largest of the four ADT derivatives, with an absorption λ_{max} at 519 nm and mirrored fluorescence pattern with a Stokes shift of 9 nm. OO-ADT has more prominent absorption peaks at 393 nm, 411 nm, and 416 nm than the other ADT derivatives, although which vibrational modes are responsible for these peaks remains unknown.



Figure 2.6: Normalized absorption and fluorescence spectra of the thioether ADT derivatives BT-ADT, HT-ADT, and OT-ADT in dilute CHCl₃ solution.

The thioether-ADT derivatives BT-ADT, HT-ADT, and OT-ADT have a band-gap of 2.20 eV, the third largest of the four ADT derivatives, with an absorption λ_{max} at 527 nm and mirrored fluorescence pattern with a Stokes shift of 10 nm.



Figure 2.7: Normalized absorption and fluorescence spectra of TES-ADT in dilute CHCl₃ solution.

The triethylsilylacetylene functionalized derivative TES-ADT has the smallest band-gap of the four at 2.09 eV, with an absorption λ_{max} at 554 nm and mirrored fluorescence pattern with a Stokes shift of 8 nm. The significant red-shifting seen for TES-ADT relative to the other three derivatives is a result of the π -orbitals of the two acetylene side chains extending the conjugation of the ADT core and lowering the HOMO/LUMO energy band-gap. It is well established that increasing the degree of conjugation in a small molecule by incorporating additional atomic orbitals into the hybrid molecular orbitals that define the HOMO/LUMO energies will decrease the HOMO/LUMO band-gap, so this red-shift is expected.

Compound	$\lambda_{onset,abs} nm$ (eV)	λ _{max,abs} (nm)	$\lambda_{max,fl}$ (nm)	
HA-ADT	540	509	516	
OA-ADT	540	509	516	
OO-ADT	554	519	528	
BT-ADT	564	527	537	
HT-ADT	564	527	537	
OT-ADT	564	527	537	
TES-ADT	592	556	562	

Table 2.1: Dilute solution photophysical parameters of ADT derivatives in CHCl₃

The absorption and fluorescence spectra show a clear relation between ADT functional group and optical band-gap. Band-gap from largest to smallest is: acetoxy-ADT > ether-ADT > thioether-ADT > TES-ADT. In order to get a more complete picture of how these heteroatom functional groups were affecting the HOMO/LUMO energies, direct measurements of their HOMO/LUMO energies were obtained using Cyclic Voltammetry (CV).



Figure 2.8: Cyclic voltammetry measurements for ADT derivatives in a 0.2 M solution of tetrabutylammonium hexafluorophosphate in anhydrous dichloromethane vs. (Fc/ Fc+) with a three electrode cell of a glassy carbon working electrode, Ag reference electrode, and Pt counter electrode.

The CV data in **Figure 2.8** was used to calculate the HOMO energy of each of the ADT derivatives. Using ferrocene as a reference material with a HOMO level of -4.8 eV, we can calculate the HOMO energy level for each of the ADT derivatives. While attempts were made to measure the LUMO energy of the ADT derivatives directly, the large band-gap of these molecules pushed their LUMO energy out to a potential range that cannot be reliably measured with dichloromethane as the solvent. The presence of oxygen reduction peaks also complicated analysis, and so we opted to calculate the LUMO energy by adding the optical band-gap from the UV-Visible absorption spectra to the CV-measured HOMO energy. These results are summarized below in **Table 2.2** and **Figure 2.9**.

 Table 2.2: HOMO and LUMO energies of ADT compounds

	0						
Compound:	HA-ADT	OA-ADT	TES-ADT	OO-ADT	BT-ADT	HT-ADT	OT-ADT
LUMO (Opt. bandgap, eV)	-2.89	-2.89	-3.13	-2.75	-2.98	-2.99	-2.94
Abs. Edge from UV/Vis (nm)	540	540	592	554	564	564	564
Optical Bandgap (eV)	2.30	2.30	2.09	2.24	2.20	2.20	2.20
HOMO (from CV, eV)	-5.19	-5.19	-5.22	-4.99	-5.18	-5.19	-5.14



Figure 2.9: HOMO and LUMO energy levels for each ADT derivative HOMO determined by CV. LUMO calculated using the HOMO energy and the optical band gap.

As shown in **Figure 2.9**, HOMO energy levels are remarkably similar across the different heteroatom functionalized ADT derivatives. With the exception of OO-ADT, all of the ADT derivatives have HOMO energy levels close enough that they are well within the experimental error range (deviations of \pm 0.1 eV are not uncommon and reported HOMO/LUMO energy levels often vary over a much larger range than that). With similar HOMO energy levels, the band-gap differences we observe between the derivatives likely results from functional groups lowering the LUMO energy level of the ADT core to different degrees.

Anthracene derivatives functionalized with thioethers have shown evidence that the sulfur atoms participate in the conjugated system, acting as a bridge between two aromatic groups on the molecule and allowing them to interact.⁴⁹ In that same work, sulfur substituents were shown to decrease the band-gap and HOMO/LUMO energy levels of anthracene to a

greater extent than an ether functionalized derivative.⁴⁹ We observe the same trend here for ADT. The OO-ADT HOMO is a good 0.2 eV higher than the other derivatives and has a larger band-gap than the sulfur derivatives.

While the acetoxy-ADT derivatives have a lower HOMO energy than oxy-ADT, as expected due to acetoxy substituents being weaker electron-donating groups, it is surprising that their effect on the HOMO/LUMO energy levels of ADT is not more pronounced.

2.5 Photo-oxidative Stability of ADT Derivatives

In transistors using linear acenes, charge carriers hop from molecule to molecule, travelling through the π -conjugated acene backbones. Charges move across these π -conjugated backbones rapidly compared to the rate at which they hop between molecules. If all other factors are held the same, long acene cores should outperform their shorter analogues. Experimentally, this has held true for single crystal OFETs made from pure acenes, where the charge mobility increased noticeably as the number of aromatic rings increased: anthracene (3 rings, 0.02 cm²/(V s)), tetracene (4 rings, 0.4–2.4 cm²/(V s)), and pentacene (5 rings, 5–40 cm²/(V s).⁵²

Because of this, significant effort has been devoted to developing longer acenes, and acenes composed of as many as nine fused aromatic rings (nonacene) have been synthesized.^{52,53} However, larger acenes are inherently unstable. As the number of fused rings increases, the molecule becomes less aromatic. This is due to the fact that any conjugated acene system has only one aromatic sextet across the whole molecule at any given point.

One aromatic sextet



Two aromatic sextets

Figure 2.10: Example of a linear acene gaining an additional aromatic ring upon degrading. This is a common driving force that leads to high acene reactivity.

Less aromaticity leads to higher reactivity. Simply put, the larger the acene is, the more susceptible it is to degradation. Any linear acene larger than anthracene (3 fused aromatic rings) is noticeably unstable and precautions must be taken to prevent the material from degrading while working with it.

Acenes most commonly decompose by two methods: dimerization, where two acene molecules covalently bond to one another as a result of close face-to-face contact through a proposed bi-acene diradical intermediate,⁵⁴ and a light-induced oxidation (photo-oxidative degradation), where oxygen binds irreversibly to the acene core in a Diels-Alder-like diene-dieneophile reaction.⁴⁷ These degradation reactions have complicated study of the linear acenes and are a major hurtle in the way of any practical application. Examples of each are shown below in **Figure 2.11**.





Figure 2.11: Example of acene dimerization and the photo-oxidative degradation reaction that commonly occurs between acenes and oxygen.

Thankfully, there are ways to overcome or minimize these degradation pathways. Incorporating heteroatom aromatic rings like thiophene into the acene core to create heteroacenes can greatly improve the stability of a linear acene to dimerization.⁵⁵ For ADT, the incorporation of thiophenes as the end rings of the acene core largely eliminates the dimerization degradation pathway under normal conditions.⁵⁶

However, the photo-oxidative degradation reaction is much harder to prevent and is the primary source of degradation in linear acenes. Despite this, it is possible to stabilize the acene core against this kind of degradation and prevent it from being completely consumed by oxygen. Attaching substituent groups to the aromatic core can strongly influence acene reactivity, either stabilizing or destabilizing the acene depending on the functional group^{46,47,54}

Some substituents have been found to increase acene stability, while other substituents destabilize them. One of the first functional groups shown to increase the stability of an acene were trialkylsilylacetylene substituents attached to pentacene, although the extent to which they stabilized pentacene and how they stabilized the core was not quantified in these early works.²⁸ It was reasoned that steric blocking of the most reactive centermost ring minimized intermolecular reactions, which helped prevent dimerization reactions. However, trialkylsilylethynyl derivatives also showed greater photo-oxidation resistance, so it is possible that these functional groups stabilize the core in different ways as well. An excellent study by Kaur et. al. looked at the effect of phenyl, trialkylsilylethynyl, and thioether functional groups on

the photo-oxidative stability of pentacene when attached to the central ring, measuring the photooxidative stability and associated half-life of twelve pentacene derivatives to measure both steric and inductive effects from substituents.⁵⁷ They found the thioether derivatives to be the most stable pentacene derivatives by far.

Fluorinating ADT derivatives makes them extremely stable due to the large electron withdrawing effect of fluorine, which pulls electron density out of the central, most reactive ring of ADT. However, this comes at the cost of functionalizing the terminal thiophene rings of ADT, preventing further functionalization of the molecule and any possibility of incorporating the ADT chromophore into a conjugated polymer system.⁴⁶

Ether functional groups were predicted to destabilize the frontier molecular orbitals due to the strong electron-donating, resonance effect of oxygen.⁵⁸ The HOMO and LUMO energy levels of any acenes they are attached to were expected to go up in a way that would destabilize them and make them more susceptible to dimerization and photo-oxidative degradation.

Given the serious limitations posed by these degradation pathways and with these previous studies in mind, we set out to measure the photo-oxidative stability of the ADT derivatives we synthesized to assess what impact each functional group had on the acene's stability.

During some of our earliest ADT synthesis work, it became clear that these ADT molecules were no exception to the acene stability rules and were found to be highly susceptible to photo-oxidative degradation when exposed to light and air simultaneously. For example, the endo-peroxide-ADT degradation product can be clearly seen on ¹H NMR in **Figure 2.12** below. The endo-peroxide degradation product displays clean, strong shifts in the ¹H NMR signal. The degraded acene core's conjugation is effectively cut in half by the addition of oxygen across the

central phenyl ring, creating significant differences in hydrogen shielding between the pure and degraded compounds.



Figure 2.12: Before and after ¹H NMR comparison of an originally pure HA-ADT solution after 30 minutes of light exposure under open air, showing the result of a photo-oxidative degradation reaction on the ¹H NMR of HA-ADT in CDCl₃.

While photo-oxidative degradation was rapid under open lab lighting and open atmosphere, the liberal application of tin foil and working under low light conditions could entirely prevent this reaction from occurring. All of the ADT compounds synthesized in this work were found to be entirely stable under open atmosphere as long as they were shielded from light exposure. The derivatives are most susceptible to degradation when dissolved in a solvent. Despite that fact, no degradation was observed even when recrystallizing them in refluxing solvent as long as they were recrystallized in relative darkness. The ADT solids can endure substantially more light exposure with no noticeable degradation, although the full extent of their solid-state stability was not characterized in this work. Measuring their photo-oxidative degradation proved to be a rather challenging experiment. While the degradation could be clearly seen on NMR, the logistics of accurately controlling light and oxygen exposure of a sample between NMR measurements ruled out that method. Instead, UV/Vis. absorption spectroscopy was chosen as a reliable method for measuring the degradation reaction (*vide infra*).

As discussed earlier in this section, the degradation reaction ends up breaking the conjugation across the acene core, creating a stark absorption difference between the pure acene and its degradation product, as less conjugation leads to a larger optical band-gap. Because of this, UV/Vis. absorption spectroscopy has been frequently utilized in the literature to monitor the degradation reaction and measure acene stability.^{49,57,54} By measuring the absorption spectra of a pure ADT solution, exposing it to lab light in timed intervals, and then measuring the absorption spectra of the degradation reaction for each ADT compound. An example of what this data looks like can be seen below in **Figure 2.13**.



Figure 2.13: UV-Visible absorption spectra showing decay of the OO-ADT absorption peak after being exposed to lab light over time. The absorption decay of the highest peak was used in the subsequent kinetics calculations.

While some researchers have used sensitizers or narrow wavelength light to trigger the photo-oxidative degradation in their ADT molecules equally,⁵⁵ we opted to measure their stability under normal working conditions using standard white fluorescent lab lighting in a windowless room, due to the already large number of factors playing a role in this experiment. While the degradation reaction is quite clean under normal lighting, exposing the ADT solutions to intense light from a handheld UV lamp generates a whole different host of degradation products that greatly complicate any attempt to characterize the reaction, making concentrated light sources less ideal. Whereas the overhead fluorescent lighting provided a more regular, easily controlled light source that only triggered the degradation we were trying to measure.

The experimental setup for photo-oxidative stability test is described below. E ach ADT compound was evaluated by exposing a cuvette with $1 - 2 \times 10^{-4}$ M CHCl₃ solutions to ambient overhead lab fluorescent lights and open air (the cuvette cap was adjusted to allow a regular flow of air into the cuvette) over time. An absorption spectra was collected after every five minutes of

light exposure (every two minutes for OO-ADT due to rapid degradation) to monitor the absorption peak decay. After each measurement, the cuvette was returned to a specific, marked location to maintain regular light exposure, the cap adjusted, and then the light turned back on. The solvent level was marked after the first absorption spectra was collected and drops of pure chloroform solvent were added as needed to maintain the original solution volume before every measurement.

A summary of the photo-oxidative stability test data for all of the ADT compounds is shown below in **Figure 2.14**.



Figure 2.14: Absorbance-time plots of the highest absorption peak of each ADT derivative in $1 - 2 \times 10^{-4}$ M CHCl₃ solutions. The log plots display pseudo-first order kinetics for each of the derivatives under these conditions.

All of the ADT derivatives exhibit pseudo-first order decay profiles, where the $ln(A_t/A_0)$ displays a strong linear decay over time. This makes sense if we assume that oxygen is present in enough excess and is constantly being replenished through air circulation that its concentration is essentially constant and does not affect the reaction rate. Based on this data, we can conclude that the ADT derivatives are all first order with respect to this reaction, while the overall reaction

with oxygen is pseudo first order due to the excess of oxygen present. This kinetics data can be summarized by calculating the half-life $(t_{1/2})$ of each ADT molecule. The half-life is a measure of how much time it takes for the concentration of the pure ADT derivative to drop to half of its original value, given the degradation reaction kinetics data. Half-life values for each ADT derivative are shown in **Figure 2.15** and **Table 2.3** below.

Compound:	Half-life (min)		
HA-ADT	215		
OA-ADT	213		
TES-ADT	90		
BT-ADT	60		
HT-ADT	56		
OT-ADT	63		
OO-ADT	19		

Table 2.3: Half-life values determined for each ADT derivative

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Photo-oxidative Stability

Figure 2.15: ADT derivatives ranked by their photo-oxidative stability as determined by their half-life.

The stability test results show strong differences in photo-oxidative stability between each of the four ADT functional groups. Our new, previously unknown acetoxy-ADT derivatives were the most stable by far with a half-life of 213 minutes. TES-ADT proved to be the second most stable derivative with a half-life of 90 minutes. The thioether-ADT derivatives were the third most stable, with a half-life between 56 and 63 minutes that varied slightly for the different alkyl chain lengths. The ether derivative OO-ADT was the least stable by far with a half-life of 19 minutes, decaying so quickly that we had to take absorption spectra every two minutes instead of every five minutes, in order to get clean results and ensure that oxygen remained in excess to maintain the pseudo-first order kinetics rate..

One key point we would like to make before evaluating these results is that these half-life values reported here are extremely situational and would likely change depending on the spectral composition and intensity of the light source used. Having said that, we believe that the stability trends we observe here will hold true regardless of light intensity. Put another way, if one were to make his/her own ADT solutions and measure these half-life values, the actual half-life time one would record may not match the half-life we report here. However, we expect that one would still find the same trend in stability (ether-ADT < thioether-ADT < TES-ADT < acetoxy-ADT).

Some of our data fits with trends we expected to see based on literature reports, while other results were quite surprising. It was predicted that ether functional groups on the central ring of an acene (as with OO-ADT here) would increase its reactivity with oxygen, due to the fact that ethers are relatively good electron donors to aromatic rings. However, there were no reported measurements of the stability of a linear acene with ether functional groups on the central ring. Our OO-ADT results confirm what Zhang et. al. researchers had predicted.⁵⁵ OO-ADT was the least stable derivative by a wide margin due to the destabilizing influence of the ether substituents.

Taking these stability results in hand with the HOMO/LUMO data collected earlier, our OO-ADT results reinforce the claim⁵⁵ that a higher HOMO energy level (~ -5.0 eV for OO-ADT) leads to increased reactivity with oxygen. OO-ADT was the only ADT derivative with a HOMO energy level that high (**Table 2-2**).

Unlike OO-ADT, our TES-ADT and thioether-ADT results are interesting. A previous study by Kaur et. al. found that thioether substituents stabilized pentacene against photo-oxidative degradation up to 2× better than trialkylsilylacetylene substituents did using a similar experimental design.⁵⁷ Our results here contradict this earlier work; however the difference we observe here might result from the different acene cores we are testing. Acene dimerization is a significant degradation pathway in linear benzylic acenes like pentacene, whereas ADT does not dimerization to any significant extent. Further supporting this idea, the acetylene portion of the

TES function group has also been known to serve as a dienophile in a Diels-Alder degradation reaction with a nearby acene core (acting as the diene), which ADT is less susceptible to. This would explain why TES substituents were found to be less stable than thioethers when bound to pentacene, but more stable than thioethers when bound to ADT in our study.

Turning now to the acetoxy-ADT derivatives, it appears that we may have discovered a new, most stabilizing functional group for acenes. The acetoxy-ADT derivatives were both remarkably long lasting compared to the other three derivatives. Acetoxy-ADT had a half-life over twice that of TES-ADT and almost four times higher than the thioether-ADT derivatives. The HOMO/LUMO energy results provide us with no explanation, as all three of these derivatives have essentially identical HOMO energy levels and somewhat similar band gaps. It is possible, however unlikely, that acetoxy-ADT, with the largest bandgap of the four compounds, simply absorbed less light than the other ADT derivatives. However, if this were true, we would have expected the second highest bandgap ADT derivative, OO-ADT, to display a much longer half-life than it did considering their absorption edges differed by only 10-15 nm. Without more rigorous control over the light source and profile, we cannot know how much of a role differences in light absorption played.

Despite this uncertainty, it is clear that the acetoxy-ADT derivatives exhibit remarkable photo-oxidative stability for a five-fused ring linear acene, and may prove to be an excellent tool for stabilizing and solubilizing larger acenes like heptacene and nonacene.

2.6 Impact of Heteroatom Functionalization on ADT Crystal Packing

While the effect of acene substituents thus far has focused on electrochemical differences and changes in stability, the most important impact that acene side chains have on the properties of these derivatives is how they alter the molecular packing of the solid-state acene. If an acene

does not adopt a crystal structure that provides good overlap between acene core π -orbitals in a way that leads to the formation of charge transport pathways, then it will be of little use in OFETs and lead to devices with low charge mobility. As a frame of reference, systems with high charge-carrier mobility typically have plane-to-plane distances that range from 3.3 to 3.8 Å, so any conjugated π -orbital overlap within that distance is presumed to facilitate charge transport.⁵⁹

This has been convincingly shown in a series of trialkylsilylacetylene functionalized ADT studied by Marcia et al. who found that even small changes in the size of the three alkyl chains on the silicon atom (from methyl to ethyl to isopropyl) could drastically change the crystal packing and resulting OFET mobilities.⁶⁰ The best performing derivative (TES-ADT) displayed good π -orbital overlap between ADT cores and packed in a 2-D brickwork pattern that allowed for charge transport in multiple directions.⁶⁰ This resulted in uniform, high quality thin films that displayed a good hole mobility of 1.0 cm²/V·s with a high on/off current ratio (10⁷), whereas the trimethylsilylacetylene-ADT derivative could not form uniform films and packed in a way that did not allow for any charge transport. Such a drastic change in performance resulted from a very small change to the molecule at large, which demonstrates exactly how profound small changes in molecular structure can be.

In order to gain insight into how these functional groups impact the crystal packing of ADT, we collaborated with Dr. David Mitzi and Dr. Kezhao Du at Duke University, who ran single crystal x-ray diffraction (XRD) on large crystals we grew of each ADT compound. The crystal structures are individually discussed below.



Figure 2.16: Crystal structure of OO-ADT. **a**) Top view looking down the OO-ADT stacks in the slip-stack direction. **b**) Side and front view of three molecules in an individual ADT stack, showing the distances between molecules in the same stack. **c**) Side view of the same stacks shown in part a. OO-ADT stacks exhibit herringbone packing, with an 87° tilt angle relative to adjacent stacks. Red arrows denote the most likely directions for charge transport.

Single crystal X-ray diffraction (XRD) was run on OO-ADT crystals grown by slow recrystallization in isopropyl alcohol and resulted in the crystal structure shown in **Figure 2.16** above. OO-ADT packs in a series of 1-D slip-stacks, while the stacks themselves exhibit herringbone packing. As seen in **Figure 2.16b**, there is strong π -orbital overlap between ADT cores within a stack (with a separation of 3.69 Å between ADT cores), which will allow charge transport through the stack, forming a path of least resistance for charges. This kind of packing arrangement is most frequently seen in acene systems with large side chains. The large 87° tilt angle seen between ADT stacks that create the herringbone pattern is a result of weak edge-to-face C-H… π interactions that provide a driving force for the highly tilted crystal packing seen here. While this type of crystal packing does create 'highways' for charge transport, the 1D nature of charge transport through these stacks makes them very susceptible to disorder and crystal grain boundaries disrupting the packing. If the slip-stack is interrupted, charges will be largely cut-off from neighboring ADT slip-stacks and will have nowhere to go. Factors such as these are believed to be the most likely explanation of the traditionally poor OFET performance of 1-D slip-stack acenes.

The crystal structure of OO-ADT shows strong interactions in only one direction, with ADT core face-to face π - π interactions creating the 1-D slip-stacks. The only additional interactions are either edge-to-face π ···H-C interactions or weak van der Waals interactions, none of which are particularly closely bound according to the crystal structure. The ether heteroatom functional groups do not play a significant role in the crystal packing of this compound.

2.6.2 Butanethiol-ADT Crystal Structure



Figure 2.17: BT-ADT chemical structure and the BT-ADT single crystals used to resolve the crystal structure.

Single crystal x-ray diffraction (XRD) was run on BT-ADT crystals grown by slow recrystallization, in the dark, from a two phase dichloromethane:methanol solvent system that slowly mixed by diffusion, growing the BT-ADT crystals in the process, shown in **Figure 2.17** above. The crystal structure obtained is shown below in **Figure 2.18**.



Figure 2.18: Crystal structure of BT-ADT. **a**) Top view looking down the ADT stacks. **b**) Side and front view of three molecules in an individual ADT stack, showing the distances between molecules in the same stack. **c**) A small subsection of the whole BT-ADT crystal structure outlined in a red triangle in part a, that shows the three ADT stack orientations that repeat throughout the structure. These BT-ADT stacks exhibit herringbone-like packing, with a 77° tilt angle relative to adjacent stacks. Red arrows denote the most likely directions for charge transport.

BT-ADT has a complex and truly unexpected crystal packing motif. While the packing of the ADT cores within a stack remains familiar (the BT-ADT cores pack in a series of 1-D slipstacks), the overall ordering of the slip-stacks relative to one another is what makes this crystal structure so unique. We could not find any other example of an acene packing like this molecule. This crystal structure is well outside the standard packing motifs.

Running close-contact calculations on the crystal structure, where the scaled sum of the van der Waal's radii is calculated for each pair of atoms in the crystal structure and compared to

the distances they actually display, provides a better clue as to what is driving formation of this unique structure. The closest contacts in the entire crystal structure are between the thioether functional group sulfur atoms and the hydrogens on the thiophene ends of the ADT core, measured at 2.89 Å or 2.99 Å, depending on whether the ADT core is facing toward or away from the thioether. Mixtures of both are present in the actual crystal. Those end hydrogens are the most acidic hydrogens on the ADT core and likely the entire molecule. While this interaction is not hydrogen bonding and nowhere near as strong, it does not seem like a coincidence that the most acidic hydrogen on the ADT core is very close to an electronegative sulfur functional group. We believe it is fair to say that these interactions are a driving force in why BT-ADT packs the way it does, and that this crystal structure would not occur without the thioether heteroatom function group interactions promoting this packing motif.

A closer inspection of the crystal structure also reveals that the sulfur atoms of the BT-ADT thiophenes are actually extremely close together in the center of the red triangle sub-cell unit that repeats throughout the crystal structure. These sulfur atoms are only 3.55 Å apart, which is within the scaled sum of the van der Waal's radii and similar distances have been used in the literature as proof of solid state sulfur-sulfur interactions.^{13,61} If the crystal structure is to be believed, these sulfur-sulfur interactions descend in a helical pattern down the group of three BT-ADT 1D-slip stacks outlined by the red triangle.

One last oddity of the BT-ADT crystal structure that we would like to address is the regular periodic voids that are present in the crystal structure. These voids are about 7 Å wide and it is possible that they are actually filled by residual solvent molecules, although we were not able to observe any from the XRD data. Molecules in the organic solid state are usually closely packed.⁶² Voids such as these are extremely uncommon and are not a feature one would expect

to develop in a crystal structure where the forces driving crystal formation are primarily thought to be weak van der Waals interactions. Most organic compounds that form large voids in their crystal structure are a result of strong hydrogen bonding moieties (R-NH₂, R-OH, R-COOH).⁶² Compounds such as 1,4-benzenedicarboxylate or 1,3,5-benzenetricarboxylate naturally form crystals with voids and are well known examples of this phenomenon. ^{62,63} However, BT-ADT has no strong hydrogen bonding moieties, and we could find no other example of a conjugated aromatic molecule forming crystals in this way.

As seen in **Figure 2.18b**, there is strong π -orbital overlap between BT-ADT cores within a stack (with a separation of 3.47 Å between cores, which is closer than it was for OO-ADT), which will allow charge transport through the stack. BT-ADT is particularly interesting because while it remains a 1-D slip-stack material, it is a 1-D slip-stack network, where the stacks are clearly interacting with each other in a way that helps orient them relative to one another, aligning the stacks in one particular direction.

2.6.3 Hexanethiol-ADT Crystal Structure



Figure 2.19: HT-ADT chemical structure and the HT-ADT single crystals used to resolve the crystal structure

Single crystal x-ray diffraction (XRD) was run on BT-ADT crystals grown by slow recrystallization, in the dark, from a two phase dichloromethane:methanol solvent system that slowly mixed by diffusion, growing the BT-ADT crystals in the process, shown in **Figure 2.19** above. The crystal structure obtained is shown below in **Figure 2.20**.



Figure 2.20: Crystal structure of HT-ADT. **a**) Top view looking down the ADT stacks. **b**) Side and front view of three molecules in an individual ADT stack, showing the distances between molecules in the same stack. **c**) Side view of the same stacks shown in part a. HT-ADT stacks exhibit herringbone packing, with an 82° tilt angle relative to adjacent stacks. Red arrows denote the most likely directions for charge transport.

Single crystal X-ray diffraction (XRD) was run on HT-ADT crystals grown by slow recrystallization in isopropyl alcohol and resulted in the crystal structure shown in **Figure 2.20** above. HT-ADT, much like OO-ADT, packs in a series of 1-D slip-stacks, while the stacks themselves exhibit herringbone packing. As seen in **Figure 2.20b**, there is strong π -orbital overlap between ADT cores within a stack (with a separation of 3.53 Å between ADT cores, smaller than the gap for OO-ADT), which will allow charge transport through the stack. This kind of packing arrangement is most frequently seen in acene systems with large side chains, so the thioethers reverting back to this packing motif as alkyl chains lengthen is certainly possible. It is surprising to see just how much the crystal structure changes moving from BT-ADT to HT- ADT, though to some extent the change in crystal packing makes sense. The circular voids in the BT-ADT crystal structure do not have enough room to accommodate an additional two carbons from each of the six ADT derivatives lining the circle. As a result, we suspect that even if HT-ADT can interact in the same way BT-ADT does, it cannot do so consistently or in a way that can accommodate the alkyl chains of HT-ADT. The extended reach of the HT-ADT alkyl chains may also make it more difficult for the ADT cores to make contact with one another. The bond angle of an R-S-R' thioether is roughly 100° in these systems, so the alkyl chains are nearly perpendicular to the acene core.

That last explanation may also explain why we were unable to grow any crystals of OT-ADT. Although numerous conditions were tested, OT-ADT never grew crystals larger than a fine powder. It is possible the large size and steep angle of the octanethiol alkyl chains simply prevents OT-ADT from having significant crystallinity.

2.6.4 Hexanoate-ADT Crystal Structure



Figure 2.21: HA-ADT chemical structure and the HA-ADT pure product

Single crystal x-ray diffraction (XRD) was run on HA-ADT crystals grown by slow recrystallization, in the dark, from DMF. The HA-ADT and OA-ADT crystal structures and the forces producing those crystal structures are similar enough that they will be discussed together in the next section.



Figure 2.22: Crystal structure of HA-ADT a) Top view looking down the ADT stacks. b) Side and front view of three molecules in an individual ADT stack, showing the distances between molecules in the same stack. c) Side view of the same stacks shown in part a. Individual ADT stacks are tilted 67° relative to adjacent stacks. Red arrows denote potential directions for charge transport.
2.6.5 Octanoate-ADT Crystal Structure



Figure 2.23: OA-ADT chemical structure and the OA-ADT single crystals grown from toluene

Single crystal x-ray diffraction (XRD) was run on OA-ADT crystals grown by slow recrystallization, in the dark, from a two phase dichloromethane:methanol solvent system that slowly mixed by diffusion, growing the OA-ADT crystals in the process, shown in **Figure 2.23**. OA-ADT crystals could also be grown by recrystallizing from toluene.



Figure 2.24: Crystal structure of OA-ADT. a) Top view looking down the ADT stacks. b) Side and front view of three molecules in an individual ADT stack, showing the distances between molecules in the same stack. c) Side view of the same stacks shown in part a. Individual ADT stacks are tilted 68.5° relative to adjacent stacks. Red arrows denote potential directions for charge transport.



Figure 2.25: Significant interactions/close contacts between HA-ADT molecules within the crystal structure. **a**) One central HA-ADT molecule and the six neighboring HA-ADT molecules it interacts with. **b**) Interactions between the central HA-ADT molecule and the two HA-ADT molecules within the same π -stack. **c**) Interactions between the central HA-ADT molecule and the four HA-ADT molecules on neighboring π -stacks.

The acetyl-oxy-ADT derivatives also exhibited a very unique crystal structure that we have not seen before in the literature. Much like the BT-ADT crystal structure, the HA-ADT crystal packing seems to be a direct result of the functional group heteroatoms influencing the way that the ADT core packs. Here, the carbonyl functional groups of the acetyl-oxy substituents seem to be driving the structure formation. Both HA-ADT and OA-ADT exhibit roughly the same crystal structure, but some differences in alkyl chain arrangement and packing distances exists.

While a bis(butanoate)-ADT (BA-ADT) derivative was successfully synthesized (as seen by ¹H-NMR), its low solubility hindered efforts to purify the crude product and we were never able to grow crystals of sufficient quality for XRD. As a result, no further study was done on BA-ADT and we cannot make a direct comparison between BA-ADT and BT-ADT. From what we have learned of the acetoxy-ADT series, the heteroatom interactions of the ester functionality appear to be stronger than those of the other heteroatom derivatives and disrupt co-facial π - π orbital stacking to a higher degree than seen in the other derivatives. This notion, along with the presence of additional steric hindrance from of carbonyl functionality, leads us to believe that the crystal structure of BA-ADT would be unlikely to mimic the packing displayed by BT-ADT. However, further experiments would be needed to know definitively.

Running close-contact calculations on the crystal structure, where the scaled sum of the van der Waal's radii is calculated for each pair of atoms in the crystal structure and compared to the distances they actually display, provides a better clue as to what is driving formation of this unique structure. The closest contacts in the entire crystal structure are between the acetyl-oxy functional group carbonyl oxygen and the once again the hydrogens on the thiophene ends of the ADT core, measured at 2.45 Å or 2.95 Å depending on whether the ADT core is facing toward or away from the carbonyl. Those end hydrogens are once again the most acidic hydrogens on the ADT core. Since the heteroatom in question is oxygen this time, there is a very real chance this is an example of weak hydrogen bonding helping guide crystal formation. In fact, if we look at the top down view of the crystal structure shown in **Figure 2.25a**, we can see that the ends of the ADT core extend out toward the ester carbonyls on the neighboring molecule. If not for the influence of the acetyl-oxy carbonyl groups, we believe the acetyl-oxy derivatives would adopt a crystal packing much closer to the one displayed by OO-ADT.

However, the influence of these acetyl-oxy carbonyls is not all positive. The carbonyls are attached so close to the ADT cores that they severely limit the amount of π -orbital overlap present within a stack of HA-ADT molecules. The ADT cores are shifted 4.42 Å off center from one another for HA-ADT and 4.19 Å off center for OA-ADT, which makes them pack more like a staircase than a compact slip-stack. Despite this, there are promising signs that π -orbital interactions still exist within HA-ADT stacks. The second closest contact on the HA-ADT molecule is actually between a carbon atom of the ADT core and the oxygen atom bridging the ADT core and the acetyl side chain of the ADT molecule above or below it. This contact is extremely close, 3.15 Å, and is more than close enough to indicate oxygen lone pair interactions with the π -orbital of the carbon atom on the next molecule. While these oxygen electron lone pair- π orbital interactions create a narrow and limited connection between ADT cores within a stack, each core is extending a π -interacting oxygen linker over the π -orbitals of its neighbor and as interacting with the oxygen linker from that same neighboring ADT core.

One study by Mooibroek et. al. looking at interactions between lone pairs of electrons and π -orbital systems in the Cambridge Structure Database found that in crystal structures with R-O-R' to aromatic π -orbital interactions, a distance of 3.07 Å to 3.22 Å was indicative of clear medium strength interactions between the two systems.⁶⁴ For HA-ADT, we observe a distance of 3.15 Å from the acetoxy oxygen, the one bridging the ADT core and the side chain, to the conjugated ADT core of the neighboring ADT molecule. This is a clear side-chain heteroatom interaction that is helping drive crystal formation and possibly facilitating intermolecular interactions between ADT cores, but it is far from the only heteroatom interaction present in this system.

Due to the ~67 ° tilt between ADT cores in adjacent ADT stacks, it is difficult to tell if there is significant π -orbital interaction between the slip-stacks. However, what we can say for certain is that the 1-D acetyloxy-ADT slip stacks are very close together. At their closest, neighboring ADT stacks have edge-to-face H $\cdots \pi$ interactions that are only 2.80 Å apart or S \cdots π interactions that are 3.47 Å apart, depending on what direction the neighboring ADT end thiophene faces. The closest ADT core C \cdots C distance between slip-stacks is 3.60 Å, which is certainly close enough for π - π interactions, but the true extent of π -orbital interaction is still unknown and complicated by the twisting inter-stack angle these derivatives have. Further study will be required in order for us to know the extent of effective overlap between acetyloxy-ADT derivatives; however, what we can say is that HA-ADT and OA-ADT take on a very unique packing motif that exhibits 2-D interactions and may enable 2-D charge transport in OFETs.

These ADT crystal structures are very interesting and the influence of heteroatom functional groups on the crystal packing of the molecules can be clearly seen. However, we are ultimately concerned with their device performance, and so we set out to make OFETs from these various ADT molecules.

2.7 ADT OFET Fabrication and Characterization

Having characterized their crystal structures, we set out to make thin films and ultimately OFET devices out of these ADT materials. Elizabeth Keenan in the You Group helped us work out the thin film casting conditions, fabricated the OFET devices, and tested their mobility. All of the transistors were fabricated on Si/SiO₂ substrates with 300 nm of SiO₂. Depending on the sample, Ti/Au drain and source contacts were thermally evaporated before or after thin film deposition to make bottom or top contact OFET devices respectively. The OFETs were testing using a probe station with a Keithley 2636b. Measurements were performed in the dark due to

the known photo-oxidative stability troubles these ADT molecules have, as we have proven earlier.

Different methods were tested to try and create uniform thin films of ADT, including spin coating, drop casting, and blade-coating. The conditions used to make thin films of the small molecules can have a huge impact on the resulting OFET performance.^{52,10,65} The thin film and OFET results obtained for our ADT derivatives are shown below.

2.7.1 **TES-ADT**

We first created transistors using TES-ADT as a reference material. TES-ADT has been well studied in the literature and by replicating OFET conditions previous reported,⁶⁵ we can establish a baseline to compare our materials to. Previous reports used spin-casting to make TES-ADT thin films for OFETs, so we used spin-casting here as well.

A 20 mg/mL toluene solution of TES-ADT was heated to 80 °C, filtered with a 0.45 μ m filter, and spun cast at 3000 rpm for 1 minute onto Si/SiO₂ with gold source-drain contacts deposited on it. **Figure 2.26** below shows microscope images of the TES-ADT devices made by spin-coating. TES-ADT coated the surface of the substrate well, and the OFETs worked.



Figure 2.26: Two different microscope images of TES-ADT films formed by spincasting from a toluene solution onto a silicon wafer with gold contacts The field-effect mobility and on/off ratio of these TES-ADT OFETs were determined using the OFET transfer curves shown below in **Figure 2.27**.



Figure 2.27: Electronic measurements of TES-ADT transistors a) Transfer curve of TES-ADT OFET. b) Log plot of TES-ADT OFET.

TES-ADT was a p-type material as reported, and provided a mobility of $0.02 \text{ cm}^2/\text{V} \cdot \text{s}$ with an on/off ratio of 10^4 . While these numbers are lower than those reported in the literature for TES-ADT ($1.00 \text{ cm}^2/\text{V} \cdot \text{s}$, on/off ratio = 10^7)⁶⁰ we did not extensively optimize or retest our casting conditions. These numbers are within an order of magnitude of those reported for TES-ADT ⁶⁰ and that is not unusual when comparing OFETs produced in different research groups. As such, this is a good enough measurement to use as a point of comparison.

2.7.2 OO-ADT

OO-ADT OFETs were produced by the same conditions used for TES-ADT. However, the OO-ADT thin films were nowhere near as consistent as those produced by TES-ADT. We found that by altering the spin-speed while spin coating, we could form drastically different thin films of OO-ADT. Some examples of the different kinds of films formed are shown in **Figure 2.28** below.



Figure 2.28: Several microscope images of OO-ADT films formed by spin-casting from a toluene solution onto silicon wafers. These films were created using different spin-speeds, but the results were not always consistent. The blue color seen behind the films is from the silicon wafer.

The OO-ADT films were not particularly uniform like the TES-ADT films were. The high degree of variability in the thin films indicates that there might be several different kinds of packing motifs present. Several OO-ADT thin films showed a tendency to form small needle-like crystals instead of continuous films. However, these results are not unexpected. A lack of strong interactions outside of the OO-ADT 1-D slip-stacks, that it is known to pack in from its crystal structure, would explain why this compound does not tend to form good quality thin films.

Despite the trouble OO-ADT has forming thin films; we were able to get OFET results for it using both bottom and top contact devices. Those device results are shown below in **Figure 2.29**.



Figure 2.29: Electronic measurements of OO-ADT transistors a) Transfer curve of top contact OO-ADT OFET. b) Log plot of top contact OO-ADT OFET. c) Transfer curve of bottom contact OO-ADT OFET. d) Log plot of bottom contact OO-ADT OFET.

The top contact OO-ADT transistors had a mobility of $2.8 \times 10^{-4} \text{ cm}^2/\text{V} \cdot \text{s}$ and an on/off ratio of ~ $10^{2.5}$. The bottom contact OO-ADT transistors had a mobility of $1.2 \times 10^{-4} \text{ cm}^2/\text{V} \cdot \text{s}$ and an on/off ratio of ~ 10^3 . It did not seem to matter if the devices were top or bottom contact. The performance was roughly the same either way. These results match well with the OFET performances reported for other 1-D slip-stacked acene molecules.²⁹

2.7.3 BT-ADT

BT-ADT OFETs were produced by the same conditions used for TES-ADT. Unlike OO-ADT, BT-ADT thin films coated the silicon substrate extremely well. We found that by altering the spin-speed while spin coating, BT-ADT would create thin films that were visually very distinct, but all of them coated the substrate well. Some examples of the different kinds of films formed are shown in **Figure 2.30** below.



Figure 2.30: Several microscope images of BT-ADT films formed by spin-casting from a toluene solution onto silicon wafers. These films are visually different at different spin-speeds, but they all coat the substrate well. The blue color seen behind the films is from the silicon wafer.

These BT-ADT thin film results are especially interesting when the crystal packing exhibited by BT-ADT is taken into account. The BT-ADT crystals formed a 1-D slip-stack network, where stacks of BT-ADT molecules were drawn close together and produced an interesting long-range order due to heteroatom interactions. While we will need further experimental data in order to prove it for sure, it looks as though the interactions that were driving the formation of the crystal structure are also responsible for the excellent film coverage properties we see here.

Despite this fascinating data, the OFET results for BT-ADT were still well within the expected performance range for a 1-D slip-stacked acene. BT-ADT OFETs transfer curves are shown in **Figure 2.31** below.



Figure 2.31: Electronic measurements of BT-ADT transistors a) Transfer curve of BT-ADT OFET. b) Log plot of BT-ADT OFET

BT-ADT exhibited a mobility of 2.9×10^{-4} cm²/V·s and an on/off ratio of ~10³. While these results are a bit disappointing, please note that BT-ADT OFETs were only made once and so the casting conditions are far from optimized. The visually different films produced at different spin-speeds indicate that there is a great deal of optimization that could be done for this material. The fact that the BT-ADT stacks seem to align with one another in the crystal structure could lead to very good OFET performance in a well optimized system. The theoretical mobility of a 1-D slip-stacked acene is not much lower than that of a 2-D acene. It is the favorable multidirectional organization of 2-D packing acenes when self-assembling that leads to better results in the real world. These BT-ADT materials seem to be self-assembling in a similar way and we hold out hope that better results for this molecule can be obtained.

2.7.4 HT-ADT

Unfortunately, no high quality, continuous thin films of HT-ADT could be grown by spin-casting. This is shown in **Figure 2.32** below. The few OFETs we did attempt to make did not work. It seems that whatever was driving such good thin-film formation in BT-ADT is not present in HT-ADT, despite how similar the molecules are. This is consistent with their crystal

structures, but it is still interesting to see just how different their properties are on a macroscopic level under the same casting conditions.



Figure 2.32: Several microscope images of HT-ADT films formed by spin-casting from a toluene solution onto silicon wafers. These films do not coat the substrate well. The blue color seen behind the films is from the silicon wafer.

2.7.5 OT-ADT

We attempted to produce OT-ADT OFETs by the same conditions used for TES-ADT. While OT-ADT produced continuous thin films, the material coating the transistor was essentially amorphous. It seems that the alkyl chains are simply too long to allow for any significant crystallinity. This is consistent with our observations when attempting to grow OT-ADT crystals, where nothing beyond an amorphous red solid powder was ever obtained regardless of the crystallization solvent.



Figure 2.33: Several microscope images of OT-ADT films formed by spin-casting from a toluene solution onto silicon wafers. These films coat the substrate well, but have low crystallinity and the OFETs made do not work. The blue color seen behind the films is from the silicon wafer.

2.7.6 HA-ADT & OA-ADT

While the previous ADT derivatives could be deposited by spin-coating, the acetyl-oxy ADT derivatives were much more difficult to convert into a uniform thin film. From working with these materials in the lab, it was already clear that they are extremely crystalline, more difficult to dissolve than the other derivatives, and in general are different from the other linear acenes. Attempts to spin-cast acetyl-oxy ADT derivatives resulted in very sparsely covered films. No matter which solvent we tried, the acetyl-oxy ADT derivatives would largely de-wet from the silicon substrate or grow large, blocky crystals. Examples of these attempts can be seen in **Figure 2.34** below.



Figure 2.34: Several microscope images of HA-ADT films formed by spin-casting and drop casting onto silicon wafers. None of these conditions result in good coverage of the substrate. The blue color seen behind the films is from the silicon wafer.

While these previous casting methods failed, we were able to find a way to successfully coat HA-ADT and OA-ADT into continuous thin films. It turns out that blade-coating them onto a heated substrate from a hot trichlorobenzene solution can produce continuous thin films. This can be seen below in **Figure 2.35**.



Figure 2.35: Several microscope images of HA-ADT and OA-ADT films formed by blade-coating trichlorobenzene solutions onto heated silicon substrates. These films generally exhibited excellent coverage and visually striking results.

Encouraged by these good quality films, we set out to make bottom contact OFETs from HA-ADT and OA-ADT under these conditions. The electronic properties of these materials were the best of any of the ADT derivatives we tested. The best HA-ADT device exhibited a hole mobility of $0.69 \text{ cm}^2/\text{V} \cdot \text{s}$ and the on/off ratio of 10^4 . The transfer curves are show below in **Figure 2.36**. These mobility results are comparable with values seen from 2-D charge transport acene materials and is an encouraging indicator that there may indeed be 2-D charge transport pathways present for these materials as we predicted from their crystal structures.



Figure 2.36: Electronic measurements of HA-ADT transistors a) Transfer curve of HA-ADT OFET. b) Log plot of HA-ADT OFET2.8 Conclusion

Heteroatom functionalization was shown to have an enormous impact on the properties, crystal packing, and OFET performance of anthradithiophene small molecules. While the huge impact of substituent groups on the properties and packing of linear acenes was well established, there has been essentially no evaluation of the impact of any substituent groups other than trialkylsilylacetylene in the literature. In this work, we synthesized five never-before reported and two previously reported functionalized ADT molecules and studied the structure-property relationship in these compounds, expanding our understanding of this crucial relation in way that will enable us to design better materials.

We found that acetyl-oxy ADT derivatives are at least twice as stable to photo-oxidative degradation as their TES-ADT counterparts and at least three times more stable than thioether-functionalized ADT derivatives. Acetyl-oxy substituents could very well be the best reported functional group for stabilizing larger acenes against degradation, which is the biggest barrier to their synthesis and further development.^{54,66}

Analysis of the crystal packing of these ADT materials revealed two new molecular packing motifs where substituent heteroatoms attached to the ADT core play a major role in determining the resulting crystal structure. For the thioether-ADT derivatives, we discovered that small changes in alkyl chain length can produce drastic changes in the molecular packing and resulting thin film formation properties of the material. The acetyl-oxy-ADT derivatives demonstrated the potential of acetyl-oxy functional groups, which exerted more influence on the resulting crystal structure than any of the other heteroatom substituents tested. These results reinforce the idea that functional groups can play a key role in guiding the molecular packing of even large organic molecules like linear acenes, and the new discoveries made in this work show that there is still a great deal left to be discovered in the field of crystal engineering.

2.9 Experimental Section

All chemicals were purchased from commercial source (Sigma-Aldrich, Fisher, Matrix, etc.) and were used as received except when specified. THF was distilled over sodium and benzophenone before use. Anhydrous toluene was purchased in sealed bottle from Fisher. For reactions performed under an inert atmosphere, the reaction flask was flame dried under vacuum and cycled between vacuum and argon three times before any reagents were added.

¹H and ¹³C nuclear magnetic resonance (NMR) measurements were recorded with Bruker DRX spectrometers (400 MHz, 500 MHz or 600 MHz). Mass Spectrometry was run on a Q Exactive

Orbitrap (ThermoFisher, Bremen, Germany) mass spectrometer and analyzed via Xcalibur (ThermoFisher, Breman, Germany). UV-visible absorption spectra were obtained with a Shimadzu UV-2600 spectrophotometer. The film thicknesses were recorded by a profilometer (Alpha-Step 200, Tencor Instruments).

Cyclic Voltammetry (CV)

CV measurements were carried out on dichloromethane solutions of the compounds using a Bioanalytical Systems (BAS) Epsilon potentiostat with a standard three-electrode configuration. A three electrode cell of a glassy carbon working electrode, Ag reference electrode, and Pt counter electrode were used. A 0.2 M solution of tetrabutylammonium hexafluorophosphate in anhydrous dichloromethane was used as the supporting electrolyte. Scans were carried out under an argon atmosphere at a scan rate of 100 mV/s. The reference electrode was calibrated using a ferrocene/ferrocenium redox couple. The HOMO in electron volts was calculated from the onset of the oxidation potential (E_{ax}) using the following equation:

$$HOMO = -[4.8eV + e(E_{ox} - E_{Fc/Fc^+})]$$

2-(thiophen-3-yl)-1,3-dioxolane (1)

12.03g (107.3 mmol) of freshly distilled (0.7 torr at 25° C), clear thiophene-3carboxaldehyde was mixed with 130 mL toluene in a 250mL round-bottom flask with stir bar, before 33.27g (536 mmol, 5 eq) ethylene glycol and 0.323g (1.61 mmol, 0.015 eq) ptoluenesulfonic acid monohydrate was added to the solution. A Dean Stark apparatus and condenser was attached to the flask, and the reaction mixture was stirred and refluxed at 130°C for 17 hours before cooling to room temperature. The now black reaction mixture was poured into a 1L separatory funnel, diluted with 100mL ethyl acetate, and washed twice with 125mL of saturated aqueous sodium hydrogen carbonate (NaHCO₃) solution. The organic layer was dried with magnesium sulfate (MgSO₄), vacuum filtered, and concentrated by rotary evaporation to provide 15.7g (93% yield) of crude product as a dark amber oil. The crude product was used in the next step without further purification.

Yield: 15.7 g (93% yield) crude product.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.39 (m, 1H), 7.32 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.16 (dd, *J* = 5.0, 1.2 Hz, 1H), 5.91 (s, 1H), 4.15 – 3.97 (m, 4H).

3-(1,3-dioxolan-2-yl)thiophene-2-carbaldehyde (2)

To a flame dried, argon refilled (3x) 250 mL round-bottom flask with stir bar, was added 15.6 g (100 mmol) of crude 2-(thiophen-3-yl)-1,3-dioxolane (1) by cannula, followed by 100mL of freshly distilled, dry tetrahydrofuran. The reaction mixture, under argon, was then cooled to - 78°C in a dry ice/acetone bath. 44.3 mL (110.6 mmol, 1.1 eq) of a 2.5 M n-BuLi solution in hexane was added dropwise to the stirring -78°C reaction mixture with a syringe. The dark red reaction mixture was stirred for 45 minutes at -78°C (warmed briefly to restore stirring when the reaction mixture froze), before 9.4 mL (120 mmol, 1.2 eq) of dry DMF was added dropwise to the -78°C reaction mixture. The stirring reaction mixture was slowly warmed to room temperature overnight. The reaction mixture was concentrated by rotatory evaporation to remove the THF, taken up in 200 mL ethyl acetate, and washed twice with 200mL of saturated brine solution. The organic layer was dried with MgSO₄, vacuum filtered, and concentrated by rotary evaporation to provide the crude product as 14 g of dark amber oil. The crude product was used without further purification.

Yield: 14 g (76% yield) crude product as a dark amber oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 10.24 (d, *J* = 0.9 Hz, 1H), 7.65 (dd, *J* = 5.0, 0.9 Hz, 1H), 7.26 (d, *J* = 4.7 Hz, 1H), 6.24 (s, 1H), 4.17 – 4.05 (m, 4H).

thiophene-2,3-dicarbaldehyde (3)

To a stirring solution of 14 g (76 mmol) crude 3-(1,3-dioxolan-2-yl)thiophene-2carbaldehyde (2) in THF (80 mL) was added 100 mL of aqueous 1 M HCl solution dropwise with an addition funnel. The reaction was monitored by TLC in 2:1 dichloromethane/hexane. After stirring for 2 hours at room temperature, the reaction was complete. The reaction mixture was concentrated by rotatory evaporation to remove the THF, taken up in 350 mL dichloromethane, and washed twice with 200 mL of saturated brine solution. The organic layer was dried with MgSO₄, vacuum filtered, and concentrated by rotary evaporation to provide the crude product as a dark red solid. The crude product was taken up in and washed through a short silica gel plug using 2:1 dichloromethane/hexane to remove the dark baseline impurities. Removal of the solvent provided 8.6 g of product as a yellow-white solid. Further purification was achieved by recrystallization of the product in 550 mL of boiling hexanes. After cooling to room temperature, the solution was further cooled in the fridge for 3 hours. The recrystallized product was collected by vacuum filtration, providing 7.35 g of solid white product.

Yield: 7.35 g (69% yield) as a white solid. (49% yield overall from compound 1)

¹H NMR (400 MHz, Chloroform-*d*) δ 10.49 (s, 1H), 10.38 (s, 1H), 7.74 (d, *J* = 5.0 Hz, 1H), 7.64 (d, *J* = 5.1 Hz, 1H).

anthra[2,3-b:6,7-b']dithiophene-5,11-dione (4) (ADT Quinone)

6 g (42.8 mmol, 2.1 eq) of thiophene-2,3-dicarbaldehyde (3) and 2.28 g (20.36 mmol, 1.0 eq) of 1,4-cyclohexane dione were dissolved in 600 mL of ethanol in a 1 L flask. The clear, yellow solution was stirred rapidly, and then 25 mL of aqueous 15% KOH (4 eq) solution was added in one portion. The mixture quickly turned dark green and thickened as a large amount of yellow solid precipitated out of solution. After stirring for 3 hours, the crude yellow solid was

isolated by vacuum filtration and washed with an additional 500 mL ethanol. The solid was then suspended in 150 mL of ethanol, sonicated for 5 minutes to break up the muddy solid, and once again filtered to provide 5.46 g of product as a muddy yellow solid.

Yield: 5.46 g (83% yield) muddy yellow solid (syn/anti mixture)

¹H NMR (400 MHz, Chloroform-*d*) δ 8.93 (s, 2H), 8.84 (s, 2H), 7.79 (d, *J* = 5.5 Hz, 2H), 7.61 (d, *J* = 5.6 Hz, 2H).

5,11-bis(hexanoate)anthradithiophene (5) (HA-ADT)

1.04 g (3.12 mmol, 1.0 eq) ADT Quinone (4), 2.16 g (15.61 mmol, 5.0 eq) K₂CO₃, and 2.04 g (31.21 mmol, 10 eq) activated Zn powder (100 mesh) were added to a flame dried 250 mL RBF with a reflux condenser under inert atmosphere. The flask was purged with argon for 10 minutes, and then 160 mL of dry THF was added. The mixture was vigorously stirred and 10.8 mL (46.8 mmol, 15 eq) of hexanoic anhydride was added the RM in one portion. After shielding the flask from light with tin foil, the stirring reaction mixture was heated to 45°C in an oil bath overnight. The next morning, the now orange reaction mixture was cooled to room temperature and the THF was removed by rotatory evaporation, providing an orange wet solid. The orange solid was taken up in 200 mL DCM and vacuum filtered to remove the Zn Powder and K₂CO₃. The DCM filtrate was concentrated down to a wet orange solid and then mixed with 200 mL of methanol to crystallize the product. The solution was cooled in the fridge for 2 hours, providing 1.15g of crude product as bright orange crystals that were collected by vacuum filtration. The crude product was recrystallized using 500 mL of hot EtOAc. After cooling to room temperature, the solution was further cooled in the fridge overnight. The recrystallized product was collected by vacuum filtration, providing 0.929 g bright orange needle-like crystals.

Yield: 0.929 g (57% yield)

¹H NMR (600 MHz, Chloroform-*d*) δ 8.45 (s, 2H), 8.39 (s, 2H), 7.52 (d, *J* = 5.6 Hz, 2H), 7.38 (d, *J* = 5.6 Hz, 2H), 3.04 (tt, *J* = 7.6, 2.5 Hz, 4H), 2.09 – 2.00 (m, 4H), 1.66 – 1.56 (m, 4H), 1.56 – 1.47 (m, 4H), 1.04 (tt, *J* = 7.3, 2.3 Hz, 6H).

5,11-bis(octanoate)anthradithiophene (6) (OA-ADT)

0.204 g (0.637 mmol, 1.0 eq) ADT Quinone (4), 0.435 g (3.18 mmol, 5.0 eq) K₂CO₃ and 0.410 g (6.37 mmol, 10 eq) activated Zn powder (100 mesh) were added to a flame dried 50 mL RBF with a reflux condenser under inert atmosphere. The flask was purged with argon for 10 minutes, and then 30 mL of dry THF was added. The mixture was vigorously stirred and 2.84 mL (9.55 mmol, 15 eq) of octanoic anhydride was added the RM in one portion. After shielding the flask from light with tin foil, the stirring reaction mixture was heated to 51° C in an oil bath overnight. The next morning, the now orange reaction mixture was cooled to room temperature and the THF was removed by rotatory evaporation, providing an orange wet solid. The orange solid was taken up in 40 mL DCM and vacuum filtered to remove the Zn Powder and K₂CO₃. The DCM filtrate was concentrated down to a wet orange solid and then mixed with 100 mL methanol to crystallize the product. The solution was cooled in the fridge overnight, providing 0.302 g of crude product as bright orange crystals that were collected by vacuum filtration. The crude product was recrystallized from boiling IPA. After cooling to room temperature, the solution was further cooled in the fridge overnight. The recrystallized product was collected by vacuum filtration, providing 0.154 g bright orange needle-like crystals.

Yield: 0.154 g (42% yield)

Note: IPA recrystallized product was at least 95% pure by ¹H NMR after the first recrystallization. However, with longer alkyl chains, OA-ADT is sufficiently soluble in a viable solvent system to be purified using silica gel column chromatography. A later batch of OA-ADT

was purified by column chromatography using 1:1 Hexane/DCM with 1% triethylamine as a solvent system. 0.32 g of crude product was loaded onto the column, and 0.248 g of pristine OA-ADT was collected (37% yield for that reaction)

¹H NMR (600 MHz, Chloroform-*d*) δ 8.45 (s, 2H), 8.39 (s, 2H), 7.52 (d, *J* = 5.6 Hz, 2H), 7.38 (d, *J* = 5.6 Hz, 2H), 3.04 (t, *J* = 7.6 Hz, 4H), 2.04 (p, *J* = 7.5 Hz, 4H), 1.63 (p, *J* = 7.3 Hz, 4H), 1.53 – 1.45 (m, 4H), 1.43 – 1.34 (m, 8H), 0.99 – 0.90 (m, 6H).

5,11-bis(butanethiol)anthradithiophene (7) (BT-ADT)

0.202 g (0.389 mmol, 1.0 eq, 0.05 M) 5,11-bis(hexanoate)anthradithiophene (5) and 0.150 g (0.798 mmol, 2.05 eq, 0.1 M) p-toluene sulfonic acid were added as solids to a flame dried, argon-filled 25 mL RBF with a stir bar. The flask was then cycled between high vacuum and inert atmosphere three times to remove any residual oxygen or water. Then, 8.1 mL of fresh butanethiol was added to the reaction mixture by syringe while in a hood (The thiol is volatile and very smelly). The reaction mixture was stirred and heated to 80°C with minimal light exposure. The solution turned from orange to red within 30 minutes, and complete consumption of the SM was observed after 3 hours by ¹H NMR. After 3 hours and 15 minutes, the RM was removed from the hot oil bath and left to stir and cool to RT under argon slowly overnight. The next morning, the RM was diluted with hexanes and purified directly by flash chromatography through a silica gel column with hexanes. 70 mg of pure product was obtained as a bright red solid.

Yield: 0.070g (38% yield)

¹H NMR (400 MHz, Chloroform-*d*) δ 9.68 (s, 2H), 9.60 (s, 2H), 7.56 (d, *J* = 5.7 Hz, 2H), 7.51 (d, *J* = 5.7 Hz, 2H), 2.95 (tt, *J* = 7.9, 4.1 Hz, 4H), 1.57 – 1.49 (m, 4H), 1.47 – 1.35 (m, 4H), 0.82 (tt, *J* = 7.2, 2.3 Hz, 6H).

5,11-bis(hexanethiol)anthradithiophene (8) (HT-ADT)

0.202 g (0.389 mmol, 1.0 eq, 0.05 M) 5,11-bis(hexanoate)anthradithiophene (5) and 0.150 g (0.798 mmol, 2.05 eq, 0.1 M) p-toluene sulfonic acid were added as solids to a flame dried, argon-filled 25 mL RBF with a stir bar. The flask was then cycled between high vacuum and inert atmosphere three times to remove any residual oxygen or water. Then, 8.1 mL of fresh hexanethiol was added to the reaction mixture by syringe while in a hood (The thiol is volatile and very smelly). The reaction mixture was stirred and heated to 100°C with minimal light exposure. Complete consumption of the SM was observed after 3 hours by ¹H NMR. After 3 hours and 15 minutes, the RM was removed from the hot oil bath and left to stir and cool to RT under argon slowly overnight. The next morning, the RM was diluted with hexanes and purified directly by flash chromatography through a silica gel column with hexanes. 82 mg of pure product was obtained as a bright red solid.

Yield: 0.082 g (40% yield)

¹H NMR (400 MHz, Chloroform-*d*) δ 9.68 (s, 2H), 9.60 (s, 2H), 7.56 (d, *J* = 5.7 Hz, 2H), 7.50 (d, *J* = 5.7 Hz, 2H), 2.94 (tt, *J* = 7.5, 4.0 Hz, 4H), 1.58 – 1.48 (m, 4H), 1.45 – 1.34 (m, 4H), 1.24 – 1.11 (m, 8H), 0.81 (tt, *J* = 7.2, 2.3 Hz, 6H).

5,11-bis(octanethiol)anthradithiophene (9) (OT-ADT)

0.200 g (0.386 mmol, 1.0 eq, 0.05 M) 5,11-bis(hexanoate)anthradithiophene (5) and 0.154 g (0.810 mmol, 2.1 eq, 0.1 M) p-toluene sulfonic acid were added as solids to a flame dried, argon-filled 25 mL RBF with a stir bar. The flask was then cycled between high vacuum and inert atmosphere three times to remove residual oxygen or water. Then, 8.1 mL of fresh octanethiol was added to the reaction mixture by syringe while in a hood (The thiol is volatile and very smelly). The reaction mixture was stirred and heated to 92°C under inert atmosphere

with minimal light exposure. Complete consumption of the SM was observed after 3 hours by ¹H NMR. After 3 hours and 20 minutes, the RM was removed from the hot oil bath and left to stir and cool to RT under argon slowly overnight. The next morning, the reaction mixture was extracted with 100 mL EtOAc, washed twice with 100 mL distilled water and once with 100 mL sat. sodium bicarbonate solution. The EtOAc layer was dried with magnesium sulfate, filtered, and concentrated. With the acid removed, the remaining octanethiol was removed from the dried organic layer using vacuum distillation (~83°C under 0.6 torr). The RM was then taken up in 9:1 hexanes/dichloromethane with 1% triethylamine and purified by column chromatography through silica gel using the same solvent. 76 mg of pure product was obtained as a bright red solid.

Yield: 0.076 g (34% yield)

¹H NMR (400 MHz, Chloroform-*d*) δ 9.67 (s, 2H), 9.60 (s, 2H), 7.56 (d, *J* = 5.8 Hz, 2H), 7.50 (d, *J* = 5.8 Hz, 2H), 2.94 (tt, *J* = 7.6, 3.9 Hz, 4H), 1.57 – 1.46 (m, 4H), 1.44 – 1.34 (m, 4H), 1.21 – 1.14 (m, 16H), 0.83 (t, J = 6.9 Hz, 6H).

5,11-bis(octyloxy)anthradithiophene (10) (OO-ADT)

Octyloxy-ADT was synthesized followed the published procedure reported by Younhee et. al.⁴²

Yield: 0.401g (25% yield)

¹H NMR (600 MHz, Chloroform-*d*) δ 8.80 (s, 2H), 8.76 (s, 2H), 7.49 (d, *J* = 5.6 Hz, 2H),

7.43 (d, *J* = 5.6 Hz, 2H), 4.26 (p, *J* = 6.9 Hz, 4H), 2.20 – 2.09 (m, 4H), 1.79 – 1.66 (m, 4H), 1.53

- 1.47 (m, 4H), 1.46 - 1.39 (m, 4H), 1.40 - 1.31 (m, 8H), 0.98 - 0.89 (m, 6H).

APPI-MS: 546.26086 m/z

5,11-bis(triethylsilylacetylene)anthradithiophene (11) (TES-ADT)

TES-ADT was synthesized follow the procedure reported by Anthony et. al.⁹

Yield: 0.604 g (70% yield)

¹H NMR (600 MHz, Chloroform-*d*) δ 9.17 (s, 2H), 9.12 (s, 2H), 7.56 (dd, *J* = 5.6, 2.2 Hz,

2H), 7.46 (d, *J* = 5.6 Hz, 2H), 1.25 (tt, *J* = 7.8, 3.0 Hz, 18H), 0.92 (q, *J* = 7.9 Hz, 12H).

Chapter 3 Development of New Tricyano-Furan Electron Acceptors for Use in Organic Photovoltaics

3.1 Molecular Engineering of A-D-A Non-Fullerene Acceptors

A-D-A molecule research has seen extensive growth over the last few years, and A-D-A NFAs development is one of the most active and promising areas in organic photovoltaics research. As discussed in **Section 1.5**, using A-D-A molecules that absorb strongly in the visible spectrum as electron acceptors in OPVs instead of fullerene derivatives can greatly expand the effective absorption range of the device. Solar cells with A-D-A electron acceptors have two light absorbers (the donor polymer and the A-D-A acceptor) and as a result can reach higher power conversion efficiencies than fullerene devices. While the concept of replacing fullerene with a better light-absorbing acceptor has been around for years, it is only recently that electron acceptors capable of outperforming fullerene have emerged. The last few years have seen a flurry of papers produced on the topic, and advances in A-D-A NFA design have pushed organic solar cell efficiencies significantly higher.^{24,67 68,69} In May of 2017, Zhao et. al. used a fluorinated ITIC derivative to obtain a record high PCE of 13.1%.⁶⁹

These advances are a true step forward in OPV research; however, there are currently more questions than answers when it comes to A-D-A molecule design. A small handful of A-D-A molecules have been extremely effective (primarily ITIC and its analogues), but it has been difficult to explain what distinguishes them from the myriad of other small molecule acceptors or A-D-A molecules that have failed to perform as well. A look at the highest performing A-D-A acceptors reveals them to be remarkably similar in molecular design.^{22, 70}

Small changes like the addition of methyl or halogen substituents on ITIC have yielded superior devices, but ultimately the scope of modifications that improve A-D-A performance remains surprisingly narrow. While the field has made great strides forward, it is also quite stagnant. The IDTT donor core and IC acceptor units outperform most other A-D-A molecules and are the conjugated core framework used in the vast majority of all A-D-A molecules.

In order for the field to grow, we need diversity in A-D-A molecule design. We need a better understanding of what aspects of the A-D-A structure are crucial to their properties and device performance. We need to learn what is producing the phenomenal results seen from ITIC derivatives, and why those same results have not been seen elsewhere. Thankfully, we are not starting from a blank slate. There are some properties that we know are crucial for good A-D-A performance.^{22,25,71}

Key properties to consider when designing new A-D-A NFA molecules:

1) A-D-A chromophores should have intense and broad absorption in the visible and near-IR regions of the solar spectrum, in order to maximize the range of light absorbed by the solar cell. This is the area where NFAs can offer a serious advantage over fullerene acceptors, and any alternatives we propose should take advantage of this property. Ideally, the A-D-A acceptor should absorb light in the 650-850 nm window (or beyond 850 nm), which would give it complimentary absorption with donor polymers that have already been developed while still giving it a large enough band-gap.

2) If possible, A-D-A molecules should be built and tuned through scalable methods and using molecules and procedures that have been thoroughly explored in the design of donor polymers. Push-pull donor-acceptor copolymers have been the subject of a staggering amount of research over the last few decades and we can use that broad knowledge base to our advantage.

3) We should try to develop A-D-A derivatives that push the acceptor LUMO energy as high as possible to maximize the open circuit voltage (V_{oc}), while maintaining an absorption window that is complimentary to most donor polymers, allowing a high short circuit current (J_{sc}). Additionally, a low enough HOMO energy is necessary in order to facilitate charge splitting with the donor material.

4) A-D-A acceptors should exhibit high electron mobility and be able to form charge transfer networks when blended into a BHJ with a donor polymer. Even if all the other properties are good, an electron acceptor that cannot pass charges along will not be a very effective material.

Small molecule acceptors are actually much like acenes in their requirements for favorable charge transport. They should be structured and functionalized in a way that promotes constructive and common intermolecular interactions between individual A-D-A molecules. Charges are highly localized in organic molecules and charge transport takes place through a hopping mechanism between molecules. If the charges cannot hop their way to the electrodes, then they cannot be collected.

5) A-D-A molecules should have good solubility in common organic solvents. A molecule that is not soluble cannot be easily purified or incorporated into OPVs.

6) A-D-A molecules should be chemically stable. While this is somewhat of a long-term problem that the entire OPV field faces, it does us no good to develop materials that we cannot keep stable long enough to purify or evaluate.

While this is a demanding list of requirements, the limited diversity in A-D-A molecule design provides us with many different potential avenues of research. There are numerous strong acceptors that have never been evaluated for use in A-D-A acceptors, and may prove to be

a viable alternative to IC. With this in mind, we searched through the literature for potential IC alternatives and one acceptor unit in particular caught our eye.

3.1.1 Tricyano-Furan (TCF) Acceptor Units

TCF is a strong electron acceptor that could potentially be an alternative to IC in A-D-A NFAs. TCF has the proper energetics to be an electron acceptor in OPVs and it is one of the champion electron acceptor materials in non-linear optics (NLOs) which rely on a strong D-A transition across the molecule to function.⁷² Despite wide use as electron deficient units in NLO chemistry, TCF has seen essentially no use outside of that field. Despite the lack of precedence in the OPV literature, TCF has the capacity to greatly increase the solubility of A-D-A acceptor moieties, while preserving the favorable energetics an A-D-A molecule needs to split excitons with a donor material and still provide complimentary absorption.



Figure 3.1: TCF and IC acceptor units. The hydrocarbons that are deprotonated during a Knoevenagel condensation reaction with the donor material are colored red. The red carbon is where the acceptor connects to the donor core.

It was anticipated that the two R-groups (methyl substituents or larger) on the TCF core would ensure solubility of the material in common organic solvents, without adding excessive steric bulk to the end units of the molecule. One of the biggest limitations of the IC acceptor units is that they require extremely soluble donor cores in order to make the overall A-D-A molecule soluble enough to work in a BHJ device. This is one of the reasons that other donor cores have not seen more use in A-D-A molecules.

From our perspective, an acceptor unit, like TCF, that provides a good degree of solubility while preserving desirable opto-electric properties would open up the door for a whole host of currently neglected donor cores that are not as solubilizing as IDTT to be used in A-D-A NFAs. This would help us develop a better understanding of the structure-property relationship in A-D-A molecules, learn which molecular features are most important, and may provide answers to a number of interesting questions:

- Is it necessary that the accepter units of the A-D-A molecule be completely flat?
- If not, how much bulk on an acceptor unit is too much?
- How important are the quaternary carbon-linked side-chains on the donor core to the A-D-A molecule solubility and packing?

Even if our TCF A-D-A derivatives do not result in high efficiency OPVs, they may still provide us with the answer to these questions and further our understanding of the structural requirements important to A-D-A NFA performance.

If the methyl TCF derivatives worked well, we would then explore replacing the methyl substituents with longer chains to probe what effect that would have on the acceptor properties.

Given the promising electrochemical outlook of TCF and high solubilizing potential it presented, we set out to synthesize TCF-based A-D-A molecules and incorporate them into polymer solar cells.

3.2 Design and Synthesis of BnDT-Core and Tricyano-Furan (TCF) Capped A-D-A Electron Acceptors

A general overview of the various A-D-A units we used as building blocks for this study are shown in **Figure 3.2** below.



Figure 3.2: Design envisioned for A-D-A molecules in this work.

In order to properly explore the viability of TCF A-D-A acceptors and the advantages they can provide over IC A-D-A acceptors, we synthesized a series of A-D-A molecules using either BnDT or IDT type donor cores with TCF and IC acceptor end units. This allows us to properly compare TCF to the champion IC acceptor units optically, electrochemically, and in OPV devices. By comparing these two systems, we hoped to gain a better understanding of how these changes to the chemical structure of the A-D-A acceptor impact its performance.

TCF acceptor molecules with various R' groups were synthesized in two steps from their $(R')_2(C=O)$ ketone precursors following a procedure outlined in the NLO literature.⁷² The synthesis of these TCF derivatives is the result of R'-ketols reacting with 2 equivalents of malono-nitrile under basic conditions.

3.2.1 Synthesis of BnDT Core A-D-As

Benzodithiophene (BnDT) has seen extensive use as a donor unit in D-A copolymers, and is used in many of the highest performing donor polymers in OPVs.^{23,73} Despite extensive use in OPVs, BnDT has only been used as a donor unit for an A-D-A NFA once to the best of our knowledge.⁷⁴ This lack of BnDT-core based NFAs is surprising, as BnDT is a high performance, planar donor that has well-developed synthesis procedures and can be made with a wide variety of functional groups.⁷⁵ It is possible that the lack of BnDT donors among published A-D-A acceptors is a result of the high solubility requirement that A-D-A acceptors must meet. BnDT is a rigid and planar core that can result in a very insoluble product if proper solubilizing groups are not used. Current high performance A-D-A acceptors utilize IDTT donor cores in order to counter-balance the extreme insolubility of their acceptor units, like IC.

However, TCF is a much more soluble acceptor unit that has many of the same properties as IC. Thus, when using TCF, we should be able to make processable A-D-A NFAs using BnDT as our donor core, without the strict requirement of having quaternary side-chain carbons on the donor core.

A summary of the BnDT donor core synthesis is shown in **Scheme 3.1** below.



Scheme 3.1: Reaction conditions for the synthesis of BnDT A-D-A donor cores and their dialdehyde functionalized derivatives.

The BnDT quinone core was bought from SunaTech, and used without further purification. The functionalized BnDT cores **1a**, **1b**, **1c** were synthesized using one of two methods. **1a** and **1b** were synthesized by lithiation of the side chain SM, followed by addition of the BnDT quinone core to the reaction mixture, where the lithiated side chains react with the BnDT quinone ketones groups. Subsequent removal of the ketone hydroxides by tin chloride produces **1a** and **1b** in good yield.⁷⁶ **1b** undergoes one additional reaction not shown in **Scheme 3.1**, where the alkyne groups on the side chains are fully reduced to hydrocarbons by hydrogen gas with palladium on carbon as a catalyst. This procedure has been well outlined in the literature.⁷⁷ Compound **1c**, on the other hand, if functionalized by reducing the BnDT quinone to the oxy-anion, which then undergoes a S_2N reaction with an alkyl-bromide, providing the ether functionalized BnDT derivative **1c** in moderate yield.

Once the BnDT cores are functionalized, the thiophenes of the BnDT core can be easily deprotonated with n-BuLi, and then reacted with DMF at – 78°C in order to provide the dialdehyde BnDT derivatives **2a**, **2b**, and **2c** in good yield. If trimethyltinchloride is added instead of DMF, then the stannylated derivatives **3a** and **3c** can be obtained in good yield. These stannyl BnDT compounds can then be coupled with 5-bromo-2-thiophenecarboxaldehyde using a palladium catalyzed, Stille coupling reaction, run under inert atmosphere overnight in refluxing dry toluene to produce thiophene-bridged BnDT cores **4a** and **4c** in good yield.

These dialdehyde derivatives can then be reacted directly with two or more equivalents of IC or TCF acceptor units in a Knoevenagel condensation reaction catalyzed by pyridine in CHCl₃. This reaction proceeds quickly for IC, which is the easier of the two derivatives to deprotonate with pyridine and reacts with the donor dialdehyde. TCF requires a higher ratio of pyridine to chloroform solution and often requires heat to fully react, but TCF A-D-A derivatives can also be obtained in moderate yield using the same basic reaction procedure. The BnDT-core A-D-A derivatives are shown below in **Scheme 3.2**.



Scheme 3.2: Reaction conditions for the synthesis of BnDT A-D-A and A-t-D-t-A products.

While we had a definite end goal in mind for the molecules we developed for this project, there were numerous unknown solubility, stability, and purification challenges that arose during their synthesis that had to be dealt with. This was particularly problematic when synthesizing BnDT core A-D-A molecules. We cycled through several BnDT iterations before finding a core with suitable solubilizing chains and appropriate planarity of the A-D-A backbone. Since we could not predict which compounds would meet the laundry list of A-D-A molecule requirements outlined in **Section 3.1**, we were forced to proceed in a trial and error fashion, where we would target one or two BnDT A-D-A products and devote our efforts to making those derivatives quickly in order to assess their solubility, absorption window, and HOMO/LUMO

energy levels. By doing this, we could determine how stable, processable, and viable an A-D-A series was before attempting to make all the variants of that molecule.

We discovered that BnDT cores with linear alkyl or ether side-chains did not provide enough solubility for either TCF or IC A-D-A molecules to be processable. We also learned that 2-octyldodecyl-oxy functionalized BnDT cores (compounds **1c-6c** from **Scheme 3.1** and **3.2** above), while sufficiently soluble, were inherently unstable once the final A-D-A molecule was made. The ether-linked alkyl side-chains on the BnDT core would detach in a way that was very noticeable on NMR. This prevented their use in OPVs, as any attempt to purify them led to significant degradation of the A-D-A molecule. We also discovered what appears to be significant steric hindrance in A-D-A molecules where the donor side chains are too close to the acceptor units, which will be discussed further in **Section 3.3**. This led us to synthesize BnDT core A-D-A derivatives with a thiophene linker that helps spatially separate the donor and acceptor units, improving the planarity of the conjugated core.

These road-blocks and discoveries led us to synthesize many different BnDT A-D-A derivatives, tuning the chemical structure in order to obtain more desirable A-D-A properties. However, the many iterations of A-D-A molecules we synthesized for this project were not in vain. From this large body of synthetic work, we are able to make some interesting comparisons between A-D-A molecules with different R groups on BnDT. We could also compare directly-bound A-D-A derivatives (**5-IC** and **5-TCF** in **Scheme 3.2**) to derivatives (**6-IC** and **6-TCF** in **Scheme 3.2**) composed of the same D and A units separated by thiophene linkers (A-t-D-t-As). These comparisons will be discussed in further detail in **Section 3.3**.

Purifying and characterizing the final A-D-A molecules provided a lot of insight into both the challenges of working with large 'small' molecules and the interesting properties that an
A-D-A type molecule exhibits. All of the A-D-A molecules shown above absorb light remarkably well. Any appreciable concentration of the A-D-A molecule dissolved in solution would quickly turn the whole solution opaque and black. So much so that it was often difficult to know if the material had dissolved or even recrystallized because of just how well they absorbed light.

 Aa
 6a-IC
 6a-TCF
 6a-TCF

This can be seen below in Figure 3.3.

Figure 3.3: Some dilute CHCl₃ solutions of several A-D-A product molecules, along with their di-aldehyde precursor 4a.

The general lack of IC functionalized A-D-A derivatives like **5-IC** and **6-IC** in the literature made more sense once we attempted to synthesize them for ourselves. While we were able to crystallize a number of **5-IC** and **6-IC** derivatives in order to purify them, they were far too insoluble for column chromatography and were a constant challenge to dissolve and work with. The quaternary carbon solubilizing side-chains of IDTT clearly play a huge role in making the IC A-D-A compounds soluble and processable.

As predicted, the TCF-based A-D-A compounds **5-TCF** and **6-TCF** proved remarkably soluble. These derivatives were so soluble it almost became a problem. The only solvent we could find that they were not highly soluble in was hexanes and for some derivatives diethyl-

ether. Their solubility was truly impressive, and they were readily purified through column chromatography.

The **5a**, **5b**, and **6a** derivatives of both acceptors proved to be stable enough to survive any purification steps needed. However, all of the **5c** and **6c** derivatives degraded whenever purification was attempted. Column chromatography, recrystallization from alcohols, and solvent extractions would all result in the loss of the branched oxy side-chains on the BnDT core, although the exact product of this reaction remained unknown. This problem was serious enough to prevent any further work on the ether functionalized BnDT derivative, but the A-D-A molecules were synthesized and characterized by UV/Vis. absorption spectroscopy, which will be discussed in **Section 3.3**.

3.2.2 Synthesis of IDT and IDTT A-D-As

While we learned a lot from synthesizing BnDT A-D-A derivatives, we needed to create A-D-A molecules with a well-studied donor core if we wanted to make a fair comparison between TCF and IC acceptor units. These molecules serve as a good frame of reference by which to measure the performance of TCF relative to IC and evaluate the effect of using BnDT as an A-D-A donor core.

In order to make a fair comparison between the BnDT derivatives made here and an IDTT-like donor core, we synthesized both the smaller indaceno-di(thiophene) (IDT or ID) to serve as a direct comparison with BnDT. We also synthesized IDTT cores, although IDTT is more difficult to make than IDT, so we had only a very limited quantity of it to work with. The synthesis is shown below in **Scheme 3.3**.



Scheme 3.3: Reaction conditions for the synthesis of ID and IT A-D-A molecules These reactions proceeded smoothly under similar conditions to those used for BnDT-core A-D-As. Having synthesized both BnDT and ID/IT donor core A-D-A molecules with IC and TCF acceptor units, we set out to characterize the properties of these new derivatives.

3.3 Optical and Electrochemical Properties

The A-D-A derivatives were first characterized by UV/visible absorption spectroscopy. While their exact molar extinction coefficients were not measured, all of the A-D-A derivatives were found to be strong light absorbers. This is a well-documented property of D-A type molecules and is one of the main reasons D-A molecules and polymers are used in OPVs for both donors and acceptors.

The D–A structure of these molecules leads to more favorable double-bond interactions between donor and acceptor units. The conjugated backbone adopts a more planar configuration to facilitate π -electron delocalization along the conjugated backbone, resulting in a smaller optical band-gap, large transition dipole moment between the HOMO and LUMO energy levels, and localization of the HOMO and LUMO energy levels on the donor moiety and the acceptor moiety, respectively.⁴⁰ These D-A characteristics also mean that small structural differences between A-D-A molecules can produce large changes in the optical properties of the molecule if those differences promote or hinder D-A interactions.

While there are many comparisons that could be made using the large number of A-D-A derivatives we have synthesized, we will focus on a few particular examples and discuss possible causes, although more definitive evidence and thorough studies will be required to determine the source of some of these differences. This project is still an active area of research in the You group, and we are still in the process of understanding this system.

3.3.1 Effect of BnDT Substituent Groups on TCF and IC A-D-A Absorption

The UV/Vis absorption spectra for a series of BnDT core A-D-A molecules (**5a-c IC** and **5a-c TCF**) are shown in **Figure 3.4** below.



Figure 3.4: Normalized UV/Vis. absorption spectra of a) IC and b) TCF functionalized BnDT core A-D-A molecules with different substituent groups, measured from very dilute CHCl₃ solutions.

It is clear from looking at the absorption spectra above that the side chains on the BnDT core have an effect on the relative distribution of the absorption peaks. Normally, the solution

absorption spectra produced by a series of conjugated organic molecules with the same core, but different side chains, will be nearly identical. However, if the side chains are a source of significant steric hindrance, they can result in twisting of an otherwise planar conjugated core. While conjugated organic molecules usually adopt planar conformations that maximize π -orbital interaction between sp² hybridized carbons, steric hindrance driven twisting of the conjugated backbone can greatly affect the nature of the molecular orbital energy levels (i.e. the molecule's HOMO/LUMO energy levels) that define the optical and electrochemical properties of the molecule.

This is particularly relevant in D-A type molecules, as their unique properties and lower band-gap are a direct result of the internal charge transfer that occurs between the donor and acceptor moieties. D-A molecules commonly exhibit two major absorption peaks in the visible spectrum: a low-wavelength, higher energy peak that can be attributed to a π - π * transition and a high-wavelength, lower energy peak that is thought to be a transition produced by intramolecular D-A charge transfer across the molecule.^{78,79} Our A-D-A derivatives shown in **Figure 3.4** are no exception; they all exhibit two distinct absorption peaks. By looking at the absorption ratio between the two peaks, we can make a crude assessment of the degree of conjugated backbone twisting created by the side chains on the BnDT core.

In planar, strongly interacting D-A type molecules, the intramolecular D-A charge transfer absorption will dominate the absorption spectrum and dwarf the π - π * absorption peak in intensity. The more distorted the conjugated backbone becomes, the weaker the intramolecular D-A charge transfer transition becomes. Since BnDT is known to be a good electron-rich donor moiety and TCF/IC are strong electron-deficient acceptor moieties, a fully planar A-D-A molecule composed of these groups should have an absorption spectra dominated by

intramolecular D-A charge transfer. Applying this concept to the absorption spectra shown in **Figure 3.4**, we can draw three clear conclusions.

First, all of the A-D-A derivatives above have π - π * absorption peaks with intensities greater than or roughly equal to their intramolecular D-A charge transfer absorption peak. This indicates that there is a significant degree of backbone twisting present in all of these A-D-A derivatives that is hindering D-A interactions across the molecule.

Second, of the three different BnDT side chains shown (**5a**, **5b**, **5c**), **5b** displays a noticeably higher intramolecular D-A charge transfer peak intensity for both IC and TCF derivatives compared to **5a** and **5c**, whose two peak intensity ratios are similar to one another. This indicates that that the branched alkyl chains on **5b** produce relatively less steric hindrance than the side chains on **5a** and **5c**, although they are clearly still interfering with intramolecular charge transfer.

Third, the **5-TCF** A-D-A molecules shown in **Figure 3.4b** display a higher degree of intramolecular D-A charge transfer than the **5-IC** molecules in **Figure 3.4a**. This indicates that the TCF A-D-A molecules are less sterically hindered than their IC A-D-A counterparts when they are this close to the side chains on the donor core.

The presence of significant π - π * absorption peaks and relatively weak intramolecular D-A charge transfer absorption in these smaller BnDT A-D-A molecules led us to synthesize larger thiophene-bridged A-thiophene-D-thiophene-A derivatives **6-IC** and **6-TCF** that would spatially separate the donor and acceptor moieties and promote stronger intramolecular D-A charge transfer absorption. It also led us to synthesize IDT/IDTT core A-D-As (**ID-IC**, **ID-TCF**, **IT-IC**, **IT-TCF**) that do not exhibit this same steric hindrance problem. We believe is because the side chains on the IDT/IDTT donor cores are distributed asymmetrically across the donor, preserving

space on one side of the donor core where the acceptor moiety can stay in plane with the donor free of steric hindrance from the side chains.

3.3.2 Effect of Donor Core Identity on TCF and IC A-D-A Absorption

Comparing the absorption spectra of our A-D-A derivatives composed of different donor cores (**5a**, **6a**, and **ID/IT**) with the same IC or TCF acceptor units gives us a better understanding of how the various molecular aspects of the donor core (symmetric/asymmetric side chains, degree of rotational freedom across the backbone, distance between the donor and acceptor units, etc.) effect the planarity and subsequent optical properties of the A-D-A molecule. The absorption spectra of four different IC functionalized A-D-A derivatives are shown in **Figure 3.5** below.



Figure 3.5: UV/Vis. absorption spectra of IC functionalized BnDT, ID, and IT core A-D-A molecules, taken from very dilute CHCl₃ solutions.

Figure 3.5 clearly shows that lower energy intramolecular D-A charge transfer absorption is dominant for all of the IC A-D-A derivatives except **5a-IC**, where we believe significant twisting of the conjugated backbone is occurring. It appears that the addition of thiophene linkers to the A-D-A molecule **6a-IC** has largely resolved the significant steric hindrance present in **5a-IC**. By spatially separating the donor and acceptor moieties, it becomes easier for the A-D-A molecule to adopt a fully planar conformation, promoting D-A CT absorption. As a result, **6a-IC** has an absorption spectra shape that closely resembles **IT-IC**, albeit with significantly wider peaks and a somewhat higher π - π * transition absorption. This result supports the hypothesis that steric hindrance is responsible for the odd absorption spectra **5a-IC** has and is the reason it does not more closely match **ID-IC**, despite having an equivalent number of aromatic rings making up the conjugated A-D-A backbone.

The narrow peak distribution observed for IT-IC compared to 6a-IC is an interesting difference that can be explained using the Franck-Condon Principle, which states that electronic transitions (e.g., light absorption and emission) occur so much faster than vibrational or rotational transitions that effectively no change in nuclear configuration occurs during the electronic transition.⁸⁰ As a result, any rotational degrees of freedom present can alter the planarity and consequentially the extent of π -orbital interaction and exciton molecular orbital distribution across segments of the conjugated A-D-A backbone. Rotational changes between segments of the molecule will be essentially fixed in place for the lifetime of the electronic excitation and will lead to a distribution of molecular conformations absorbing at slightly different wavelengths, broadening and blue-shifting the molecule's absorption peaks. This should be true for any C-C single bonds linking conjugated sections of the A-D-A molecule, and will be present in our data for any rotations with an energetic barrier lower than kT. With this in mind, the absorption difference between IT-IC and 6a-IC begins to make sense. The low number of rotational degrees of freedom across the conjugated backbone of **IT-IC** (two rotating C-C single bonds along the backbone total) means there are few rotational transitions that can

impact electronic transitions. Almost all of the aromatic rings making up the conjugated backbone of **IT-IC** are fused together in a way that forces them to remain planar. This is why **IT-IC** has an absorption window that is so narrow. Meanwhile, **6a-IC** has a very broad absorption window as a result of the four rotating C-C single bonds along its backbone. One piece of evidence that supports this notion is the extremely similar absorption band-edge that **IT-IC** and **6a-IC** have. The lowest energy absorption band-edge is commonly used as the optical band-gap that represents the HOMO-LUMO energy difference. Any deviations away from a fully planar molecule will push this absorption energy higher, but the band edge is the energetic floor for the molecule. **IT-IC**'s peak absorption is close to its absorption edge, while **6a-IC**'s peak absorption is much farther away from that same absorption edge.

Figure 3.6 below shows the same donor cores used in **Figure 3.5**, but now with methyl functionalized TCF acceptors instead of IC.



Figure 3.6: UV/Vis. absorption spectra of TCF functionalized BnDT, ID, and IT core A-D-A molecules, taken from very dilute CHCl₃ solutions.

The same general trends present in **Figure 3.5** are also present for the TCF derivatives in **Figure 3.6**. Lower energy intramolecular D-A charge transfer absorption peaks are dominant for

all TCF A-D-A derivatives except **5a-TCF**, where we believe twisting of the conjugated backbone is occurring. The addition of thiophene linkers to the A-D-A molecule **6a-TCF** has largely resolved the significant steric hindrance present in **5a-TCF**, although the intensity of the intramolecular D-A charge transfer absorption relative to the π - π * transition is not as high for the TCF A-D-As, when compared with ICNC A-D-As (**Figure 3.5**). Nevertheless, **6a-TCF** has an absorption spectral shape that closely resembles that of **IT-TCF**, albeit with significantly wider peaks.



Figure 3.7: UV/Vis. absorption spectra of IC and TCF functionalized ID/IT core A-D-A molecules, taken from very dilute CHCl₃ solutions.

Figure 3.7 compares the ID/IT core A-D-A derivatives with both IC and TCF acceptor units. It is interesting to note that **ID-TCF** has a significantly different absorption shape compared to **IT-TCF**, which was not the case for **ID-IC** and **IT-IC**. This could indicate that there is steric hindrance occurring between the TCF acceptor units and the IDT/IDTT side chains that is not an issue for the more planar IC acceptor. Although additional experiments will need to be run in order to see if this is indeed the case.



Figure 3.8: HOMO and LUMO energy levels for each A-D-A derivative. HOMO energies determined by CV. LUMO energy was determined two different ways: **a**) LUMO calculated by adding the optical band gap to the CV measured HOMO. **b**) LUMO as measured by CV. Color correlates with the identity of the donor core.

Cyclic voltammetry measurements of the A-D-A derivatives were run in a 0.2 M solution of tetrabutylammonium hexafluorophosphate in anhydrous dichloromethane vs. (Fc/ Fc+) with a three electrode cell of a glassy carbon working electrode, Ag reference electrode, and Pt counter electrode. Using ferrocene as a reference material with a HOMO level of -4.8 eV, we can calculate the HOMO and LUMO energy levels of each of the derivatives. The LUMO energy level of these A-D-A molecules were measured electrochemically and also calculated by adding the optical band-gap to the measured HOMO energy level of the A-D-A derivatives.

The CV data shown in **Figure 3.8** indicates that the HOMO energies of all the A-D-A derivatives should be low enough to act as electron acceptors when blended with a high performance electron donor polymer like FTAZ. The LUMO energies measured by CV are quite clear, but do conflict with the LUMO values we would expect from the optical bandgap. It is interesting that adding thiophene linkers between the donor and acceptor units when moving

from **5a-IC** and **5a-TCF** to **6a-IC** and **6a-TCF** causes the HOMO and LUMO energies to drop, when the additional of more electron rich thiophenes usually raises the HOMO and LUMO energies of the molecule. This could be the result of increased A-D-A planarity allowing the acceptor units to have a greater impact on the HOMO and LUMO energies of the A-D-A molecule. This would fit well with the changes we observed in the UV/Vis absorption data and makes sense when considering the detrimental effect that twisting of the conjugated backbone has on the D-A character of the molecule.

3.4 Photovoltaic Properties

The photovoltaic properties of these A-D-A acceptors were investigated in bulk heterojunction (BHJ) solar cells with a standard device configuration: indium doped tin oxide (ITO)/ZnO/FTAZ:A-D-A blend/MoO₃/Al with a 1:1 weight ratio of FTAZ donor polymer vs. A-D-A acceptor molecule. Detailed results of the photovoltaic properties are summarized in **Figure 3.9** and **Figure 3.10** below.



Figure 3.9: Photovoltaic properties of BHJ solar cells made with BnDT donor core A-D-A molecules as electron acceptors.

Figure 3.9 clearly shows that none of the BnDT core A-D-A molecules we synthesized performed well when incorporated into a BHJ solar cell. None of the derivatives in **Figure 3.9** even broke 1% PCE. However, we believe that the poor performance of the IC and TCF

derivatives likely stem from different root causes. Derivatives **5a-IC** and **6a-IC** were primarily synthesized to serve as a reference material by which to judge the performance of the TCF A-D-A derivatives **5a-TCF** and **6a-TCF**. Even before **5a-IC** and **6a-IC** were used in a solar cell device, it was clear that they would perform poorly due to their low solubility and possible energetic mismatch with common donor polymers like F-TAZ. Their low solubility in common organic solvents made them difficult to purify, characterize, and would complicate efforts to incorporate them into a polymer solar cell blend. Their low solubility undoubtedly had a large effect on the micro-structure of BHJ blends made using these materials. Their low solubility meant they were likely not very miscible with the FTAZ donor polymer and would not form finely mixed BHJ domains that are required to facilitate efficient charge separation and obtain good OPV performance. The lack of a proper BHJ blend would lead to severely reduced current and poor fill factor as charge are either not able to reach the interface before recombining or are unable to find a charge transport pathway through the BHJ that would allow charges to reach the proper electrode and be collected. Both **5a-IC** and **6a-IC** display low current and poor fill factors. The BnDT donor core does not provide nearly enough solubility to make IC -based A-D-A acceptors work well, and that lack of solubility is believed to be the root cause of their poor performance.

While we knew their performance would be poor, it was interesting to see how compound **5a-IC**, which we suspected had significant twisting of its conjugated backbone, was the only derivative unable to produce any meaningful current. We suspected that strong steric hindrance in this compound would isolate the two acceptor units of the A-D-A molecule and prevent charges from easily moving across the conjugated backbone, rendering it a completely ineffective charge transport material. Additionally, the CV measurements of 5a-IC show

significantly different HOMO/LUMO energy levels compared to other A-D-A molecules, which would be expected if there was notable steric hindrance across the A-D-A molecule. However, it is also possible that the two IC end units are just too strong of electron acceptors for the BnDT donor core, which would result in less hybridization of their orbitals and favor higher energy π - π^* excitations over donor-acceptor interactions. If either of these situations are true, then 5a-IC would be expected to perform poorly in OPVs, which matches the results we obtained.

The TCF derivatives **5a-TCF** and **6a-TCF** exhibit much higher solubility than the IC functionalized A-D-A molecules, so we don't believe that poor miscibility with the donor is to blame for their low PCE results. It seems that the TCF derivatives may suffer from the opposite problem, where the TCF moieties are hindering intermolecular A-D-A interactions and disrupting crystallinity in the A-D-A films, without which there can be no charge transport pathways formed through the A-D-A material.^{81,82} Further reading into their past use in NLO systems indicates that TCF acceptors are actually prized for their highly anisotropic structure and variable R-groups that can prevent TCF D-A molecules from crystallizing even when just methyl substituents are used.^{83,84} In short, the properties of TCF that made it so useful in NLO research may preclude it from finding use in A-D-A acceptors for organic photovoltaics. While this discovery was troubling, we needed further. However, since all of the A-D-A derivatives performed so poorly, we wanted to make sure that it was not just the BnDT core that was dragging down their performance. In order to learn if TCF was truly the problem, we turned to the IDT/IDTT core A-D-A derivatives shown in **Figure 3.10** below.



Figure 3.10: Photovoltaic properties of BHJ solar cells made with IDT/IDTT core A-D-A electron acceptors.

The OPV results in **Figure 3.10** for ID/IT-TCF compared to ID/IT-IC helped confirm that it was indeed the TCF acceptor units that were to blame for the poor OPV performance of their A-D-A molecules. Despite all of the synthetic challenges addressed in this work and the promising optical and electrical properties exhibited by the TCF based A-D-A molecules, in the end they turned out to be very poor electron acceptors in a bulk heterojunction solar cell. The highest PCE obtained by a device utilizing TCF functionalized A-D-A electron acceptors was a dismal 0.68% for **ID-TCF**. Meanwhile, devices using IC functionalized A-D-A derivatives with the same donor core (**ID-IC**) obtained PCE values as high as 5.58%, over eight times higher than its TCF counterpart. This difference is too great to simply be an optimization problem and attempts to further optimize the devices have not improved the efficiencies. A difference in OPV performance this large in spite of the very similar properties displayed by IC and TCF functionalized A-D-A molecules is an indication that TCF is disrupting or hindering a crucial intermolecular interaction either between individual TCF A-D-A molecules or the donor polymer.

The most likely explanation appears to be that TCF is unable to interact with other molecules of itself strongly enough to form effective charge transport pathways that allow split exciton charges to make their way through the BHJ and be collected at the electrode. The anisotropic nature of TCF almost completely prevented these materials from crystallizing to any extent that could be seen macroscopically, and films cast of these materials were largely amorphous. This helped make the TCF A-D-A molecules very soluble, but likely created serious issues in the BHJ blends. This lack of crystallinity would make it extremely difficult to form charge transport pathways through the material and possibly led to a sub-optimal morphology. With a more phase-separated microstructure, it is possible we would have seen reduced charge recombination in the blend, and reasonable current from these devices.

Another detrimental factor that could have affected device performance was the overlapping absorption profile of our donor and acceptor compounds. Ideally we would want to have complimentary absorption between our donor and acceptor materials in order to cover more of the solar spectrum. In these devices, our TCF A-D-A molecules overlapped with our donor absorption for the most part; however, overlapping absorption windows would not produce the drastically different PCE results we observe here.

One recently published paper may help shed some light on why IC based A-D-As perform so well.⁸⁵ It appears that the large, flat IC acceptor units lead to pervasive intermolecular interactions between individual A-D-A molecules, where the IC moieties stack on top of one another making it easy for charges to hop from A-D-A molecule to A-D-A molecule. XRD results show that these IC acceptor ends are 3.8 Å apart, which is more than close enough

to facilitate intermolecular π -orbital interactions.⁸⁵ This appears to be one of the most crucial structural features needed to preserve good charge transport properties for an A-D-A molecule. If this is true, then the TCF functionalized A-D-A derivatives performed so poorly because the TCF acceptor moieties did not overlap strongly enough for efficient intermolecular charge hopping. It is also possible that the anisotropic nature of TCF prevented the A-D-A molecules from forming long-distance charge transport pathways. This would explain the large difference in current between the IC and TCF OPV devices, as charges would not be able to make their way out of the TCF BHJ blend before recombining.

While the voltage of the TCF A-D-A solar cells is a good 0.2 V lower than their IC functionalized counterparts, it is difficult to know if this is a result of a lower A-D-A acceptor LUMO for the TCF derivatives compared to the IC derivatives or if the voltage has been affected by the overall poor performance of the TCF devices.

3.5 Conclusion

In summary, we synthesized a range of A-D-A electron acceptor molecules from four donor units (**5**, **6**, **ID**, and **IT**) and two different acceptor units (**IC** and **TCF**). Both IC and TCF A-D-A derivatives showed significantly different optical properties when bound with different donor cores. This difference highlights the existence of commonly underestimated steric hindrance between solubilizing side chains and the conjugated backbone that is not accounted for in theoretical calculations.

This study showed that side chains are not just passive actors in A-D-A molecules; they can impact the planarity of the A-D-A backbone and the extent of intramolecular charge transfer transitions across the molecule, which directly alters the opto-electronic properties of the material. All of the A-D-A derivatives were found to be strong light absorbers and exhibited

appropriate HOMO/LUMO energies needed to act as electron acceptors when blended with a high performance FTAZ donor polymer.

Curiously, solar cells made with TCF functionalized A-D-A derivatives as the electron acceptor showed surprisingly poor performance, providing solar cells with PCE< 1%. Given the generally favorable optical and electrochemical properties displayed by the TCF derivatives, these poor solar cell results hint at a larger problem with intermolecular interactions between TCF capped A-D-A molecules.

This indicates that there are still aspects of A-D-A molecular design that have not been well explored. We hypothesize that the lack of aggregation in the TCF A-D-A molecules leads to low local charge mobility with a negative impact on charge generation and increases geminate recombination. Although further tests will be needed in order to confirm that this is truly the case.

Recently published XRD data of ITIC films hints at the importance of ensuring that acceptor moieties are fully planar in order to facilitate intermolecular charge transport between individual A-D-A molecules.^{81,86} This concept has not previously been outlined as a key design criterion for A-D-A electron acceptor compounds. This is because the field has largely advanced using 'guess and check' methods, where champion materials are found serendipitously and not through careful molecular design. To some extent this is understandable, given that A-D-A electron acceptor research has only recently seen a huge surge in interest and potential over the last three years, but it is not an efficient way for the field to advance.

Discovering what the crucial structural features of successful A-D-A molecules are and creating design rules that help guide future exploration and materials development will be critical to advancing the NFA field. Our TCF A-D-A OPV results affirm the crucial role that planar,

intermolecular interaction-promoting acceptor units play in forming charge transport pathways in the BHJ solar cell blend.

Overall, this project demonstrates that there are certain design rules in A-D-A design that need to be followed in order to harness their full potential as electron acceptors and to control intermolecular interactions. For an A-D-A NFA molecule to work, strong absorption and appropriate energy levels are not enough. Researchers must also consider how charges will move through these A-D-A molecules and what chemical functionalities with help or hinder that process. This work helps highlight just how strict those structural guidelines can be.

Further study of the morphology, charge recombination, and charge mobility of the bulk heterojunction blends of donor polymers with these TCF and IC acceptor A-D-A molecules can offer insights into how the molecular structure of A-D-A molecule affects the morphological features of the blends and the solar cell performance, which could potentially provide a guideline for A-D-A material design for OPVs.

3.6 Experimental Section

All chemicals were purchased from commercial source (Sigma-Aldrich, Fisher, Matrix, etc.) and were used as received except when specified. THF was distilled over sodium and benzophenone before use. Anhydrous toluene was purchased in a sealed bottle from Fisher. For reactions performed under an inert atmosphere, the reaction flask was flame dried under vacuum and cycled between vacuum and argon three times before any reagents were added.

¹H and ¹³C nuclear magnetic resonance (NMR) measurements were recorded with Bruker DRX spectrometers (400 MHz, 500 MHz or 600 MHz). Mass Spectrometery was run on a Q Exactive Orbitrap (ThermoFisher, Bremen, Germany) mass spectrometer and analyzed via Xcalibur (ThermoFisher, Breman, Germany). UV-visible absorption spectra were obtained with a

Shimadzu UV-2600 spectrophotometer. The film thicknesses were recorded by a profilometer (Alpha-Step 200, Tencor Instruments).

Cyclic Voltammetry (CV)

CV measurements were carried out on dichloromethane solutions of the compounds using a Bioanalytical Systems (BAS) Epsilon potentiostat with a standard three-electrode configuration. A three electrode cell of a glassy carbon working electrode, Ag reference electrode, and Pt counter electrode were used. A 0.2 M solution of tetrabutylammonium hexafluorophosphate in anhydrous dichloromethane was used as the supporting electrolyte. Scans were carried out under an argon atmosphere at a scan rate of 100 mV/s. The reference electrode was calibrated using a ferrocene/ferrocenium redox couple. The HOMO in electron volts was calculated from the onset of the oxidation potential (E_{ox}) using the following equation:

$$HOMO = -[4.8eV + e(E_{ox} - E_{Fc/Fc^+})]$$

4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (1a)

3.95 g (18.16 mmol, 4.0 eq) 2-(2-ethylhexyl)thiophene was added to a flame dried 100 mL RBF with a reflux condenser under inert atmosphere. The flask was purged with argon for 10 minutes, and then 50 mL of dry THF was added. The mixture was cooled to 0°C, stirred, and 8.17 mL (20.43 mmol, 4.5 eq) of 2.5 M n-BuLi in Hexanes was added to the RM dropwise. After stirring at 0°C for 45 minutes, the stirring reaction mixture was then heated to 50°C in an oil bath for 2 hours. After 2 hours had passed, 1.03 g (4.54 mmol, 1.0 eq) BnDT Quinone dissolved in 12 mL of dry THF solution was added to the still heated RM dropwise. After 1.5 hours at 50°C, the reaction mixture was cooled to room temperature over 35 minutes, at which point 9.4 g (41.5 mmol, 9.2 eq) SnCl₂ in 23 mL of 10% HCl was added to the reaction mixture in one portion. The reaction mixture was then left to stir overnight. The next morning, the THF was removed by

rotatory evaporation, providing a viscous yellow oil. The crude RM was taken up in DCM and washed with water three times. The organic solution was dried over magnesium sulfate, vacuum filtered, and concentrated via rota-vap. The product was purified with silica column chromatography in straight hexanes.

Yield: 2.1 g (77% yield)

¹H NMR (600 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 5.7 Hz, 2H), 7.46 (d, *J* = 5.7 Hz, 2H), 7.30 (d, *J* = 3.4 Hz, 2H), 6.89 (d, *J* = 3.4 Hz, 2H), 2.86 (d, *J* = 6.8 Hz, 4H), 1.71 – 1.65 (m, 2H), 1.49 – 1.41 (m, 4H), 1.42 – 1.35 (m, 4H), 1.37 – 1.29 (m, 8H), 0.95 (t, *J* = 7.4 Hz, 6H), 0.92 (t, *J* = 6.9 Hz, 6H).

4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-dicarbaldehyde (2a)

0.815 g (1.408 mmol, 1.0 eq) Compound 1a was added to a flame dried 250 mL RBF under inert atmosphere. The flask was purged with argon for 10 minutes, and then 150 mL of dry THF was added. The mixture was cooled to -78°C, then 1.46 mL (3.66 mmol, 2.6 eq) of 2.5 M n-BuLi in Hexanes was added to the RM dropwise. After stirring at -78°C for 25 minutes, the stirring reaction mixture was brought to RT for 30 minutes, then cooled back down to -78°C for 20 minutes. 1.25 mL (14.08 mmol, 10.0 eq) dimethylformamide dissolved in 1.8 mL of dry THF solution was added to the -78°C RM dropwise. The RM was left to stir and slowly warm back to RT overnight. The next morning, the THF was removed by rotatory evaporation. The crude RM was taken up in DCM and washed with water three times. The organic solution was dried over magnesium sulfate, vacuum filtered, and concentrated via rota-vap. The product was purified with silica column chromatography in 2:1 hexane:dichloromethane.

Yield: 0.70 g (78% yield)

¹H NMR (600 MHz, Chloroform-*d*) δ 10.10 (s, 2H), 8.36 (s, 2H), 7.35 (d, J = 3.5 Hz, 2H), 6.97 – 6.92 (m, 2H), 2.88 (d, J = 6.8 Hz, 4H), 1.73 – 1.66 (m, 2H), 1.48 – 1.41 (m, 4H), 1.41 – 1.37 (m, 4H), 1.37 – 1.30 (m, 8H), 0.96 (t, J = 7.4 Hz, 6H), 0.92 (t, J = 7.0 Hz, 6H). (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-

diyl)bis(trimethylstannane) (3a)

1.023 g (1.768 mmol, 1.0 eq) Compound 1a was added to a flame dried 250 mL RBF under inert atmosphere. The flask was purged with argon for 10 minutes, and then 176 mL of dry THF was added. The mixture was cooled to -78°C, then 2.62 mL (5.30 mmol, 3.7 eq) of 2.5 M n-BuLi in Hexanes was added to the RM dropwise. After stirring at -78°C for 25 minutes, the stirring reaction mixture was brought to RT for 60 minutes, then cooled back down to -78°C for 30 minutes. 12 mL (12 mmol, 6.8 eq) 1 M Me₃SnCl in Hexanes was added to the -78°C RM dropwise. The RM was left to stir and slowly warm back to RT overnight. The next morning, the THF was removed by rotatory evaporation. The concentrated RM was used in the next reaction within further purification. RM looks very clean by NMR.

Yield: 1.44 g (90% yield)

¹H NMR (600 MHz, Chloroform-*d*) δ 7.68 (s, 2H), 7.31 (d, *J* = 3.4 Hz, 2H), 6.91 – 6.89 (m, 2H), 2.87 (t, *J* = 6.3 Hz, 4H), 1.73 – 1.65 (m, 2H), 1.48 – 1.42 (m, 4H), 1.41 – 1.36 (m, 4H), 1.36 – 1.30 (m, 8H), 0.97 – 0.93 (m, 6H), 0.91 (t, *J* = 7.0 Hz, 6H), 0.67 (s, 18H).

5,5'-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-

diyl)bis(thiophene-2-carbaldehyde) (4a)

0.77 g (0.851 mmol, 1.0 eq) compound 3a, 0.568 g (2.13 mmol, 2.5 eq) 5bromothiophene-2-carbaldehyde, and 0.098 g (0.085 mmol, 0.1 eq) Pd(PPh₃)₄ were added to a flame dried 100 mL RBF with a reflux condenser under inert atmosphere. The flask was purged with argon for 10 minutes, and then 40 mL of dry toluene was added. The mixture was then stirred, heated to 104°C, and left to react overnight. The next morning the crude RM was cooled to RT, taken up in DCM, and washed with water three times. The organic solution was dried over magnesium sulfate, vacuum filtered, and concentrated via rota-vap. The product was purified with silica column chromatography in 2:1 dichloromethane:hexanes

Yield: 0.270 g (40% yield)

¹H NMR (600 MHz, Chloroform-*d*) δ 9.88 (s, 2H), 7.86 (s, 2H), 7.69 (d, *J* = 3.9 Hz, 2H), 7.36 (d, *J* = 3.9 Hz, 2H), 7.32 (d, *J* = 3.4 Hz, 2H), 6.95 (d, *J* = 3.5 Hz, 2H), 2.94 – 2.86 (m, 4H), 1.76 – 1.68 (m, 2H), 1.50 – 1.44 (m, 4H), 1.44 – 1.39 (m, 4H), 1.39 – 1.33 (m, 8H), 0.98 (t, *J* = 7.4 Hz, 6H), 0.94 (t, *J* = 7.0 Hz, 6H).

2,2'-((2Z,2'Z)-((4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6diyl)bis(methanylylidene))bis(3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile (5a-IC)

0.050 g (0.0787 mmol, 1.0 eq) compound 2a and 0.061 g (0.315 mmol, 4 eq) 2-(3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile were added to a flame dried 25 mL RBF with a reflux condenser under inert atmosphere. The flask was purged with argon for 10 minutes, and then 6 mL of dry chloroform and 0.2 mL Pyridine were added. The mixture was stirred, heated to 70°C, and left to react overnight. The crude RM was cooled to RT and run through a short silica gel plug with DCM. The eluted green product solid was then recrystallized twice from boiling ethanol to remove residual acceptor starting material.

Yield: 0.053g (68% yield)

¹H NMR (600 MHz, Chloroform-*d*) δ 8.84 (s, 2H), 8.72 – 8.68 (m, 2H), 8.42 (s, 2H), 8.01 – 7.96 (m, 2H), 7.82 – 7.77 (m, 4H), 7.44 (d, *J* = 3.4 Hz, 2H), 7.01 (d, *J* = 3.4 Hz, 2H), 2.93

(d, *J* = 6.9 Hz, 4H), 1.76 (p, *J* = 6.3 Hz, 2H), 1.53 – 1.47 (m, 4H), 1.47 – 1.43 (m, 4H), 1.42 – 1.35 (m, 8H), 1.00 (t, *J* = 7.4 Hz, 6H), 0.94 (t, *J* = 7.0 Hz, 6H).

2,2'-(((1E,1'E)-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6diyl)bis(ethene-2,1-diyl))bis(3-cyano-5,5-dimethylfuran-4(5H)-yl-2(5H)-

ylidene))dimalononitrile (5a-TCF)

0.202 g (0.317 mmol, 1.0 eq) compound 2a and 0.164 g (0.787 mmol, 2.5 eq) 2-(3-cyano-4,5,5-trimethylfuran-2(5H)-ylidene)malononitrile were added to a flame dried 50 mL RBF with a reflux condenser under inert atmosphere. The flask was purged with argon for 10 minutes, and then 24 mL of dry chloroform and 0.8 mL Pyridine were added. The mixture was stirred, heated to 75°C, and left to react for 26 hours. The crude RM was cooled to RT, then concentrated via rota-vap. The crude product was purified with silica column chromatography in 4:1 dichloromethane:hexanes, which was switched to straight DCM to elute the product once higher Rf impurities cleared the column. The product was then recrystallized from hot ethanol twice in order to remove excess TCF starting material.

Yield: 0.178 g (56% yield)

¹H NMR (600 MHz, Chloroform-*d*) δ 7.96 (s, 2H), 7.91 (d, *J* = 15.9 Hz, 2H), 7.32 (d, *J* = 3.5 Hz, 2H), 6.99 (d, *J* = 3.5 Hz, 2H), 6.73 (d, *J* = 15.9 Hz, 2H), 2.92 (d, *J* = 6.8 Hz, 4H), 1.77 (s, 12H), 1.74 – 1.69 (m, 2H), 1.49 – 1.43 (m, 4H), 1.42 – 1.38 (m, 4H), 1.38 – 1.31 (m, 8H), 0.97 (t, *J* = 7.4 Hz, 6H), 0.92 (t, *J* = 6.9 Hz, 6H).

2,2'-((2Z,2'Z)-(((4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6diyl)bis(thiophene-5,2-diyl))bis(methanylylidene))bis(3-oxo-2,3-dihydro-1H-indene-2,1diylidene))dimalononitrile (6a-IC) 0.093 g (0.116 mmol, 1.0 eq) compound 4a and 0.054 g (0.246 mmol, 3.0 eq) 2-(3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile were added to a flame dried 25 mL RBF with a reflux condenser under inert atmosphere. The flask was purged with argon for 10 minutes, and then 6 mL of dry chloroform and 0.3 mL Pyridine were added. The mixture was stirred, heated to 83°C, and left to react for 1 day. (A higher pyridine ratio would have sped up the reaction.) The crude RM was cooled to RT and the resulting crude solid was filtered into a Soxhlet thimble and extracted with ethyl acetate, hexanes, THF, and chloroform. None of these fractions contained significant amounts of product. The product remained in the sohxlet thimble as a gold solid. This solid was dissolved into hot chlorobenzene, and the product was precipitated out in methanol. The solid obtained was dried under vacuum. NMR shows the desired product, but has a very weak signal due to its low solubility.

Yield: 0.073g (54% yield)

¹H NMR (600 MHz, Chloroform-*d*) δ 8.88 (s, 2H), 8.72 (d, *J* = 7.6 Hz, 2H), 8.01 (s, 2H), 7.96 (d, *J* = 8.4 Hz, 2H), 7.82 (s, 2H), 7.81 – 7.74 (m, 4H), 7.49 (d, *J* = 4.0 Hz, 2H), 7.35 (d, *J* = 3.4 Hz, 2H), 7.00 (d, *J* = 3.4 Hz, 2H), 2.94 (t, *J* = 6.5 Hz, 4H), 1.80 – 1.71 (m, 2H), 1.50 (s, 4H), 1.47 – 1.43 (m, 4H), 1.42 – 1.35 (m, 8H), 1.01 (t, *J* = 7.5 Hz, 6H), 0.96 – 0.91 (m, 6H). 2,2'-(((1E,1'E)-((4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6diyl)bis(thiophene-5,2-diyl))bis(ethene-2,1-diyl))bis(3-cyano-5,5-dimethylfuran-4(5H)-yl-2(5H)-ylidene))dimalononitrile (6a-TCF)

0.095 g (0.116 mmol, 1.0 eq) compound 4a and 0.059 g (0.246 mmol, 3.0 eq) 2-(3-cyano-4,5,5-trimethylfuran-2(5H)-ylidene)malononitrile were added to a flame dried 25 mL RBF with a reflux condenser under inert atmosphere. The flask was purged with argon for 10 minutes, and then 6 mL of dry chloroform and 0.3 mL Pyridine were added. The mixture was stirred, heated to 83°C, and left to react for 3 days. (A higher pyridine ratio would have sped up the reaction.) The crude RM was cooled to RT, concentrated via rota-vap, then loaded directly onto a silica gel column. The crude product was purified with silica column chromatography in straight DCM, which was switched to 20:1 DCM/EtOAc to elute the product once higher Rf impurities cleared the column.

Yield: 0.086 g (64% yield)

¹H NMR (600 MHz, Chloroform-*d*) δ 7.84 (s, 2H), 7.77 (d, *J* = 15.8 Hz, 2H), 7.44 – 7.40 (m, 2H), 7.36 (d, *J* = 4.0 Hz, 2H), 7.33 (d, *J* = 3.4 Hz, 2H), 6.98 (d, *J* = 3.4 Hz, 2H), 6.66 (d, *J* = 15.9 Hz, 2H), 2.91 (dd, *J* = 6.7, 3.1 Hz, 4H), 1.76 (s, 12H), 1.75 – 1.70 (m, 2H), 1.50 – 1.45 (m, 4H), 1.44 – 1.40 (m, 4H), 1.39 – 1.34 (m, 8H), 0.98 (t, *J* = 7.4 Hz, 6H), 0.94 (t, *J* = 7.0 Hz, 6H). **4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene-2,7-**

dicarbaldehyde (ID-dialdehyde)

The ID dialdehyde molecule was synthesized using a procedure previously reported in the literature.⁸⁷

Yield: 0.212 g (63%)

¹H NMR (500 MHz, Chloroform-*d*) δ 9.83 (s, 2H), 7.66 (s, 2H), 7.59 (s, 2H), 7.13 (d, *J* = 8.3 Hz, 8H), 7.09 (d, *J* = 8.3 Hz, 8H), 2.61 – 2.47 (m, 8H), 1.62 – 1.56 (m, 8H), 1.40 – 1.23 (m, 24H), 0.90 – 0.83 (m, 12H).

2,2'-(((1E,1'E)-(4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-s-indaceno[1,2-b:5,6b']dithiophene-2,7-diyl)bis(ethene-2,1-diyl))bis(3-cyano-5,5-dimethylfuran-4(5H)-yl-2(5H)ylidene))dimalononitrile (ID-TCF)

0.055 g (0.057 mmol, 1.0 eq) ID-dialdehyde and 0.057 g (0.285 mmol, 5.0 eq) 2-(3cyano-4,5,5-trimethylfuran-2(5H)-ylidene)malononitrile were added to a flame dried 50 mL RBF with a reflux condenser under inert atmosphere. The flask was purged with argon for 10 minutes, and then 6 mL of pyridine was added. The mixture was stirred, heated to 70°C, and left to react overnight. The pyridine was removed via rota-vap, and the product was crystallized from hot ethanol.

Yield: 0.055 g (73%)

¹H NMR (600 MHz, Chloroform-*d*) δ 7.43 (s, 2H), 7.24 (d, *J* = 4.9 Hz, 2H), 7.16 (d, *J* = 8.3 Hz, 8H), 7.05 (d, *J* = 8.3 Hz, 8H), 7.00 (d, *J* = 4.9 Hz, 2H), 2.58 – 2.53 (m, 8H), 1.58 (p, *J* = 7.5 Hz, 8H), 1.38 – 1.24 (m, 24H), 0.88 (t, *J* = 6.9 Hz, 12H).

Chapter 4 CONCLUSION AND FUTURE DIRECTION

4.1 Conclusion

The design of malleable, tunable, and processable conjugated organic small molecules and polymers has been the driving force behind the improvements realized in the field of organic electronics that is moving us closer to wide-spread utilization with every passing year. The field of organic electronics has made regular progress towards these goals, and yet, many unanswered questions and unknown variables remain regarding the inherent structure-property relationships that define and control the electronic performance of these materials.

This dissertation has focused on the structural design, synthesis, and characterization of new conjugated organic small molecule derivatives that can hopefully give us some insight into what role chemical structure plays in device performance. We hope that the study of these new derivatives can be used to create even better next generation materials and elucidate important design rules or at the very least which structural features to avoid.

In Chapter 2, we detailed the synthesis of several new anthradithiophene (ADT) derivatives and evaluated the effect of heteroatom functional groups on the opto-electric properties, crystal packing, and OFET device performance they exhibit. One new ADT substituent (acetoxy-ADT) greatly increased the photo-oxidative stability of the ADT core compared to other known stabilizing groups, offering a new means of solubilizing and stabilizing larger acene compounds. Two previously unreported linear acene crystal packing motifs, believed to be driven by heteroatom interactions, were discovered for BT-ADT and HA-ADT/OA-ADT. Thin film formation of the ADT derivatives showed some interesting differences between functional groups, and at least one functional group (acetoxy-ADT) showed very promising initial blade-coated OFET results that were on par with other high performance linear acene OFETs (HA-ADT devices exhibited hole mobility as high as $0.69 \text{ cm}^2/\text{V} \cdot \text{s}$ and an on/off ratio of 10^4). Further optimization and study of acetoxy-ADT derivatives could produce better results.

Chapter 3 dealt with the synthesis, characterization, and OPV results of a series of new A-D-A molecules functionalized with TCF acceptor units. We compared these new A-D-A compounds with similar molecules functionalized by the current top acceptor unit IC.

Our TCF A-D-A OPV results affirmed the crucial role that planar, intermolecular interaction-promoting acceptor units play in forming charge transport pathways in the BHJ solar cell blend. Overall, this project demonstrated that there are certain design rules in A-D-A design that need to be followed in order to harness their full potential as electron acceptors and to control intermolecular interactions. For an A-D-A NFA molecule to work, strong absorption and appropriate energy levels are not enough. Researchers must also consider how charges will move through these A-D-A molecules and what chemical functionalities with help or hinder that process. This work helps highlight just how strict those structural guidelines can be, and clearly underscores the importance of preserving planarity on the ends of the A-D-A molecule in order to facilitate charge transport through these materials.

4.2 Future Work

4.2.1 ADT Project

While good progress has been made in this project, there are still a number of areas that would benefit from further research. While we have the crystal structures and are fairly confident in the forces driving structure formation, the extent of π -orbital overlap between

several of these ADT derivatives has not been quantified in any meaningful way. Running further calculations to determine the extent of ADT intermolecular interactions between ADT cores in the solid state based on crystal structure data we already have, would allow us to assess both the strength of their current intermolecular interactions and how best to further modify their structures in order to obtain even better results. For example, several of the crystal structures described in this work seemed to involve interaction, or at the very least close contact, between the terminal hydrogens on the thiophene end units of ADT and heteroatom functional groups on a neighboring molecule. By replacing those terminal hydrogens with other atoms like fluorine or chlorine, it may be possible to change the crystal structure entirely. The packing motif may be better or it may be worse, but it would almost certainly have an effect and fluorine functionalization at that position has already been found to greatly improve the packing, stability, and performance of ADT derivatives.⁴⁶ It would be a logical next step to try out a similar approach with these new substituents.

We were also unable to explore what role the odd-even effect might play in the crystal packing of these materials, as has been observed in other systems.^{52,13} This would be an interest concept to explore in these heteroatom acenes that clearly show strong differences in packing for different alkyl chain lengths.

4.2.2 Further Evaluation of the TCF A-D-A Solar Cell Blends

We plan to further explore the reason that the TCF A-D-A derivatives are providing such poor performance compared to their IC counterparts by studying charge separation and recombination dynamics in these solar cell blends. Running photoluminescence quenching (PLQ) studies on the blends will help us understand if the poor performance seen from the TCF

derivatives is due to unfavorable exciton splitting between the donor and the A-D-A acceptor, or if their performance is a result of poor charge transport pathways through the BHJ as we suspect.

Space-charge-limited current (SCLC) measurements of these blends would also help us determine the electron mobility of TCF A-D-As in the blend. If the TCF A-D-As have a suitably high electron mobility that would indicate that their poor performance in OPV devices may be attributed to something besides poor intermolecular interactions that limit charge transport.

4.2.3 Development of BP A-D-A Molecules

While we are still testing the TCF A-D-A molecules to determine exactly where they went wrong, we have been looking for ways to modify TCF in a way that will help promote better intermolecular interactions between A-D-A derivatives. The easiest way to do this would be to find a way to flatten TCF while preserving its strong electron withdrawing properties. Luckily, we believe we have found a way to do just that. The general idea is outlined below in **Figure 4.1**.



Figure 4.1: The envisioned modifications that could lead to a planar acceptor similar to TCF. By adding another carbon to the TCF ring, we should be able to insert an aromatic ring where the R groups would normally be, creating a new benzopyran type acceptor.

There was one example reaction in the literature of the same chemistry used to form the five-membered TCF ring also working on a six-membered ring derivative.⁷² While the authors described subsequent reactions that occur for the six membered ring version and only briefly explored it, we saw real potential as a way to flatten out TCF by replacing the two R groups on TCF with a flat phenyl ring and obtain an acceptor moiety as flat as IC, which should promote intermolecular interactions. This method has the added bonus of coming from a very cheap precursor, 2-hydroxyacetophenone, which can be readily functionalized to make derivatives with substituent groups on the phenyl ring.

While this is an ongoing project, we have made some very promising initial progress born from our work on TCF, shown below in **Figure 4.2**.



Figure 4.2: Initial synthesis work towards making the benzopyran-based FCNBP acceptor.

The initial easy synthesis scheme, where two equivalents of malononitrile are added directly, does not work for this derivative, as the six-membered ring will break open and tautomerize in a way that prevents the desired product from forming. However, if we replace the cyano group directly attached to the benzopyran ring with a fluorine substituent, we can eliminate the irreversible tautomerization and actually obtain the desired product FCNBP, which should be very close energetically to TCF which was already a strong acceptor molecule. This work is still in its infancy, and so we have not been able to make a finished A-D-A molecule with these new FCNBP acceptors attached. However, we have absolutely confirmed the identity of the FCNBP acceptor, so the only remaining step is to find the right conditions needed to bind it to a donor core. In this way, we are applying the A-D-A molecule design principles that came out of the TCF A-D-A project in order to develop a new generation of new acceptor moieties. We will continue developing this new line of acceptor molecules for use in A-D-A derivatives, and hopefully see the development of a new class of A-D-A acceptor moieties.

APPENDIX: CHEMICAL NMRs

Chemical NMRs for Chapter 2








128

5.0 f1 (ppm) 4.5

4.0

3.5

1.77

7.5

7.0

6.5

6.0

5.5

1.76

9.0

8.5

8.0

1.0 9.5

8.37 3.73 16.77-

1.5

4.00

3.0

2.5

2.0

6.46

0.5 0.

1.0













di(thiophene-2-carboxaldehyde)-bis(2-(2-ethylhexyl)thiophene)-BnDT (4a)

1H NMR (600 MHz, Chlorofond) 5 9.88 (s, 2H), 7.86 (s, 2H), 7.69 det 3.9 Hz, 2H), 7.36 (d,= 3.9 Hz, 2H), 7.32 (d,= 3.4 Hz, 2H), 6.95 (d,= 3.5 Hz, 2H), 2.94 - 2.86 (m, 4H), 1.76 - 1.68 (m, 2H), 1.50 - 1.44 (m, 4H), 1.44 - 1.39 (m, 4H), 1.39 - 1.33 (m, 8H), 0.98 (d,Hz, 6H), 0.94 (d,= 7.0 Hz, 6H).

















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