2015

Designing Anthradithiophene Derivatives Suitable For Applications in Organic Electronics and Optoelectronics

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Rawad Kamal Hallani, Student

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Dr. Dong-Chang Yang, Director of Graduate Studies
DESIGNING ANTHRADITHIOPHENE DERIVATIVES
SUITEABLE FOR APPLICATIONS IN ORGANIC
ELECTRONICS AND OPTOELECTRONICS

DISSERTATION

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

By
Rawad Hallani
Lexington, Kentucky

Director: Dr. John Anthony
Lexington, Kentucky
ABSTRACT OF DISSERTATION

DESIGNING ANTHRADITHIOPHENE DERIVATIVES SUITABLE FOR APPLICATIONS IN ORGANIC ELECTRONICS AND OPTOELECTRONICS

Anthradithiophene (ADT) derivatives have proven to be a front-runner in the world of small molecule semiconductors for organic electronics and optoelectronics. This is mainly due to the improved stability, easy tuning of chemical and physical properties, and impressive device performance that these molecules possess, especially in organic field effect transistors (OFET) and organic photovoltaics (OPV). The second chapter of this dissertation shows that reducing the amount of alkylsilyl ethynyl groups, used for functionalizing and solubilizing the ADT backbone, does alter the chemical, physical and crystallographic properties of ADTs. These changes offer the opportunity to study and observe different intermolecular interactions as well as monitoring their influence on sulfur scrambling in solid state. Additionally, from the early days ADTs and functionalized ADTs have been synthesized as isomeric mixtures. In chapter three, I demonstrate a new and simple method that can separate the syn and anti isomers of the F-TES-ADT and F-TEG-ADT chromatographically. The effects of isomeric purity on crystal packing and field effect transistor performance were studied extensively.

Chapter four of this dissertation reveals a new generation of acceptor (electron poor) ADT derivatives obtained by attaching cyanide as electron withdrawing group (EWG) to the ADT chromophore. An extensive study was conducted on CN-ADT (acceptor) molecules in small molecule (F-TES-ADT) donor/ small molecule (CN-ADT) acceptor binary BHJ blends as well as P3HT/CN-ADT/PCBM ternary BHJ blends. Photophysical studies of the Donor/ acceptor blends (interface, domains, and crystal orientation) were conducted to obtain a better understanding of the film morphology and its effect on solar cell performance.

Finally, the last part of the dissertation, Chapter five, focus on studying singlet fission in ADT derivatives, as well as the effect of varying the size of the alkylsilyl ethynyl functional group (used for solubilizing the ADT backbone) on altering the electronic couplings and how can that potentially affect the singlet fission rate in these molecules. We also tried to inspect the extent of the correlation between long-range order in crystal packing and singlet fission by monitoring singlet fission rate and efficiency for ADT derivatives with different thin film morphologies.
KEYWORDS: Organic Photovoltaics, isomers, field effect transistors, disorder, inversion center of symmetry, exciplex.
DESIGNING ANTHRADIOTHIOPHENE DERIVATIVES SUITABLE FOR
APPLICATIONS IN ORGANIC ELECTRONICS AND OPTOELECTRONICS

By Rawad Hallani

Dr. John E. Antony
Director of Dissertation

Dong-Sheng Yang
Director of Graduate Studies

November 19, 2015
ACKNOWLEDGMENTS

In college (Lebanese University) I decided I want to be a biochemist, not because I was interested in biochemistry or it piques my interest, but simply because I was good at it. I went through the motions and with a blink of an eye I was in my fourth year, two semesters away from graduating. This is when I had the opportunity to transfer to the University of Kentucky. I had to travel 6625 miles to get to Lexington, Kentucky. Leaving family and friends behind is tough, but what’s tougher is learning a new language. I started learning English nine months before I left my country. French was my school’s second language. Although they offered English classes, I didn’t have the luxury of time, so I had to get private lessons in the evening from a small nearby English learning centre until I was able to pass the TOEFL test and meet the UK requirements (special thanks to the American centre). In Lexington, I struggled with the language the first six months. Not being able to understand or decipher the majority of the conversations was very hard, but not as hard as being incapable of speaking properly (for a person that talks a lot it is a real struggle). This immediately got better thanks to my “American roommates” who instantly became my friends and helped me with almost everything, from taking me grocery shopping, since I didn’t have a car, to helping me opening a bank account, getting my driving licence, and most importantly learning the language. Thank you Nicholas Hantle, your help has been very important and a major reason to why and how I managed to make it seven years in the US.

At UK, I got to know the instructor of my advanced organic synthesis lab, Dr. Mark Watson, who introduced me to the field of organic electronic that I didn’t even know it exists. Through Dr. Watson I met Dr. John Anthony at a faculty poster session. I remember that I didn’t understand most of Dr. Anthony’s explanation about organic semiconductors and the focus of his research, yet I found myself very interested in the organic electronic field, and for the first time I felt like I found something I finally like. I joined the Anthony group couple weeks later and I have been working there ever since. Thus, I owe Dr. Watson a big thank you for helping me finding what I am interested in and introducing me to my future advisor. Lots of
graduate students and post docs have been part of my journey, from former group members: Balaji Purushothaman, Zhong Li, Ying Shu, Marsha Loth, and Emily Ripaud, to current group members: Jennifer Washbourne, Devin Granger, Marcia Payne, Anthony Petty, Karl Thorley, Sam Mazza, Thilanga Liyanage, and Paige Higdon. Thank you all, you made work more enjoyable and created a fun and friendly environment.

A special thank you to my biggest fan group, my family. My number one fan, my dad Kamal Hallani, who has dedicated his life to make sure I m getting a good education, while offering everything he can to get me to the place I am at today. Thank you dad! I also would like to thank my Mom, my sisters, and my brother: Hannaa, Tania, Nada, Sarah, Nadine, and Ibrahim Hallani. You guys rock!

Thank you for my committee members Dr. Mark Meier, Dr. Jason Derouchey, and Dr. Joseph Brill. Also a special thank you to the best and most helpful crystallographer I know, Dr. Sean Parkin, who was willing to answer my questions (even the not so sharp ones) on crystallography with lots of enthusiasm, and a little of British sarcasm, which I enjoyed. Thank you Dr. Parkin. Thanks for the graduate school, the chemistry department and the grants that supported my work the last five years. Also thank you to our collaborators, Prof. Lynn Loo, and Anna Hailey from Princeton University, Prof. Oana Jurchescu, Katelyn Goetz, and Yaochuan Mei from Wake Forest University, Dr. Chaw Keong from University of Cambridge, and Prof. Oksana Ostroverkhova from Oregon State University.
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<tr>
<td>TIPS:</td>
<td>Tri-iso-propylsilylacetylene</td>
</tr>
<tr>
<td>HOMO:</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>LUMO:</td>
<td>Lowest occupied molecular orbital</td>
</tr>
<tr>
<td>EWG:</td>
<td>Electron withdrawing group</td>
</tr>
<tr>
<td>EDG:</td>
<td>Electron donating group</td>
</tr>
<tr>
<td>P3HT:</td>
<td>Poly-3-hexylthiophene</td>
</tr>
<tr>
<td>OFET:</td>
<td>Organic field effect transistor</td>
</tr>
<tr>
<td>OSC:</td>
<td>Organic solar cell</td>
</tr>
<tr>
<td>OLED:</td>
<td>Organic light emitting diode</td>
</tr>
<tr>
<td>PDI:</td>
<td>Polydispersity index</td>
</tr>
<tr>
<td>M_w:</td>
<td>Weight average molecular weight</td>
</tr>
<tr>
<td>M_n:</td>
<td>Number average molecular weight</td>
</tr>
<tr>
<td>TFT:</td>
<td>Thin film transistor</td>
</tr>
<tr>
<td>C_60:</td>
<td>Fullerene</td>
</tr>
<tr>
<td>PCE:</td>
<td>Power conversion efficiency</td>
</tr>
<tr>
<td>ADT:</td>
<td>Anthradithiophene</td>
</tr>
<tr>
<td>TT:</td>
<td>Tetracenothiophene</td>
</tr>
<tr>
<td>BTBT:</td>
<td>Benzothienobenzothiophene</td>
</tr>
<tr>
<td>PMMA:</td>
<td>Polymethylmethacrylate</td>
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<tr>
<td>PVP:</td>
<td>Poly-4-vinylphenol</td>
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<tr>
<td>PEDOT:PSS:</td>
<td>Poly(3,4-ethylenedioxythiophene):</td>
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<tr>
<td>B polystyrene sulfonate</td>
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<td>BGBC:</td>
<td>Bottom gate/ bottom contact</td>
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<tr>
<td>BGTC:</td>
<td>Bottom gate/ top contact</td>
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<tr>
<td>TGBC:</td>
<td>Top gate/ bottom contact</td>
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<tr>
<td>TGTC:</td>
<td>Top gate/ Top contact</td>
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<td>Threshold voltage</td>
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<tr>
<td>V_GS:</td>
<td>Gate/source voltage</td>
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<td>Subthreshold slope</td>
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<tr>
<td>SAM:</td>
<td>Self assembled monolayer</td>
</tr>
<tr>
<td>AFM:</td>
<td>Atomic force microscopy</td>
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<tr>
<td>GIXD:</td>
<td>Grazing incident x-ray diffraction</td>
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<tr>
<td>OPV:</td>
<td>Organic photovoltaic</td>
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<tr>
<td>TES:</td>
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<td>BHJ:</td>
<td>Bulk heterjunction</td>
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<td>J_sc:</td>
<td>Short circuit current</td>
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<td>Phenyl-C_71-butyric acid methyl ester</td>
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<td>Threshold voltage</td>
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<td>Electron withdrawing group</td>
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<tr>
<td>EDG:</td>
<td>Electron donating group</td>
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<tr>
<td>P3HT:</td>
<td>Poly-3-hexylthiophene</td>
</tr>
<tr>
<td>OFET:</td>
<td>Organic field effect transistor</td>
</tr>
<tr>
<td>OSC:</td>
<td>Organic solar cell</td>
</tr>
<tr>
<td>OLED:</td>
<td>Organic light emitting diode</td>
</tr>
<tr>
<td>PDI:</td>
<td>Polydispersity index</td>
</tr>
<tr>
<td>M_w:</td>
<td>Weight average molecular weight</td>
</tr>
<tr>
<td>M_n:</td>
<td>Number average molecular weight</td>
</tr>
<tr>
<td>TFT:</td>
<td>Thin film transistor</td>
</tr>
<tr>
<td>C_60:</td>
<td>Fullerene</td>
</tr>
<tr>
<td>PCE:</td>
<td>Power conversion efficiency</td>
</tr>
<tr>
<td>ADT:</td>
<td>Anthradithiophene</td>
</tr>
<tr>
<td>TT:</td>
<td>Tetracenothiophene</td>
</tr>
<tr>
<td>BTBT:</td>
<td>Benzothienobenzothiophene</td>
</tr>
<tr>
<td>PMMA:</td>
<td>Polymethylmethacrylate</td>
</tr>
<tr>
<td>PVP:</td>
<td>Poly-4-vinylphenol</td>
</tr>
<tr>
<td>PEDOT:PSS:</td>
<td>Poly(3,4-ethylenedioxythiophene):</td>
</tr>
<tr>
<td>B polystyrene sulfonate</td>
<td></td>
</tr>
<tr>
<td>BGBC:</td>
<td>Bottom gate/ bottom contact</td>
</tr>
<tr>
<td>BGTC:</td>
<td>Bottom gate/ top contact</td>
</tr>
<tr>
<td>TGBC:</td>
<td>Top gate/ bottom contact</td>
</tr>
<tr>
<td>TGTC:</td>
<td>Top gate/ Top contact</td>
</tr>
<tr>
<td>I_DS:</td>
<td>Drain/source current</td>
</tr>
<tr>
<td>V_th:</td>
<td>Threshold voltage</td>
</tr>
<tr>
<td>V_GS:</td>
<td>Gate/source voltage</td>
</tr>
<tr>
<td>μLin:</td>
<td>Linear regime mobility</td>
</tr>
<tr>
<td>μ_sat:</td>
<td>Saturated regime mobility</td>
</tr>
<tr>
<td>STS:</td>
<td>Subthreshold slope</td>
</tr>
<tr>
<td>SAM:</td>
<td>Self assembled monolayer</td>
</tr>
<tr>
<td>AFM:</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>GIXD:</td>
<td>Grazing incident x-ray diffraction</td>
</tr>
<tr>
<td>OPV:</td>
<td>Organic photovoltaic</td>
</tr>
<tr>
<td>TES:</td>
<td>Triethylsilyl</td>
</tr>
<tr>
<td>BHJ:</td>
<td>Bulk heterjunction</td>
</tr>
<tr>
<td>J_sc:</td>
<td>Short circuit current</td>
</tr>
<tr>
<td>V_oc:</td>
<td>Open circuit voltage</td>
</tr>
<tr>
<td>FF:</td>
<td>Fill factor</td>
</tr>
<tr>
<td>EQE:</td>
<td>External quantum efficiency</td>
</tr>
<tr>
<td>IQE:</td>
<td>Internal quantum efficiency</td>
</tr>
<tr>
<td>R_s:</td>
<td>Series resistance</td>
</tr>
<tr>
<td>R_p:</td>
<td>Shunt resistance</td>
</tr>
<tr>
<td>PC61BM:</td>
<td>Phenyl-C_61-butyric acid methyl ester</td>
</tr>
<tr>
<td>PC71BM:</td>
<td>Phenyl-C_71-butyric acid methyl ester</td>
</tr>
</tbody>
</table>
HBL: Hole blocking layer
EBL: Electron blocking layer
BT: Benzothiazole
DCV: Dicyanovinyl
TPD: 5-alkylthieno[3,4-c]pyrrole-4,6-dione
SF: Singlet fission
S0: Ground state
S1: Singlet excited state
Kff: Singlet fission rate constant
IC: Internal conversion
ISC: Intersystem crossing
A: Absorbance
F: Fluorescence
P: Phosphorescence
1(TT): Triplet pair state
E0: Energy of the singlet state
E1: Energy of the triplet state
CT: Charge transfer
TSBS: Tri-sec-butylsilyl
DIBAL-H: Di-isobutylAluminum hydride
n-BuLi: n-Butyl lithium
MeOH: Methanol
THF: Tetrahydrofurane
NaBH4: Sodium borohydride
SnCl2: Tin(II) chloride
Fc: Ferrocene
Bu4NPF6: Tetra (n-butyl)ammonium hexafluorophosphate
DSC: Differential scanning calorimetry
HMDS: Hexamethyldisilazane
PFBT: Pentafluorobenzenthioi
TES: Triethylsilyl
RCh: Channel resistance
Rc: Contact resistance
L: Channel length
W: Channel width
AC: As casted
TA: Thermally annealed
DCM: Dichloromethane
TEG: Triethylgermyl
CDCl3: Deuterated Chloroform
√I1\text{D}: Square root of the drain current
LiHMDS: Lithium hexamethyldisilazide
CN: Cyano
DMF: Dimethylformamid
Zn(CN)2: Zinc cyanide
FRET: Förster resonance energy transfer
TA: Transient absorption
SC: Spin casted
ZC: Zone casted
F2-EHT-ADT: 2,8-difluoro-5,12-bis(2-ethylhexylthienyl)

anthra[2,3-b;6,7-b']dithiophene

Et₃N: Triethylamine
Chapter 1 Introduction

1.1 Semiconductors

A semiconductor is a substance with electrical conductive properties that lay between a conductor and an insulator (Figure 1.1). Theoretically, a semiconductor behaves as an insulator at absolute zero (0 K). In order for a semiconductor to conduct electricity, electrical, thermal, or photonic energy is required to overcome the band gap energy.

Inorganic semiconductors such as silicon and germanium are made of a covalently bonded network of atoms, with all the outer shell electrons of these atoms participating in bond formation (Figure 1.2). By providing enough energy, electrons can escape the valence band, generating charge carriers that are free to move across the lattice through a continuous conduction band, Figure 1.3.

Figure 1.1 Diagram of energy levels in semiconductors compared to conductors and insulators.

Figure 1.2 Diagram showing the energy levels in conductors, semiconductors, and insulators.

Figure 1.3 Diagram illustrating the movement of charge carriers in a conduction band.
Organic semiconductor films on the other hand, are made of molecular subunits. The covalent bonds that form the backbone of the molecule subunits are made of overlapped sp² hybridized atomic orbitals of carbon atoms. The remaining atomic orbitals of these carbons are made of \( P_z \) orbital that can also overlap to produce \( \pi \) bonding molecular orbital or the highest occupied molecular orbital (HOMO), and \( \pi^* \) antibonding molecular orbital or the lowest unoccupied molecular orbital (LUMO). HOMO’s and LUMO’s are also known as the frontier orbitals.

These molecular subunits are held together via weaker intermolecular van der Waals interactions that assist molecules self-assembly in an ordered fashion (Figure 1.2b). As a result, strings of HOMOs and LUMOs with correlative yet non-degenerate energy levels (pseudo-degenerate) are produced that can emulate the performance of a valence and a conduction band correspondingly (Figure 1.3).

Getting an electron in the LUMO can be achieved through the direct injection of an electron from an electrode at the molecule/electrode interface (Transistors), or by applying sufficient energy to promote an electron from the HOMO to the LUMO (organic solar cells). Once the electron is in the LUMO, the only way for it to navigate through the organic semiconductor network is by hopping from one molecule to another (Figure 1.3), causing a series of intermolecular and intramolecular relaxations in the lattice. This type of
movement, which is described by Marcus theory of electron-transfer reactions, is the major reason for the significant drop of conductivity in organic semiconductor materials.

1.2 P-type and n-type semiconductors

The addition of a small percentage of foreign atoms to a semiconductor lattice can cause dramatic changes in its electrical properties. For instance, adding phosphorus will provide surplus electrons to the silicon lattice, producing an n-type semiconductor. Adding boron on the other hand, will cause an electron shortage in the lattice, which increases hole carrier concentration, generating a p-type semiconductor. This technique is called doping and it is frequently used in the inorganic field to alter the semiconductor affinity toward electrons or holes.

Figure 1.3 Continuous conductive energy band for inorganic materials (left) vs. pseudo degenerate LUMO energy levels for organic materials (right).

Figure 1.4 (Left) n-doping: an electron is transferred from the dopant to the host. (Right) p-doping: an electron is extracted from the host by the p-doped materials generating a hole.

The doping process for organic semiconductors is similar to that of inorganic semiconductors, with electron donor or acceptor dopants being added to the organic
material, producing a surplus of charge carriers.\textsuperscript{1,2} To generate \textit{n}-type doping the dopant has to donate electrons to the LUMO of the organic material, while a \textit{p}-type dopant must extract electrons from the HOMO of the organic material to generate holes. More studies are still needed in order to improve and understand the microscopic origin of doping in organic semiconductors (Figure 1.4).\textsuperscript{3,4}

The more common approach, especially for organic small molecules, to prepare intrinsic organic semiconductors with \textit{n}-type and \textit{p}-type character is by directly tuning the HOMO and LUMO of the organic materials via introducing electron withdrawing groups (EWG) or electron donating groups (EDG) to the chromophore.\textsuperscript{5,7} Hence, the electrochemistry of these organic molecules can be easily tailored to suit the desired application, whether the required electrochemical character is \textit{n}-type or \textit{p}-type.

\textbf{1.3 Organic semiconductors}

Heterocyclic polymers and conjugated polycyclic compounds are the two major categories of organic semiconductors.

\textbf{1.3.1 Heterocyclic polymers}

Conjugate Polymers have demonstrated great potential as organic semiconductor materials especially in organic field effect transistors (OFETs),\textsuperscript{8,9} organic solar cells (OSCs),\textsuperscript{10} and organic light emitting diodes (OLEDs).\textsuperscript{11,12} A polymer’s ability to be solution deposited, and to produce uniform films because of their intrinsic viscosity, and their
charge transport characteristics make them good candidates for solution-processed/low cost applications. However, polymers in general suffer from poor control of regioregularity and polydispersity, a major drawback that affects charge transport behavior and creates variation in batch-to-batch performance. For instance, poly-3-hexylthiophene (P3HT), a very well studied polymer semiconductor, is a derivative of polythiophene that was alkylated to be solution processed (Figure 1.5). This alkylation helps control the polymerization and increases the structural ordering. However, P3HT still suffers from low regioregularity (81%)\textsuperscript{13} that affects its charge conductivity (Figure 1.6). McCulloch and co-workers were able to unravel this dilemma by using a Ni-based catalyst that improves P3HT regioregularity to >98.5%.\textsuperscript{14, 15} Consequently, the ordering in the P3HT spin-cast films increased and its performance improved dramatically (2 to 3 order of magnitudes).\textsuperscript{16}

Polymers also need to exhibit a low polydispersity index (PDI) to afford reproducible charge transport properties. PDI is calculated by dividing the weight average molecular weight by the number average molecular weight of the polymer \((PDI = \frac{M_w}{M_n})\). PDI measures the molecule weight distribution in a particular sample. A PDI close to 1 indicates a small variation in the polymer’s molecular weight, which reduces batch-to-batch performance variation. Thus, PDI close to 1 and high regioregularity are key requirements for better device performance.

Figure 1.6 P3HT: head-to-tail arrangement (H-T), head-to-head arrangement (H-H), tail-to-tail arrangement (T-T).

1.3.2 Conjugated polycyclics
Acenes are among the most studied small molecule organic semiconductors.\textsuperscript{17, 18} Linearly fused aromatic and heteroaromatic rings are the most common template for small molecule organic semiconductors.\textsuperscript{19} The number of fused rings, as well as the count of incorporated heteroatoms can lead to a drastic impact on the molecule’s physical and chemical properties. For instance, increasing the number of fused rings in the acene chromophore can result in a loss of solubility and stability.\textsuperscript{20}

Naphthalene and anthracene are respectively the smallest two members of the acene series (n=1, n=2) that display semiconducting behavior in thin film transistors (TFT).\textsuperscript{21, 22} However, naphthalene and anthracene’s high oxidation potentials, and their small $\pi$-surface area limit their usage in organic electronics. Functionalization of these molecules is one way to improve its performance. Although, dimerization of anthracene lowers the oxidation potential and improves charge injection\textsuperscript{23}, such molecules still suffer from poor solubility.\textsuperscript{24} The solubility setback was resolved by introducing different functionalities to the anthracene chromophore.\textsuperscript{23} These derivatives have exhibited high mobility (0.18 cm$^2$/Vs) when used in thin film transistor applications.\textsuperscript{23}

Like all unsubstituted acenes, tetracene (n=3) adopts a herringbone packing motif (figure 1.7) in the solid state.\textsuperscript{25} The $\pi$-surface area expansion in tetracene increases $\pi$ stacking between the molecules, and enhances orbital overlapping, which amplifies charge transport capabilities. Tetracene however, exhibits a significant drop in stability by virtue of a lower oxidation potential (compared to naphthalene and anthracene).
Pentacene (n=4) is the most studied acene derivative in the organic electronics field. Just like tetracene, pentacene crystallizes in a herringbone fashion (Figure 1.7). High performance FET devices made from thin film vapor deposited pentacene display mobilities as high as 1.5 cm²/Vs. Additionally, pentacene showed the potential to be a p-type material for organic solar cells, with C₆₀ (fullerene) as the n-type species displaying a PCE as high as 2.7%.

Despite the improvement in its charge transport performance, pentacene suffers from poor solubility as a consequence of the added number of fused rings in its chromophore that increases molecule rigidity. Additionally, pentacene also suffers from low stability, mainly due to Photo-dimerization and endoperoxide formation. For pentacene to be a truly useful molecule the solubility needs to improve, and the decomposition pathways must be suppressed through intelligent substitution (Figure 1.8).
1.3.2.1 Bis(trialkylsilylethynyl)pentacene

The benefit of using soluble acenes in device fabrication is the ability of exploiting them in low cost, large surface area, solution processed electronic applications. However, all the examples mentioned previously suffer from low solubility. Anthony and co-workers were able to solve this problem by introducing trialkylsilylethynyl substituents as solubilizing groups at the 6 and 13 position of the pentacene chromophore (Figure 1.9).\(^{31, 32}\) In addition to the improved solubility, trialkylsilylethynyl groups provides a level of control over the π-stacking order of acenes in the solid state. Hence, by changing the size of the alkyl groups, the crystal packing of the substituted pentacene can be tuned.\(^{32}\)

Assuming the shape of the alkylsilylethynyl group is roughly spherical, the Anthony group hypothesized that when the diameter of that sphere is less than half the size of the acene chromophore, the molecules tend to pack in a 1-D slipped-stack fashion.
Additionally, when the diameter is close to half the length of the acene chromophore, the molecules tend to stack in a 2-D arrangement. However, if the diameter of the alkylsilylethynyl sphere increases to more than half the length of the acene chromophore the packing reverts back to the 1-D slipped stack, and stays this way until the diameter of the alkylsilylethynyl sphere becomes as big or exceeds the acene chromophore. Then, the molecule starts to pack in a herringbone fashion because the strongest interaction available now is the one between the alkylsilylethynyl substituent and the acene chromophore (Table 1.1).

Table 1.1 Influence of the alkyl silylethynyl size on crystal packing.  

<table>
<thead>
<tr>
<th>Pentacene substitution</th>
<th>No substitution</th>
<th>Triethylsilyl-ethynyl</th>
<th>Tri-iso-propylsilylethynyl</th>
<th>T-butyl dimethyl silyl ethynyl</th>
<th>Tri-n-propylsilyl ethynyl</th>
<th>(SiMe)_3 silyl ethynyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal structure</td>
<td>Herringbone</td>
<td>1-D slipped stacks</td>
<td>2-D stacks</td>
<td>1-D columnar stacks</td>
<td>1-D slipped stacks</td>
<td>Herringbone</td>
</tr>
</tbody>
</table>

Functionalized pentacene displays major improvements in its stability as well as its solubility. Due to the presence of the alkylsilylethynyl groups, photo dimerization is reduced and in some cases eliminated when the silyl group is large enough.

### 1.3.2.2 Heteroacenes

Isostructural and isoelectronic analogs for pentacene such as anthradithiophene (ADT), thiotetracene (TT) (Figure 1.10), and benzothienobenzothiophene (BTBT) (Figure 1.11) were introduced as potential alternatives due to their improved stability (Figure 1.10) attributable to a higher energy barrier to oxidation. Moreover, the bigger size of the atomic radius of sulfur improves the orbital overlapping in heteroacene derivatives as a result of a d-π wave function overlap between sulfur and carbon. As the strength of orbital overlap is the predominant factor governing charge transport in organic semiconductors, heteroacenes are predicted to outperform pentacene derivatives.
Figure 1.10 Examples of some commonly used heteroacene molecules (on the left) and comparing their energy levels to that of TIPS pentacene (table on the right).

Figure 1.11 The sulfur atom can be added synthetically in a myriad of positions in the chromophore. By changing the sulfur position the chemical, physical and electrical properties of the acene can be altered.36

1.3.2.2.1 Functionalized Anthradithiophene (ADT)

ADTs are typically prepared as a mixture of isomers due to a non-regioselective aldol condensation that forms the ADT quinone.34
The same functionalization approach described previously with pentacene can be used with ADTs. Different size alkylsilylethynyl groups were added at the 5 and 11 positions (Figure 1.12) of the ADT to alter its crystal packing and improve the solubility. Additionally, the high acidity of the protons at the 2 and 8 positions allows for additional and accessible synthetic functionalization to be exploited (Figure 1.13).

**1.4 Organic field effect transistors**

Organic field effect transistor (OFET) is one of the hottest applications in the world of organic electronics. Transistors are building blocks that exist in every modern electronic device, from an electronic switch in a logic circuit to a signal amplifier converting a weak input signal to a stronger output one. A field effect transistor (FET) is made of three major components: dielectric, electrodes (gate, source, and drain), and the semiconductor thin
film layer (active layer). The most commonly used inorganic dielectrics are silicon dioxide, and aluminum oxide, while the most common organic dielectrics are polymer dielectrics such as PMMA, PVP, and Cytop, to name a few.

There are three electrodes in a FET. The source and drain electrodes are usually made of Au, Ag, Al, or an organic conducting polymer such as PEDOT: PSS. The gate electrode is usually made of doped silicon. The active layer is made of small molecule organic polycyclic, or semiconducting polymer compounds.

![Figure 1.14 OFET building design: a) BGBC; b) TGBC; c) BGTC; d) TGTC](image)

**1.4.1 Transistor design**

Based on the design of the device, OFETs can be classified into four types: bottom gate/ top contact (BGTC), bottom gate/ bottom contact (BGCBC), top gate/ top contact (TGTC), and top gate/ bottom contact (TGBC) (Figure 1.14). The most common OFET design is the BGBC (Figure 1.14, (a)) where the active layer is least affected by the different treatments necessary during the fabrication of the device since it is deposited last. However, TGBC (Figure 1.12, (b)) devices should, theoretically, offer the best design and greater performance for OFET, as a result of a lower contact resistance achieved with an increased surface area between the electrodes and the active materials.
1.4.2 Operating process

Thin film transistors are straightforward devices for measuring many electronic properties of organic semiconductors. Operation of a transistor is transparent - when there is no voltage, a very small current is measured between the source and drain (\(I_{DS} \sim 0\, \text{V}\)) and the device is considered in an off state. However, when a voltage is applied at the gate, charge injection from the source electrode to the semiconductor active layer becomes more possible. Once the gate voltage exceeds the threshold voltage (\(V_{TH}\)), drain current flowing from the source to the drain, \(I_{DS}\), can be measured and the device is now switched to an on state. When \(V_{GS} > 0\, \text{V}\) positive charge accumulates at the gate dielectric interface polarizing the dielectric layer leading to negative charge accumulating at the semiconductor-dielectric interface, hence the first layer of semiconductor in contact with the dielectric is responsible for conducting negative charges in the channel between the source and drain electrodes (\(n\)-channel). When \(V_{GS} < 0\, \text{V}\) positive charges will accumulate at the semiconductor-dielectric interface creating a \(p\)-channel device. In certain cases the device operates for both \(V_{GS}\) polarities and the device is considered ambipolar.

OFET drain current can be described using this equation:\(^{43}\)

\[
(I_{SD})_{lin} = \frac{W}{L} C_i \mu_{lin} (V_G - V_{TH})V_D
\]

\(W\) is the channel width, and \(L\) is the channel length. \(C_i\) is the capacitance of the dielectric. The mobility of the charge carrier in the linear current regime (Figure 1.16, (a)) is denoted \(\mu_{lin}\), and describes the ability of charge carriers to move throughout the material.
when the transistor is on. \( V_G \) and \( V_D \) describing the gate and the drain voltage respectively, and \( V_{TH} \) defining the threshold voltage.

When the drain voltage exceeds the gate voltage the device enters the “saturated regime” (Figure 1.16, (a)), thus a new equation is necessary to describe the drain current.\(^{43}\)

\[
(I_{SD})_{sat} = \frac{W}{2L} \cdot C_i \cdot \mu_{sat} \cdot (V_G - V_{TH})^2
\]

In the saturated regime, the device no longer follows Ohm’s law and the current reaches a constant value.

Figure 1.16 (a) The output characteristics of TIPS-pentacene OFET recorded at \( V_G = -10 \) V (black), \(-20\) V (green), \(-30\) V (purple), and \(-40\) V (blue) on the left. (b) The transfer characteristics recorded at \( VSD = -40\) V.

Multiple figures of merit can be extracted from the output plots elucidated in Figure 1.15. These figures of merit are:

**The threshold voltage** (\( V_{TH} \)) is extrapolated from the \( x \)-intercept of the linear region of the blue curve (Figure 1.16, b) (\( \sqrt{I_D} \) vs. \( V_G \)). The \( V_{TH} \) describes the voltage needed to fill all the traps in the transistor before it is considered in an on state.

**The mobility** (\( \mu \)) is calculated from the slope of the blue curve in Figure 1.16b

\[
\mu = \frac{2L}{WC_i} \left( \frac{\delta \sqrt{I_D}}{\delta V_{GS}} \right)^2
\]
The on/off current ratio is extracted from the $I_D$ vs. $V_G$ transfer curve (red curve, Figure 1.16, b). The on/off current ratio is the maximum current between the source and drain when the device is in its on state divided by the leakage current when the device is in its off state. An on/off ratio $>10^5$ is required for a device to be considered functional.

The subthreshold slope (STS) is also obtained from the $I_D$ vs. $V_G$ transfer curve (red curve, Figure 1.16, b) using the equation below.

$$STS = \frac{\delta V_G}{\delta \log I_D}$$

The STS yields information about the speed the device can be switched from on to off. A STS $<1$ is needed for a device to be useful in typical high-speed applications.

1.4.3 Crystal engineering for OFET application

Low cost, large surface deposition can be accomplished via solution processing methods such as drop casting, inkjet printing, spray coating, spin casting, dip coating, blade coating, and solution shearing.44

Tailoring the HOMO/LUMO energy levels of the molecule plays a crucial role in the ease of the charge carrier injection and whether it’s an electron injection ($n$-type), hole injection ($p$-type), or both (ambipolar). Therefore the HOMO/LUMO orbitals must possess an energy that is close to that of the work function of the electrodes (source and drain). Consequently, the energy required for the charge carrier injection can be achieved at an accessible applied electric field.45

The device’s design dictates the type of crystal packing an organic semiconductor molecule must possess in order to ensure optimal performance. For OFET applications, the charge carrier path is set horizontally between the source and drain electrodes. The most efficient charge transport pathway in organic semiconductors happens along the intermolecular $\pi-\pi$ stacking of the molecules. Therefore, it is preferable that molecules pack with their $\pi$ orbitals parallel to the substrate (Figure 1.15, b and c).
Forcing the molecules to follow a specific orientation during the solution deposition can be challenging. Domain size, orientation, and morphology of the thin film layer particularly at the interfaces (active layer/dielectric, and active layer/electrodes) are some of the variables that have to be taken in consideration. For instance, silicon dioxide (SiO$_2$) is the most commonly used dielectric in OFET research. The presence of the hydroxyl groups at the surface of the SiO$_2$ increases its surface energy (hydrophilic surface). Organic semiconductors are hydrophobic by nature. Therefore, in order to create uniform films via solution deposition, the dielectric surface energy needs to be reduced. Surface treatment using self-assembled monolayers (SAMs) is one way to overcome such problems.\textsuperscript{46} SAMs are used to reduce surface roughness,\textsuperscript{47} and surface free energy,\textsuperscript{48} which increase grain sizes in the thin film. Increased grain size means formation of larger domains with the appropriate dimension to cover the transistor channel length (Figure 1.17, b and c), leading to easier and improved charge transport characteristics.

![Diagram of pentacene orientation](Image)

**Figure 1.17** a) Representation of pentacene laying flat on the surface (no charge transport), b) Pentacene orientation on an SiO$_2$ substrate,\textsuperscript{49} c) TIPS pentacene orientation on an SiO$_2$ substrate,\textsuperscript{50} d) TIPS pentacene with a non uniform film (more than one domain) reduces charge transport.

Inorganic/organic interface compatibility problems can also manifest between the electrodes and the semiconductor layer. It has been demonstrated via atomic force microscopy (AFM), grazing incident x-ray diffraction (GIXD) and many other surface analysis methods that the organic semiconductor layer orientation at the electrodes is
dramatically different. This reduces the uniformity of the thin film layer and eventually increases the contact resistance of the device due to a high charge trap density. Treatment of the gold source and drain electrodes with phenyl thiols reduces its surface energy, and leads to uniform morphology (Figure 1.18).

![Figure 1.18 Schematic of the molecular orientation on the Au surface for (111) (a), and (011) (b) orientations.](image)

Using organic dielectrics and organic electrodes can also improve the compatibility at between interfaces in OFETs. Organic dielectrics are especially used in TGBC OFET devices where the polymer dielectric and the gate electrode can also act as encapsulating agents that protect the active layer from oxygen and water which improves the lifetime of the device.

Increasing the π-π orbital overlap between the molecules creates more charge pathways and eventually improves the device’s function. Molecules that pack in 2-D stacks tend to demonstrate a superior performance in OFETs compared to other packing models (Figure 1.19). Therefore, we always try to tune the crystal packing, of our materials, to give us the highest charge transport capabilities.
Figure 1.19 Charge transport in a 2-D crystal packing (a) TIPS pentacene top view, (b) TIPS pentacene side view along the short axis. Charge transport in a 1-D crystal packing: (c) TES pentacene top view, (d) TES pentacene side view along the short axis.

1.5 Organic photovoltaics (OPV)

Solar cell (SC) devices were invented in 1954, when the first modern Si (p-n) junction was produced at Bell Laboratories. By mimicking the process of photosynthesis that plants use to convert solar energy into chemical energy, they created a system that absorbs photon energy from sunlight and converts it into electrical energy.

The simple design of an organic solar cell consists of two organic light absorbing layers (active layers) sandwiched between two electrodes (anode and cathode). One layer contains an organic semiconductor molecule with electron donor character that is capable of capturing photonic energy (excited). The second layer can also be excited by the same photonic energy, but also displays an electron accepting character, making it suitable for receiving the excited electrons from the donor molecules. Having a donor and an acceptor in the active layer facilitates charge separation, thus reduces recombination and improves device performance (Figure 1.21, c).

When light strikes the active layer of a solar cell, it excites the molecule with the high ionization potential (high HOMO). Unlike inorganic species, the electron/hole pair (exciton) of organic molecules doesn’t easily dissociate into free charges. The weak van der Waals intermolecular forces, that hold organic molecules together, make the charges less delocalized, which increase the exciton binding energy. Once excitons are formed, there are two phenomenons that can take effect: excitons diffusion and excitons...
recombination. Organic semiconductors with high conductivity facilitate excitons diffusion to the donor/acceptor interface (Figure 1.20). At the interface, the difference between the LUMO of the donor and the LUMO of the acceptor provides the necessary energy ($\Delta E$) (Figure 1.22) to overcome the exciton binding energy and help the exciton dissociate into separate charges.\textsuperscript{55} Once electrons and holes are separated the difference in the work function between the electrodes creates an electric field inside the cell that helps the charges to separate and accumulate at the their respective electrode, holes at the anode and electrons at the cathode, which leads to an electric current in the external circuit of the cell.

![Figure 1.20 Operation sequence of an organic photovoltaic cell.](image)

Low conductivity, impurities, and short exciton diffusion length are the main cause for charge recombination (non geminate, geminate, and trap assisted recombination). In organic materials, excitons acquire a short lifetime and consequently a short diffusion length, typically on the length of 10 to 20 nm.\textsuperscript{56} As such, the thickness of the semiconductor layer plays a major role in assuring that the maximum amount of excitons would reach the donor/acceptor interface. Although, organic molecules have a high extinction coefficient, the active layer cannot be very thin or the cell would suffer from low sunlight absorption, which reduces the generated current.

The first generation of organic photovoltaic (OPV) was engineered as a bilayered heterojunction solar cell (Figure 1.21, a). The deposition of the donor and the acceptor thin
layers consecutively between electrodes, yielded a 1% power conversion efficiency (PCE) in 1986 by Tang et al.\textsuperscript{57} The average active layer thickness of the donor and acceptor materials in a bilayered OSC is around 100 nm each. Hence, the majority of the excitons that form farther than 20 nm from the interface will not reach the donor acceptor Heterojunction. The excitons recombine instead, leading to a drop in the current, and ultimately the performance of the cell. Bulk heterojunction (BHJ) solar cells were introduced as the next generation of OPV (Figure 1.21, b). BHJ is obtained by blending the donor (D) and the acceptor (A) in solution and casting them onto the anode, followed by the deposition of a low-work-function cathode. The BHJ architecture increases the interface surface area between the donor and the acceptor, which leads to a larger number of excitons dissociating into free charges at the donor/acceptor heterojunction. As a result, molecules that form small crystalline domains are ideal for such application.

Ideally the D/A blend should be aligned vertically to allow a direct charge pathway to the electrodes. Controlling this type of separation (vertical separation) can be achieved thru spontaneous phase separation.\textsuperscript{58, 59} Literature reports have established that spontaneous phase separation can be managed by using high boiling point solvents,\textsuperscript{60} or by patterning the surface on which the blend is deposited using self-assembled monolayer.\textsuperscript{61} This will construct a substrate with two different surface energies, at which point a specific surface energy will favor the growth of one of the D/A materials over the other, leading to vertical phase separation. This induces the expansions of the D/A interface while controlling the size of the phases to insure the right exciton diffusion length.\textsuperscript{61}

![Figure 1.21 Donor/acceptor bilayer heterojunction (a), donor/acceptor bulk heterojunction (b), simple design of a photovoltaic cell (c).](image-url)
A wide range of parameters is used to inspect the device performance. The power conversion efficiency (PCE) depends linearly on three factors: open circuit voltage ($V_{oc}$), short circuit current ($J_{sc}$), and the fill factor (FF). $P_{in}$ is the incident solar power (1000 W/m$^2$).

\[
PCE = \frac{J_{sc}V_{oc}FF}{P_{in}}
\]

![Figure 1.22 Basic energy level diagram of a heterojunction solar cell.]

### 1.5.1 Open circuit voltage ($V_{oc}$)

The open circuit voltage is the maximum voltage a solar cell can generate when disconnected from the circuit. It is roughly dependent on the difference between the HOMO of the donor and the LUMO of the acceptor (Figure 1.22). Thus, tuning the HOMO-LUMO levels of the donor and acceptor allows us to optimize the open circuit voltage and eventually the power conversion efficiency (PCE).$^{62}$

\[
V_{oc} = \frac{1}{e} \left(|E_{donor HOMO}| - |E_{acceptor LUMO}| \right) - 0.3V
\]

$e$ represents the elementary charge, and the 0.3 V is an empirically derived constant.$^{62}$
1.5.2 Short circuit current ($J_{sc}$)

$$J_{sc} = \int_{AM\ 1.5} e\eta_{EQE}(\lambda)N_{Ph}(\lambda)d\lambda$$

The short circuit current is the maximum current a cell can provide when the circuit is shorted. Improving the short circuit current can be complicated since there is more than one variable to study and control. The absorption intensity in the visible range is critical, it has to be high for the device to harvest the maximum amount of photons. Materials with a narrow band gap and high molar extinction coefficient are necessary. $\eta_{EQE}$ is the external quantum efficiency of the cell which is defined as the ratio of number of photons impinged on the cell to the number of charges generated. $\eta_{EQE}$ is related to the entire charge generating process (absorption, exciton diffusion, exciton separation, and charge collection).

Controlling the morphology of the organic active layer is essential. As mentioned previously, once an exciton is photogenerated it must reach the donor/acceptor interface, thus materials need to have a high charge transport characteristics, long exciton diffusion length, and small domains. Additionally, even though there is still no clear understanding of the exciton dissociation process, charge dissociation at the interface also needs to be taken in consideration.

1.5.3 Fill Factor (FF)

Fill factor is the percentage of the maximum power that can be obtained by the photovoltaic cell divided by the theoretical maximum power that a cell should theoretically produce (Figure 1.23, a).

$$FF = \frac{P_{max}}{P_{theoretical}} = \frac{V_{Max}\times J_{max}}{V_{OC}\times J_{SC}}$$
The fill factor is represented by the largest rectangle that you can draw inside the I-V curve at the maximum voltage and maximum current. The squarness of the fill factor is related to the series resistance ($R_s$) and the shunt resistance ($R_p$) of the photovoltaic cell. $R_s$ is associated with the internal current of the cell. Therefore, it should be as low as possible since it describes the resistance at the interfaces (Figure 1.23, b). $R_p$ is related to the lost current of the cell. Hence, it should be as high as possible since it is inversely proportional to the current loss via recombination or any destructive process (Figure 1.23, b).

P3HT (Donor)/PC$_{61}$BM (Acceptor) is the most studied system in BHJ organic photovoltaics (Figure 1.24). PC$_{61}$BM (phenyl-C$_{61}$-butyric acid methyl ester) is one of the best-studied acceptor materials. Its spherical shape allows it to transport charges in all three dimensions and the butyric methyl ester substitution allows for solution processability. Power conversion efficiency of this system varies depending on the processing techniques: Thermal annealing, deposition techniques, addition of additives, active layer thickness, and the weight percent variation of PCBM and P3HT in the BHJ active layer blend. Despite the thorough studies in the last 10 years on the P3HT/PC$_{61}$BM system, the average PCE has been between 3 and 4 %. This has led researchers to investigate new polymers and small molecules as potential replacements for P3HT and PC$_{61}$BM.
Figure 1.24 General representation of PCBM (A)/P3HT (D) BHJ solar cell. EBL (electron blocking layer), HBL (Hole blocking layer).

Figure 1.25 Examples of small molecule acceptors

Designing molecules with large transition dipole, narrow optical gap, and the right HOMO/LUMO energy levels are necessary to ensure efficient photon absorption, charge transfer and charge separation. Havinga and coworkers demonstrated the combination of an electron deficient building block (A) (Figure 1.29) such as benzothiazole (BT), dicyanovinyl (DCV), rhodanine, indanedione, or 5-alkylthieno[3,4-c]pyrrole-4,6-dione (TPD), with an electron rich building block (D) (Figure 1.29) such as benzodithiophene,
fluorene, thiophene oligomers, or pentacene, the hybridized molecular orbital generated from the interaction between these building blocks creates Donor and acceptor molecules with a smaller optical gap (high photon absorption), and high transition dipoles, which leads to a strong oscillator strength that results in increasing photons absorptivity, charge separation, and migration. Additionally the alkyl side chains that can be attached to these units (either on the donor building block (D) or the acceptor building block (A) of the molecule) improves solubility, and film morphology.

Figure 1.26 Examples of small molecule donors

Figure 1.27 Examples of polymer acceptors
Figure 1.28 Examples of some polymer donors

Figure 1.29 Examples of donor building block units (left), and acceptor building block units (right)

Table 1.2 Summary of BHJ solar cell parameters of donors blended with PCBM. *small molecules
PCE is linearly related to $V_{OC}$, $J_{SC}$, and FF. However, it was demonstrated that $V_{OC}$ shows lower correlation with PCE, compared to $J_{SC}$ and FF. Probing donor materials in blends, with the same acceptor compound (i.e. PCBM), results in a somewhat constant $V_{OC}$ ($V_{OC}$ doesn’t vary that much in Table 1.2). This makes it feasible to examine PCE as a function of $J_{SC}$ and FF. Similarly, probing blends of different acceptors while using the same donor material (i.e P3HT) gives similar $J_{SC}$ (Table 1.3), making PCE a function of $V_{OC}$ and FF.

Although, increasing $J_{SC}$ and $V_{OC}$ almost always lead to enhanced PCE as expected (Table 1.2, and 1.3), $J_{SC}$ does however display superior impact on the cell efficiency than $V_{OC}$, as revealed with PBTff4t in Table 1.2 ($J_{SC}$ of 17.7 mA/cm² have lead to a 9.6% PCE), and PF12TBT in Table 1.3 ($V_{OC}$ of 1.26 V generated a 2.7% PCE). This expresses the importance of controlling active layer film morphology, charge transfer, and photon absorption on solar cell performance.

Table 1.3 Summary of BHJ solar cell parameters of acceptors blended with P3HT unless stated otherwise. * Small molecules

<table>
<thead>
<tr>
<th>Donors</th>
<th>$J_{SC}$ (mA/cm²)</th>
<th>$V_{OC}$ (V)</th>
<th>% η</th>
</tr>
</thead>
<tbody>
<tr>
<td>FBR75*</td>
<td>7.95</td>
<td>0.62</td>
<td>0.73</td>
</tr>
<tr>
<td>PIBT76*</td>
<td>4.7</td>
<td>0.9</td>
<td>2.5</td>
</tr>
<tr>
<td>DERH77*</td>
<td>12.6</td>
<td>0.96</td>
<td>6.1</td>
</tr>
<tr>
<td>DCV58*</td>
<td>11.1</td>
<td>0.97</td>
<td>5.2</td>
</tr>
<tr>
<td>P379</td>
<td>11.5</td>
<td>0.85</td>
<td>6.6</td>
</tr>
<tr>
<td>PTB480</td>
<td>14.8</td>
<td>0.7</td>
<td>6.1</td>
</tr>
<tr>
<td>PF12TBT83</td>
<td>17.7</td>
<td>0.76</td>
<td>10.4</td>
</tr>
<tr>
<td>PBTff4T81</td>
<td>18.6</td>
<td>0.76</td>
<td>9.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Acceptors</th>
<th>Blended with</th>
<th>$J_{SC}$ (mA/cm²)</th>
<th>$V_{OC}$ (V)</th>
<th>% η</th>
</tr>
</thead>
<tbody>
<tr>
<td>K1284*</td>
<td>P3HT</td>
<td>3</td>
<td>0.62</td>
<td>0.73</td>
</tr>
<tr>
<td>CNTCPSPn7*</td>
<td>P3HT</td>
<td>3.72</td>
<td>0.84</td>
<td>1.3</td>
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<tr>
<td>FEHIDT83*</td>
<td>P3HT</td>
<td>3.82</td>
<td>0.95</td>
<td>2.43</td>
</tr>
<tr>
<td>PF12TBT83</td>
<td>P3HT</td>
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<td>1.26</td>
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<td>PC-NDI86</td>
<td>TTV7</td>
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<td>0.88</td>
<td>3.68</td>
</tr>
<tr>
<td>P(NDI2OD-T2)87</td>
<td>PTQ1</td>
<td>8.85</td>
<td>0.84</td>
<td>4.1</td>
</tr>
</tbody>
</table>
1.6 Singlet fission (SF)

Singlet fission was first detected in tetracene single crystals in the 1960s.\textsuperscript{88} Since then, SF has been observed and studied in a very limited amount of materials most notably acenes,\textsuperscript{89} isobenzofuran,\textsuperscript{90} and oligophenyls.\textsuperscript{91} The obscurity of the SF mechanism has played a major role in restraining the development of molecules that can demonstrate such capabilities.

Figure 1.30 A simplified Jablonski energy level diagram that elucidates the different steps in a singlet fission process: Molecule 1 gets excited then shares the excitation with a neighboring molecule creating a triplet pair, which then dissociates into two triplets. Orbital mixing represents the electronic coupling between molecule 1 and molecule 2. Electronic coupling is obtained through a mixing between the frontier orbitals of two separate molecules that produces an in phase/stabilized bonding orbital (lower in energy), and an out of phase/destabilized antibonding orbital (higher in energy). The energy difference between the coupled molecular orbitals and the stabilized bonding orbital represents the electronic couplings between the two molecules.

Singlet exciton fission is a spin allowed photophysical process that can split a singlet exciton into two triplet excitons. A simplified explanation of this phenomenon involves the consideration of a pair of identical molecules in their ground (non-excited) state, referred to as a dimer ($S_0S_0$). It starts with an optically induced photo excitation ($h\nu$) of an electron from the ground state to a singlet-excited state ($S_1$). The excitation can be shared between two electronically coupled molecules, or dimer, with the overall equation of ($S_0S_0$) $\leftrightarrow (S_1S_0$). An internal spin-allowed conversion converts the singlet-excited state dimer
(S\textsubscript{1}S\textsubscript{0}) into a coupled pair of triplets \(^1TT\) via \((S\textsubscript{1}S\textsubscript{0}) \xleftrightarrow{k_{fis}} ^1TT\). This conversion is related to the electronic coupling between the singlet-excited state and the coupled pair triplet state of the dimer, however the requirements on this electronic coupling are not well understood. It is simpler to think of singlet fission as a process that involves the electronic state of two electronically coupled molecules instead of the electronic state of a single molecule. Upon formation of \(^1TT\), it can dissociate into two separate triplets \(^1TT\) \xleftrightarrow{} ^1T + ^1T, or it can recombine losing its double excitation.

\[
(S\textsubscript{0}S\textsubscript{0}) \xrightarrow{hv} (S\textsubscript{1}S\textsubscript{0}) \xleftrightarrow{k_{fis}} ^1TT \rightarrow ^1T + ^1T
\]

The rate constant of SF, \(k_{fis}\), must be exceptionally large in order to compete with other fast photophysical processes such as internal conversion and fluorescence (Figure 1.31).

![Jablonski diagram](image)

Figure 1.31 Jablonski diagram exposing the different competing photophysical processes that needs to be taken in consideration when studying singlet fission. F (fluorescence), P (Phosphorescence), IC (internal conversion), ISC (intersystem crossing).

To maximize \(k_{fis}\), three parameters need to be taken in consideration: electronic coupling, Gibbs free energy (\(\Delta G\)), and the energy of the triplet state relative to the singlet state.
It has been demonstrated that the coupling between the monomers needs to be strong enough for a high $k_{fis}$, yet weak enough to favor triplet pair dissociation over triplet pair recombination.$^{92}$ Thus, the intermolecular forces that impact the self-assembly process of the molecules in the solid state are critical for producing the desired electronic coupling.$^{93}$

![Figure 1.32 Representation of endergonic vs. exergonic molecule](image)

The energy difference between $S_0S_1$ and $^1(TT)$ has a critical affect on $k_{fis}$ and is represented by $\Delta G$ (Figure 1.32). An endergonic molecule ($\Delta G > 0$) such as tetracene exhibits a ten times slower fission rate despite having a coupling that is 20 times larger than pentacene, an exergonic molecule ($\Delta G < 0$).$^{93}$ However, if the SF process is too exergonic, as is the case in derivatives of hexacene, an activation energy barrier can be formed that can slow down the charge transfer process (Figure 1.33). This is known as the Marcus inverted regime and is believed to decrease $k_{fis}$ despite having a high degree of electronic coupling between the molecules.$^{91}$ Therefore the process needs to be slightly exergonic to undergo efficient and fast singlet fission.$^{93}$

![Figure 1.33 Charge transfer in Marcus Theory](image)
between the two electronic states (ΔG^0 is positive, normal regime). (b) No activation energy required (ΔG^0 is negative, exergonic, normal regime) and the charge transfer is favorable. (c) In this case ΔG^0 is more negative creating an activation energy barrier that slows down the charge transfer process (ΔG^0 is more negative leading to an inverted Marcus regime).

Finally, molecules with triplet energy approximately half the energy of the singlet state (E_T ≥ 2E_s) have demonstrated a higher singlet fission rate, which makes designing molecules with such features a requirement to ensure high k_fis.93

### 1.6.1 Singlet fission in organic photovoltaics

Because singlet fission converts a high-energy singlet into two lower energy triplets, exploiting this phenomenon could theoretically double the photocurrent generated from high-energy photons in photovoltaics.94 Thus, a solar cell with singlet fission capability could potentially offer external quantum efficiency (EQE) as high as 200% at certain wavelengths (Figure 1.34).

BHJ solar cells generate one electron from each absorbed photon. According to the Shockley-Queisser principle, the maximum efficiency of a single junction solar cell is limited to 33% due to inevitable energy losses such as recombination and thermal energy.95 Singlet fission can increase the single junction cell efficiency by theoretically doubling the photocurrent generated in the solar cell via dissociating the photogenerated exciton into two lower energy excitons.

Figure 1.34 Energy transfer process at the heterojunction. Blue arrow represents the absorbance of the donor molecule. CT1: Direct charge transfer of singlet exciton generated from the
photoexcitation. CT2: charge transfer of the two excitons generated from the singlet exciton fission process.

On the other side, the newly generated two triplet excitons (T\textsubscript{1}+T\textsubscript{1}) have now half the energy of the singlet state (\textit{1}(TT) or S\textsubscript{1}), which negatively affect the voltage of the cell and reduces its open circuit voltage, despite doubling its generated photocurrent. As a result, the maximum cell efficiency of a single junction solar cell that exhibits singlet fission abilities can theoretically be improved to no more than 42\%.\textsuperscript{96}
Chapter 2 The effect of desymmetrization on anthradithiophene derivatives

2.1 Mjölnir TSBS-ADT

Common silylethynyl functionalization strategy have revealed that trialkysilyl groups direct the crystallization of the aromatic core. The bigger the alkylsilyl group the more space it occupies, leading to a shift in the long and short axis of the molecule in the crystal stack (Figure 2.1). As a result, different styles of crystal packing can be achieved (i.e. 1-D slip stacks, 1-D columnar stacks, and 2-D stacks). However, the presence of alkylsilylethynyl groups can also inhibit charge injection between donor and acceptor molecules in OPV applications, as well as reducing orbital overlapping between molecules of the same stack. Thus, in this work I demonstrate a new category of desymmetrized anthradithiophene derivatives obtained by the attachment of one alkylsilylethynyl group to the ADT chromophore. The single alkylsilylethynyl group will allow for some steric control of the packing in the solid state, much like that observed in the bis(alkylsilylethynyl) ADTs, as well as providing solubility and stability. Additionally, the presence of only one sterically demanding group should result in an alternating columnar $\pi$-stacking (Figure 2.1) opening up one edge of the ADT chromophore to interact with an adjacent $\pi$ cloud through edge-to-face interactions, similar to that observed in the unfuctionalized (bare) acenes. All in all, we expect a hybrid molecule, which combines the edge to face interactions of an unfunctionalized ADT, with the solubility and stability of bis(silylethynyl) ADT. Due to the resemblance to the hammer of Thor, I refer to this class of molecules in this chapter as the Mjölnir compounds (Figure 2.1).

![Figure 2.1](image.png)

Figure 2.1 Effect of the solubilizing groups on the crystal packing of anthradithiophene. The absence of one solubilizing group should drive the molecule to pack in an alternating fashion,
which creates less steric hindrance. As a result, we should observe a shift in the molecule packing along the long axis that leads to columnar packing.

2.1.1 Synthesis

The desymmetrized ADT (mjölnir) derivatives (Scheme 2.1) were prepared from the isomeric mixture of ADT quinones 2-1. Addition of one equivalent of tri-sec-butyldil acetylene (TSBSA) gave an isomeric mixture of intermediate 2-2. The reduction of 2-2 was completed using DIBAL-H, and the resulting diol was treated with stannous chloride to yield the mjölnir ADT. The Mjölnir ADT isomers were separated by chromatography on silica gel using hexanes as the eluent to yield 40% of isomers 2-3a (Rf = 0.3), 2-3b (Rf = 0.26), and 2-3c (Rf = 0.23). All three isomers were recrystallized from hexanes.

Scheme 2.1 Synthetic scheme of mjölnir TSBS-ADT, and mjölnir TIPS-ADT. S-butyl = sec-butyl, ipr=iso-propyl.
Figure 2.2 Recrystallization of 2-3a, 2-3b, and 2-3c by slow evaporation from hexanes gave pink/red needles (2-3a and 2-3b), and sheet-like crystals for 2-3c.

Single crystal X-ray diffraction analysis revealed that the three desymmetrized isomers (Figure 2.8) show improved aromatic overlap (compared to bis(silylethynyl) ADTs) along the long axis, as expected. Molecules of 2-3a and 2-3b pack as isolated π-stacked pairs, with the paired molecules overlapping the solubilizing groups of adjacent pairs in the stack (Figure 2.4, 2.5). In contrast, 2-3c packs with both pairwise face-to-face and edge-to-face interactions, leading to contiguous aromatic overlap in one dimension (Figure 2.6, and 2.7).

2.1.2 X-Ray crystallography

Figure 2.3 Ellipsoid plots of isomer 2-3a, 2-3b, 2-3c and its isomeric mixture.
Figure 2.4 Side view along the chromophore’s long axis showing isolated $\pi$-stacked pairs of isomers 2-3a, and 2-3b (packs in a very similar fashion). TSBS groups were omitted for more clarity.

Figure 2.5 Top view showing the crystal packing between the isolated pairs of isomer 2-3a and (2-3b packs in a very similar fashion). TSBS groups were omitted for more clarity.
Figure 2.6 Side view along the long axis of isomer 2-3c showing pseudo-1D crystal packing. TSBS groups were omitted for more clarity.

Figure 2.7 Top view of isomer 2-3c. TSBS groups were omitted for more clarity.
As shown in Figure 2.8, similar pairwise interactions in 2-3c are also present. However, unlike in 2-3a and 2-3b, the pairs in 2-3c adopt an edge-to-face orientation with respect to adjacent molecule pairs (Figure 2.6), rather than overlapping the solubilizing hydrocarbons of the adjacent stacks (Figure 2.4). We rationalize that this difference in solid-state arrangement arises from the unhindered expanse of aromatic edge in 2-3c allowing strong C-H-π interactions to direct crystal packing; in the other two isomers, the presence of the electronegative sulfur atom yields less stabilizing S-π interactions\textsuperscript{102} causing the observed isolation of the pairwise-stacked chromophores in 2-3a and 2-3b.

Isomer 2-3c is predicted to exhibit the highest charge transport in the series due to the strong orbital overlapping to multiple surrounding molecules, leading to a 1-D charge transport pathway in crystals and crystalline films.

Figure 2.8 Representation of the packing patterns observed in isomers 2-3a, 2-3b and 2-3c. TSBS groups were omitted for more clarity
2.1.3 Photophysical studies

Figure 2.9 Normalized absorption spectra of mjölnir isomers (2-3a,3b,3c) in dichloromethane (solid lines), and emission in dichloromethane (dashed line).

In solution, all three isomers show nearly identical absorption spectra with each $\lambda_{\text{max}}$ at 517 nm, and mirror fluorescence patterns with a Stokes shift of 18 nm (Figure 2.9). Thin-film UV-Vis absorption maxima of the three isomers drop-cast from dichloromethane show a 293 cm$^{-1}$ red shift compared to the solution absorption spectrum (Figure 2.10). All isomers express the same optical properties in absorption (solution, thin film) and fluorescence (solution).

Figure 2.10 Normalized thin film absorption spectra of isomers 2-3a, 3b, and 3c.
The photostability of compound 2-3 was studied and the molecule displayed a half-life of 30 minutes. Bis(tri-sec-butylsilylthynyl) ADT (TSBS-ADT) exhibits a half-life of 52 minutes. Hence, it is likely that the absence of one solubilizing group increases the decomposition rate of molecule 2-3 via [4+4] photo-induced dimerization (Figure 2.11).

![TSBS ADT](image1)

Figure 2.11 Photostability measurements in dichloromethane for TSBS-ADT (left) \( t_{1/2} = 52 \) minutes, and the isomeric mixture of 3a, 3b, and 3c (right) \( t_{1/2} = 30 \) minutes.

### 2.1.4 Electrochemistry and physical properties

Table 2.1 Measured and calculated HOMO and LUMO levels

<table>
<thead>
<tr>
<th>Isomer</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>Gap (eV)</th>
<th>Calc. HOMO (eV)</th>
<th>Calc. LUMO (eV)</th>
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</thead>
<tbody>
<tr>
<td>2-3a</td>
<td>-5.27</td>
<td>-2.92</td>
<td>2.35</td>
<td>-4.96</td>
<td>-2.43</td>
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<tr>
<td>2-3b</td>
<td>-5.21</td>
<td>-2.89</td>
<td>2.32</td>
<td>-4.97</td>
<td>-2.43</td>
</tr>
<tr>
<td>2-3c</td>
<td>-5.22</td>
<td>-2.89</td>
<td>2.33</td>
<td>-4.96</td>
<td>-2.39</td>
</tr>
</tbody>
</table>

The three isomers also show the same electrochemical properties with a chemically reversible oxidation and reduction being observed (Figure 2.12). Assuming a HOMO level of -4.8 eV for ferrocene, the HOMO and LUMO of the mjölnir compounds was estimated at -5.2 and -2.9 eV respectively, with a band gap of 2.3 eV. Using B3LYP/6-31G(d) optimized structures, theoretical HOMO and LUMO energies were calculated by Dr. Karl J. Thorley and show very little change between isomers (Table 2.1).
Figure 2.12 Cyclic voltammetry measurements for isomers (2-3a, 3b, and 3c) in 0.2 M solution of Bu₄ NPF₆ in dichloromethane at room temperature vs. (Fc/ Fc+) with Ag/AgCl as the reference electrode.

The thermal characteristics of the mjölnir isomers were examined using differential scanning calorimetry (DSC) Figure 2.13. Since 2-3a, and 2-3b exhibit very similar crystal packing one would expect the same melting point for both isomers. Interestingly, that was not the case. Isomer 2-3b displays a melting point of 138°C, 35°C lower than isomer 2-3a. Isomer 2-3c on the other hand, melts at 151°C which is 23°C lower than isomer 2-3a. This observation can be explained by the position of the sulfur atom in the ADT chromophore. When the sulphur atom exists on the same side of the trialkylsilyl ethynyl group, the melting point of the molecule is reduced (2-3b, 2-3c), as a result of weaker intermolecular interaction.
Using the crystal structures obtained for each of the isomers, Dr. Thorley calculated the electronic coupling between pairs of molecules representing each different type of contact (UHF/6-31G(d)) using the NWChem electron-transfer module (Table 2.2). Contact A1 and B1 in Figure 2.8 for molecule 2-3a and 2-3b show the highest overall electronic coupling (Table 2.2). However, the lack of long-range A1 and B1 couplings in isomer 2-3a and 2-3b makes the overall electronic coupling, in the solid state, of these isomers very limited.

**Table 2.2 Hole electronic coupling (eV)**

<table>
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<tr>
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<th>A1/B1/C1</th>
<th>C2</th>
<th>C3</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-3a</td>
<td>0.071</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2-3b</td>
<td>0.057</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2-3c</td>
<td>0.067</td>
<td>0.018</td>
<td>0.011</td>
</tr>
</tbody>
</table>
2.1.5 Thin-film characterization

Our collaborators, Prof. Lynn Loo’s group at Princeton University, measured the grazing-incidence x-ray diffraction (GIXD) patterns for thin films of the three isomers both as cast and after thermal annealing. The GIXD shows a very intense reflection pattern for isomer 2-3c indicating a high degree of crystallinity. The GIXD for isomer 2-3a and 2-3b however, show little to no reflexion pattern indicating a low degree of crystallinity (Figure 2.14). Although, full pole figure analysis would be required to quantify the extent of crystallinity.\textsuperscript{104}

![GIXD patterns](image)

Figure 2.14 GIXD patterns of thin films of isomers 2-3a, 2-3b, and 2-3c (left to right, 2wt% solution in toluene was spin coated at 1000 RPM for 60 seconds). Top row – as-cast; bottom row - thermally annealed (90°C for 7 minutes). Measured by Anna K. Hailey (Princeton University).

Plotting intensity vs. scattering vector, q, shows that despite the low crystallinity of isomer 2-3a and 2-3b, both isomers still adopt a structure that is very close to the bulk structure judging by the peak intensity at q= 0.55Å\(^{-1}\) in both the experimental diffraction traces extracted from the grazing-incidence X-ray diffraction patterns and the powder diffraction traces derived from the single-crystal data. Figure 2.15 also shows that the as-cast film of 2-3a and 2-3b also contain another, unknown structure, indicated by the
presence of a peak at $q = 0.4 \text{ Å}^{-1}$, that disappear upon annealing. It is not unusual to observe thin-film polymorphs in organic semiconductor thin films due to competing molecule-molecule, molecule-substrate, and molecule-solvent interactions during film processing.\textsuperscript{105, 106}

Upon thermal annealing the as-cast films of 2-3\textsuperscript{a} and 2-3\textsuperscript{b} are completely converted to the known structure as the X-ray diffraction traces of the thermally annealed films showed no sign of the $q = 0.4 \text{ Å}^{-1}$ peak. Films of isomer 2-3\textsuperscript{c} are very crystalline, and under all processing conditions adopt the known crystal structure indicated by the coincidence of the primary peak, corresponding to the (100) reflection, at $q = 0.35 \text{ Å}^{-1}$ in both the X-ray diffraction trace extracted from the grazing-incidence diffraction pattern and the powder diffraction trace obtained from single-crystal data. The as-cast film of 2-3\textsuperscript{c} has an amorphous halo around 1.5 Å; the intensity associated with this halo is reduced upon thermal annealing, suggesting that these post-deposition treatments further crystallize films of 2-3\textsuperscript{c}. The effect of solvent vapor annealing was also considered, although did not offer any additional information concerning film morphology of any of the three isomers.
2.1.6 Device characterization

The hole-transport properties of the three isomers as well as the mixture of isomers were studied in bottom-gate, bottom-contact organic thin-film transistors, fabricated on 300 nm thick SiO₂ substrate treated with hexamethyldisilazane (HMDS), and gold electrodes that were treated with pentafluorobenzenthiol (PFBT). Semiconductor solution was prepared by dissolving the isomers each in toluene at a concentration of 2 wt%. Thin
films were formed on these patterned substrates by spin-coating the solution at 1000 RPM for 60 seconds. The films were then thermally annealed at 90 °C for 7 minutes. The conditions used are similar to those applied to make triethylysilethynyl (TES) ADT transistors, and were also used to form thin films for GIXD experiments. As shown in Table 2.3 there is a four order-of-magnitude difference in mobility between devices utilizing isomers 2-3a and 2-3b, with a maximum mobility of 2.10^{-6} \text{cm}^2\text{V}^{-1}\text{s}^{-1}, and devices made from isomer 2-3c, with maximum mobility of 5 \times 10^{-2} \text{cm}^2\text{V}^{-1}\text{s}^{-1}.

![Channel resistance and contact resistance in thin film transistors.](image)

The extracted (measured) mobility for all isomers is inversely proportional to the channel length of the thin film transistor (Table 2.3). The total resistance in a transistor is constituted of the channel resistance ($R_{ch}$) and the contact resistance ($R_c$) (Figure 2.16). The channel resistance depends on the channel length of the transistor, while the contact resistance depends on the semiconductor/electrodes interface. $R_{ch}$ is proportional to the length of the channel (Figure 2.16), which means measured mobility should increase upon decreasing the length of the channel. However, at very small channel length (less than 1μm), the contact resistance starts to dominate and thus the measured mobility of the semiconductor starts to decrease with decreased channel length. Thus, the increase of the measured mobility with decreasing channel length observed with our thin film devices for all three isomers suggests that channel resistance is the key factor impacting device performance. This implies that grain boundaries within the channel are bottlenecks to charge transport. Assuming a uniform grain boundary density across the organic semiconductor film, the smaller the channel area, and the fewer the grain boundaries within that channel, the higher the mobility measured across smaller device areas would be, until the device area is comparable to the size of a single grain. Since the mobility does not
saturate across the channel lengths explored, it is likely that the crystalline domains are smaller than 2.5 μm.

Table 2.3 Summary of maximum transistor mobilities extracted at different channel lengths as-cast (AC), and thermally annealed (TA) processing conditions for thin-film transistors with active layers comprising isomers 2-3a, 2-3b, 2-3c, and the mixture.

<table>
<thead>
<tr>
<th>Molecule (processing condition)</th>
<th>μ (cm²/VS) 2.5 μm channel</th>
<th>μ (cm²/VS) 5 μm channel</th>
<th>μ (cm²/VS) 10 μm channel</th>
<th>μ (cm²/VS) 20 μm channel</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-3a (AC)</td>
<td>10⁻⁶</td>
<td>8×10⁻⁸</td>
<td>8×10⁻⁸</td>
<td>8×10⁻⁸</td>
</tr>
<tr>
<td>2-3a (TA)</td>
<td>2×10⁻⁶</td>
<td>3×10⁻⁷</td>
<td>10⁻⁷</td>
<td>10⁻⁷</td>
</tr>
<tr>
<td>2-3b (AC)</td>
<td>10⁻⁶</td>
<td>10⁻⁷</td>
<td>7×10⁻⁸</td>
<td>7×10⁻⁸</td>
</tr>
<tr>
<td>2-3b (TA)</td>
<td>5×10⁻⁶</td>
<td>5×10⁻⁷</td>
<td>2×10⁻⁷</td>
<td>2×10⁻⁷</td>
</tr>
<tr>
<td>2-3c (AC)</td>
<td>8×10⁻⁴</td>
<td>3×10⁻⁴</td>
<td>2×10⁻⁴</td>
<td>2×10⁻⁵</td>
</tr>
<tr>
<td>2-3c (TA)</td>
<td>5×10⁻²</td>
<td>-</td>
<td>4×10⁻³</td>
<td>-</td>
</tr>
<tr>
<td>Mix (AC)</td>
<td>-</td>
<td>10⁻⁶</td>
<td>3×10⁻⁷</td>
<td>2×10⁻⁷</td>
</tr>
<tr>
<td>Mix (TA)</td>
<td>-</td>
<td>2×10⁶</td>
<td>8×10⁻⁷</td>
<td>10⁻⁷</td>
</tr>
</tbody>
</table>

Under all process conditions, isomer 2-3c consistently yield better performing transistors compared to isomers 2-3a and 2-3b. This observation is consistent with our analysis of the crystal structures and electronic coupling calculations, which indicate 2-3c to be the most favorable isomer for charge transport.

2.2 F-TIPS-ADT mjölnir

TSBS-ADT packs in 1-D slipped stacks (Figure 2.17). Desymmetrizing TSBS-ADT alters the crystal packing but does not offer the targeted 1-D columnar packing.

Figure 2.17 TSBS-ADT crystal packing obtained by the Anthony group.
In order to extend our knowledge about the influence of desymmetrization on crystal packing, I decided to apply the same method on the F-TIPS-ADT molecule, and generate the mjölnir version of this derivative.

2.2.1 Synthesis & crystal packing

The synthesis of 2-7 is identical to that of 2-3 and is showed in details in scheme 2.1. 4-4’ was used instead of 4-4 in the aldol condensation and reacted with 1,4-cyclohexanedione to yield 89% of F-ADT quinone (2-5). 2-5 was then reacted with one equivalent of tri-iso-propylsilyl acetylene to make the intermediate (2-6), which was then reduced using DIBAL-H to form 2-7. Unlike mjölnir TSBS-ADT (2-3), TIPS mjölnir F-ADT (2-7) isomeric mixtures were much harder to separate chromatographically, mainly due to the low solubility of 2-7. The mjölnir TIPS-F-ADT (2-7) was recrystallized from 1,2dichloroethane to yield 45% (two steps) needle shaped crystals with dark orange color.

Figure 2.18 Crystal packing of F-TIPS-ADT and mjölnir F-TIPS-ADT. (a) Top view of F-TIPS-ADT showing the stacking that this molecule demonstrates. (b) Side view along the short axis of F-TIPS-ADT chromophore. (c) Top view of mjölnir F-TIPS-ADT showing an improved π-stacking due to alternating stacking. (d) Side view along the short axis of the mjölnir F-TIPS-ADT chromophore.
The desymmetrization of F-TIPS-ADT does force molecules to pack in an alternating fashion as seen in Figure 2.18(c, and d). As a result, packing is shifted along the long axis of the molecule, creating columnar stacks just as predicted. The closest contact between the two molecules in the same column for F-TIPS-ADT is 3.47 Å, almost the same as the close contact obtained by the mjölnir F-TIPS-ADT (3.44 Å). However the orbital overlapping between the Mjölnir F-TIPS-ADT molecules does increase due to the big shift in the long axis of the molecule as well as a small shift in the short axis (Figure 2.18d).

Additionally, in order to study the effect of fluorine atoms on ADT packing I synthesized bare F-ADT derivative and compared its crystal stacking with that of bare ADT. Similarly, I tried to monitor the fluorine impact on crystal packing in the presence of alkylsilyl solubilizing groups in mono-substituted (mjölnir F-TIPS-ADT, 2-7), and bisubstituted F-ADT (F-TIPS-ADT obtained by the Anthony group) derivatives. This allows us to elucidate to what extent the impact of the fluorine is eclipsed by the alkylsilyl solubilizing groups.

**2.3 Bare F-ADT**

The synthesis begins with the fluorination of thiophene-2,3-dialdehyde (4-4) to make the 5-fluoro-2,3-thiophene dialdehyde (4-4'). This was followed with the aldol condensation of 4-4' with 1,4-cyclohexanedione to make the F-ADT quinone (isomeric mixture, 2-5). 2-5 was reduced using an excess of DIBAL-H in dichloromethane to make 5,11-dihydroxyanthradithiophene (2-8) intermediate, which was deoxygenated using HCl and tin (II) chloride to make the bare F-ADT product (2-9) (Scheme 2.2). Recrystallization of 2-9 was done in 1,2-dichlorobenzene to yield 70% of golden thin sheet shaped crystals.
Scheme 2.2 Synthesis scheme of bare F-ADT (2-9)

2.3.1 X-ray crystallography

Figure 2.19 Thermal ellipsoide plot of F-ADT (2-9)
Figure 2.20 (a) F-ADT (2-9) crystal packing compared with (b) Bare ADT crystal packing. Similar packing with almost identical close contact distances.

Single crystals suitable for X-ray crystallography were obtained via physical vapor transport by our collaborators (The Hotta group in Kyoto University, Japan). The presence of the fluorine had little impact on the crystal packing of the ADT chromophore. Single crystal analysis of 2-9 revealed that, in the same manner as the bare ADT, 2-9 packs in herringbone fashion with a small difference in the close contact (3.53 Å for F-ADT compared to 3.58 Å for bare ADT) (Figure 2.20 a). In the absence of solubilizing groups C-H-π contacts and π-π contacts dominate the intermolecular forces, and the presence of fluorine atoms exert limited impact on the crystal packing. Upon addition of one solubilizing group the alkyl silyl group inhibits the edge to face interaction seen with bare ADT and takes control over the crystal packing as discussed previously. Finally the presence of two solubilizing groups creates more steric hindrance forcing a slip in the long and short axis of the molecules of the same stack while providing the same type of intermolecular interaction seen with the mono substituted ADTs but with less orbital overlapping.
2.4 Conclusion

Attaching one solubilizing group should facilitate the charge injection from the Mjölnir derivatives (donor) to the PC$_{61}$BM (acceptor) and therefore, 2-7 (donor)/PC$_{61}$BM (acceptor) blend should be tested in BHJ solar cells. Additionally, the morphology of these derivatives in the blend along with its crystal packing orientation on the substrate are very critical to assure good charge transport and high conversion efficiency in BHJs. Finally, decreasing the symmetry of the molecule by reducing the number of solubilizing groups enhanced differences in dipoles among the isomers to allow simple chromatographic separation (when molecules possess high enough solubility). The resulting unhindered acene edge allows for enhanced aromatic edge-to-face interactions, as observed in unsubstituted acenes (2-3). Edge-to-face interactions are stabilized more strongly in isomer 2-3c, where the edge contains C-H-\pi rather than S-\pi interactions. The differences in crystal structure between the isomers gives rise to a four-order-of-magnitude increase in the hole mobility for isomer 2-3c compared to 2-3a and 2-3b. Fluorine atoms don’t seem to play a praiseworthy role in influencing the crystal packing where fluorinated bare ADT packs almost exactly the same as bare ADT molecules.

2.5 Experimental details

**General methods for entire dissertation:** Solvents were purchased from Pharmco-Aaper. Tri-sec-butylsilylacetylene, tri-iso-butylsilylacetylene, and tri-cyclopentylsilylacetylene were prepared by literature methods.$^{112}$ All other chemicals were used as supplied from Sigma-Aldrich. Gas chromatography mass spectrometry was obtained using Bruker Scion SQ mass spectrometer system. High-resolution mass spectra were recorded in MALDI mode on a Bruker Daltonics Autoflex MALDI-TOFMS or in EI mode in a JOEL JMS-700T MStation. Combustion analyses were done by Midwest Microlab (Indianapolis, IN). The silica gel used for running columns is 230-400 mesh purchased from Silicycle. All solvents were purchased in bulk form. NMR spectra were measured on a Varian Unity 400 MHz spectrometer, chemical shifts reported in ppm relative to CDCl$_3$. Melting and decomposition points were determined by differential scanning calorimetry (DSC) at 10 °C min$^{-1}$. UV-Vis spectra were measured on a StellarNet Black-Comet spectrometer, and fluorescence spectra measured on a StellarNet Silver Nova 200
spectrometer. Cyclic voltammetry was performed on a BAS CV-50W potentiostat under N2, at a scan rate of 100 mV min with Fc/Fc+ as internal standard in 0.2 M Bu4 NPF6 solution in dichloromethane. Single crystal X-ray diffraction data were collected on either a Nonius Kappa CCD or a Bruker-Nonius X8 Proteum diffractometer. The data were refined and the structures solved as described in the CIFs.

![Chemical structure](image)

Thiophene-2,3-dialdehyde (4-4): The synthesis is described in chapter 4.

![Chemical structure](image)

5-fluoro-thiophene-2,3-dialdehyde (4-4’): This molecule was synthesized following literature procedure.113

![Chemical structure](image)

ADT quinone (2-1): 2-1 was synthesized following the same procedure in ref.114

![Chemical structure](image)

F-ADT quinone (2-5): In a 250 ml round bottom flask equipped with a stir bar. Add 1,4-cyclohexanedicarboxylic anhydride (0.510 g, 4.55 mmol) to 4-4’ (1.42 g, 9.09 mmol). Dissolve it in the smallest amount possible of ethanol (4 ml of ethanol with heating) then add 2 drops of 15% KOH while stirring to form a yellow precipitate. The solid product was recovered by
filtering the solution and washing with methanol and ether to yield to 89% of a yellow amorphous solid (2-5). (MALDI-TOF, TCNQ matrix) m/z 356(100% M⁺).

5,12-bis(tri-sec-butylsilyl)anthra[2,3-b;6,7-b’]dithiophene (2-3): To a nitrogen-purged round-bottom flask was added diethyl ether (15 ml), followed by tri-sec-butylsilylacetylene (510 mg, 2.275 mmol). n-Butyllithium (1.6 M in hexanes, 1.3 mL, 2.1 mmol) was added drop wise at 0 °C and the mixture was stirred for one hour while allowing it to reach room temperature. ADT quinone34, 99 (560 mg, 1.75 mmol) was added to the flask, followed by 40 mL of diethyl ether, and the reaction was left to stir overnight at room temperature. Sodium borohydride (323 mg, 8.75 mmol) and methanol (10 mL) were added directly to the reaction mixture, which was stirred for a further five hours. Deoxygenation proceeded by the addition of stannous chloride dihydrate (2 g, 8.75 mmol) dissolved in 10 ml of 10% aqueous HCl, and the mixture was stirred for one hour. The mixture was then quenched with water and extracted with ethyl acetate, dried with magnesium sulfate, filtered, and the solvent evaporated. The crude product was purified by chromatography on silica using hexanes as the eluent to yield 40% of isomers 2-3a (Rf = 0.3), 2-3b (Rf = 0.26), and 2-3c (Rf = 0.23). The molecules were recrystallized from hexanes.

Isomer 2-3a. 1H NMR (400 MHz, CDCl₃): δ 9.09 (s, 2H), 8.57 (s, 1H), 8.51 (s, 2H), 7.51 (d, J = 5.65 Hz, 2H), 7.40 (d, J = 5.65 Hz, 2H), 2.0 (m, 3H), 1.98 (m, 6H), 1.33 (d, J = 7.32 Hz, 9H), 1.13 (t, J = 7.29 Hz, 9H). 13C NMR (CDCl₃, 100MHz) δ 139.9, 137.9, 130.4, 129.4, 128.7, 125.7, 123.8, 120.9, 120.8, 117.5, 105.1, 104.2, 19.2, 14.7, 13.8. MS (EI 70
eV) m/z 512 (100%, M⁺). Elemental analysis calculated for C₃₂H₃₆S₂Si: %C 74.95, %H 7.08. Found: %C 75.15, %H 7.16.

Isomer 2-3b. ¹H NMR (400 MHz, CDCl₃): δ 9.08 (s, 1H), 9.02 (s, 1H), 8.50 (s, 1H), 8.40 (s, 1H), 8.32 (s, 1H), 7.47 (d, J = 5.60 Hz, 1H), 7.43 (d, J = 5.65 Hz, 1H), 7.36 (d, J = 5.64 Hz, 1H), 7.31 (d, J = 5.68 Hz, 1H), 2.02 (m, 3H), 1.53 (m, 6H), 1.33 (d, J = 7.32 Hz, 9H), 1.17 (t, J = 7.29 Hz, 9H). ¹³C NMR (CDCl₃, 100 MHz) δ 140.0, 139.2, 138.9, 137.7, 130.5, 130.2, 129.4, 129.0, 128.5, 128.3, 127.0, 123.8, 123.2, 122.9, 120.9, 120.7, 119.3, 115.9, 104.6, 104.3, 25.7, 19.3, 14.7, 13.9. MS (EI 70 eV) m/z 512 (100%, M⁺). Elemental analysis calculated for C₃₂H₃₆S₂Si: %C 74.95, %H 7.08. Found: %C 76.58, %H 7.24.

Isomer 2-3c. ¹H NMR (400 MHz, CDCl₃): δ 9.08 (s, 1H), 9.02 (s, 1H), 8.50 (s, 1H), 8.40 (s, 1H), 8.32 (s, 1H), 7.47 (d, J = 5.60 Hz, 1H), 7.43 (d, J = 5.65 Hz, 1H), 7.36 (d, J = 5.64 Hz, 1H), 7.31 (d, J = 5.68 Hz, 1H), 2.02 (m, 3H), 1.53 (m, 6H), 1.33 (d, J = 7.32 Hz, 9H), 1.17 (t, J = 7.29 Hz, 9H). ¹³C NMR (CDCl₃, 100 MHz) δ 140.0, 139.2, 138.9, 137.7, 130.5, 130.2, 129.4, 129.0, 128.5, 128.3, 127.0, 123.8, 123.2, 122.9, 120.9, 120.7, 119.3, 115.9, 104.6, 104.3, 25.7, 19.3, 14.7, 13.9. MS (EI 70 eV) m/z 512 (100%, M⁺). Elemental analysis calculated for C₃₂H₃₆S₂Si: %C 74.95, %H 7.08. Found: %C 76.10, %H 7.06.
2,8-difluoro-5,12-bis(tri-iso-propylsilyl)anthra[2,3-b:6,7-b’]dithiophene (2-7): To a nitrogen-purged round-bottom flask was added diethyl ether (15 ml), followed by tri-iso-propylsilylacetylene (414 mg, 2.275 mmol). n-Butyllithium (1.6 M in hexanes, 1.3 mL, 2.1 mmol) was added drop wise at 0 °C and the mixture was stirred for one hour while allowing it to reach room temperature. F-ADT quinone34, 99 (2-5) (623 mg, 1.75 mmol) was added to the flask, followed by 40 mL of diethyl ether, and the reaction was left to stir overnight at room temperature. Di-iso-butylaluminum hydride (DIBAL-H) (8.75 ml, 1M solution in Hexane, 8.75 mmol) was added drop wise to the reaction mixture, which was stirred for an additional two hours. Excess of DIBAL-H was quenched by adding 10% aqueous HCl solution slowly at 0 °C. Deoxygenation proceeded by the addition of stannous chloride dihydrate (2 g, 8.75 mmol) dissolved in 10 ml of 10% aqueous HCl, and the solution was stirred for one hour. The mixture was then quenched with water and extracted with dichloromethane, dried with magnesium sulfate, filtered, and the solvent evaporated. The crude product was purified by chromatography on silica using 9:1 hexanes: dichloromethane as the eluent to yield 45% of 2-7. The molecule was recrystallized from 1,2-dichloroethane to yield orange needle shaped crystals. MP 218 °C. MS (MALDI, DHB matrix) m/z 507 (M-CH3)+. 1H NMR (400MHz, CDCl3): δ 8.86 (s, 1H), 8.78 (s, 1H), 8.42 (s, 1H), 8.22 (s, 1H), 8.14 (s, 1H), 6.73 (s, 1H), 6.71 (s, 1H), 1.55 (m, 3H), (1.32 (d, J = 4.71 Hz, 18H) ppm. 167.05, 164.1, 163.8, 136.5, 135.4, 133.7, 132.18, 130.7, 130.5, 128.8, 128.5, 128.1, 127.2, 126.4, 125.6, 121.6, 121.4, 121.3, 120.2, 120.1, 120, 119.6, 115.5, 103.7, 103.6, 102.6, 101.9, 18.9, 11.6 ppm.
2,8-bare F-ADT (2-9): Di-iso-butylaluminum hydride (DIBAL) (8.75ml, 1M solution in Hexane, 8.75 mmol) was added drop wise to a solution of 2-5 (625 mg, 1.75 mmol) in DCM, which was stirred for an hours. Excess of DIBAL was quenched by adding 10% aqueous HCl solution slowly at 0 °C. Deoxygenation proceeded by the addition of stannous chloride dihydrate (2 g, 8.75 mmol) dissolved in 10 ml of 10% aqueous HCl, and the solution was stirred for one hour. The precipitate was filtered out using DCM to yield 397 mg (70%) crude product. The crude product was recrystallized from 1,2-dichlorobenzene to yield 22% golden thin crystals. MP 400 °C. The product wasn’t soluble enough for carbon and proton NMR.
Chapter 3 Isomerically pure anthradithiophene derivatives

Archetype ADT derivatives such as F-TES-ADT and F-TEG-ADT have exhibited average mobilities of 1.5 and 2.3 cm²/Vs respectively in single-crystal organic field-effect transistors (OFET). This is primarily due to a 2-D packing motif that generates strong orbital overlap between the molecules and enhances charge transport characteristics. Because inhomogeneous materials are not typically expected to exhibit high charge-carrier mobilities, the excellent performance displayed by ADTs is intriguing since they are typically prepared as a mixture of isomers.34, 115, 116

Recently the Tykwinski group at the University of Erlangen-Nuremberg Germany, synthesized the syn F-TES-ADT isomer, which demonstrates a performance similar to that of the mixture.101 This observation, as well as the work presented by the Bao group (Stanford University) on thienotetracene molecules,35 has reinforced our previous hypothesis that sulfur disorder cannot be controlled in the crystal packing of thiophene based heteroacenes, despite the isomeric purity of the compound.35 However, a preparation of the pure syn and anti parent (unsubstituted) ADTs by Mamada and co-workers (Yamagata University, Japan) showed a substantial difference in semiconductor performance between the two isomers, despite having similar crystal packing.102 The anti ADT isomer demonstrates a hole mobility two orders of magnitude higher than the syn ADT isomer in top-contact thin-film transistors. This was explained by the lower degree of atomic disorder obtained for the anti isomer by virtue of an inversion center of symmetry. The literature supports this theory as all the published molecules that I found, which possess an inversion centre, have outperformed other molecules of similar
conformation, properties, and crystal packing but which lack a centre of symmetry. (Table 3.1)

Table 3.1 Different heteroacene derivatives from the literature presenting molecules with an inversion center of symmetry demonstrating higher performance in OFET.

<table>
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<tr>
<th>Molecule structure</th>
<th>Crystal packing</th>
<th>Inversion center</th>
<th>Mobility cm²V⁻¹S⁻¹</th>
</tr>
</thead>
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<td>No</td>
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</tr>
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</tr>
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</table>
3.1 Synthesis

As described in chapter two, desymmetrizing ADT derivatives enables efficient separation of the ADT isomers. I also revealed that the position of the sulfur atom in the ADT backbone plays a critical role in this separation. Due to the polarity of these sulfur atoms, ADT isomers demonstrate different degrees of interaction with silica, thereby allowing their separation by chromatography. Therefore, I hypothesized that attaching a reactive moiety such as a “free ethynyl” to the 11 position of the ADT chromophore should not hinder the sulfur/silica interactions, and thus would still allow the separation of such molecule’s isomeric mixture on silica. This would also offer a reactive site that could be exploited in additional synthetic reactions to convert this intermediate molecule into the final target molecule (bis(silylethynyl) ADT). Thus, I chose the mono-tri-iso-butylsilylethynyl anthradithiophene (3-1) as our synthetic target. The isomeric mixture of 3-1 was obtained via addition of one equivalent of tri-iso-butylsilylacetylene, and one equivalent of ethynylmagnesium bromide to the F-ADT quinone. The step that follows has proven to be delicate as our classical deoxygenation method that involves the use of 10% HCl to aromatize the ADT chromophore was impractical. I discovered that HCl (even in small quantities) is highly reactive with the free alkyne moiety in the molecule (see Figure below). Hence, the deoxygenation was completed using tin (II) chloride and 10% H$_2$SO$_4$ instead to give molecule (3-1) in 45% yield.

The isomers were separated by silica gel chromatography with hexane as the eluent. The three separated isomers were recrystallized from dichloromethane to yield dark red-colored crystals. Although slightly unstable these isomers were quickly reacted with 15% potassium hydroxide solution in a 1:1 mixture of tetrahydrofuran:methanol to yield (80%) of intermediate (3-2). Finally, (3-2) was reacted with LiHMDS, and triethylsilylchloride
(triethylgermyl chloride) to yield the final crude product(s) \(3-3a,b\) (\(3-4a,b\)). Purification by chromatography resulted in a pink solid that was recrystallized from hexane.

Scheme 3.1 Synthetic scheme of pure anti F-TES-ADT (\(3-3a\)), F-TEG-ADT (\(3-4a\)), and pure syn F-TES-ADT (\(3-3b\)), syn F-TEG-ADT (\(3-4b\)).

3.2 X-ray crystallography
X-ray quality single crystals were obtained for isomers 3-3a, 3-3b and 3-4a. All isomers adopt crystal packing that is nearly identical to their corresponding isomeric mixtures. However, upon close inspection we can see a small but relevant difference between the mix, the syn and the anti isomers in both derivatives (3-3, and 3-4).

Figure 3.1 Ellipsoid plots of mix F-TES-ADT (3-3), anti F-TES-ADT (3-3a), and their crystal packing (viewed perpendicular to the plane of the F-ADT ring system).
As mentioned previously, the disorder of the thiophene ring in the crystal packing cannot be eliminated.\textsuperscript{35,101} This appeared at first to be the case for the separated mix, syn, and anti isomers of F-TES-ADT and F-TEG-ADT. However, at very close inspection I noticed that the presence of an inversion centre of symmetry for the anti ADT isomer (3-3a and 3-4a) produces a higher degree of order for the ADT chromophore with the disorder only needing to be modelled for the thiophene ring portion of the ADT. Furthermore, by inspecting of the sulfur site occupancy in the ADT chromophore, I discovered that the disorder in the thiophene ring of the anti isomers was even lower than that of its corresponding isomeric mixture (Table 3.2). A 0.9/0.1 sulfur occupancy was found for 3-3a and 0.94/0.06 sulfur occupancy for 3-4a.
Table 3.2 Percent occupancy of sulfur in the crystal packing of F-TES-ADT and F-TEG-ADT isomers, extracted from the CIF files of the refined crystal structures.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Major sulfur occupancy (%)</th>
<th>Minor sulfur occupancy (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-3b&lt;sup&gt;101&lt;/sup&gt; (syn)</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>3-3a (anti)</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>3-3 (mix)</td>
<td>68.8</td>
<td>31.2</td>
</tr>
<tr>
<td>3-4b (syn)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3-4a (anti)</td>
<td>94.44</td>
<td>5.56</td>
</tr>
<tr>
<td>3-4 (mix)</td>
<td>70.6</td>
<td>29.4</td>
</tr>
</tbody>
</table>

The melting points for all the derivatives and their corresponding isomers were measured. 3-3 (mix) and 3-4 (mix) measured melting points are 10 to 20 degrees lower than that of 3-3a (anti) and 3-4a (anti). This could be explained by melting point depression. By eliminating one of the two isomers the product becomes extra pure, which leads to an increase in its melting point. However, what is more interesting is the significant increase in the melting point for compound 3-3a (anti) (205 °C) and 3-4a (anti) with respect to compound 3-3b (syn) (190 °C)<sup>101</sup> and 3-4b (syn) respectively. This can be explained by the existence of stronger intermolecular interactions in the anti isomers compared to the syn and the mix (see below).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Melting point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-3 (mix)</td>
<td>195</td>
</tr>
<tr>
<td>3-3b (syn)</td>
<td>190</td>
</tr>
<tr>
<td>3-3a (anti)</td>
<td>205</td>
</tr>
<tr>
<td>3-4 (mix)</td>
<td>190</td>
</tr>
<tr>
<td>3-4b (syn)</td>
<td>172</td>
</tr>
<tr>
<td>3-4a (anti)</td>
<td>189</td>
</tr>
</tbody>
</table>

Looking at the structure of the F-TES-ADT and the F-TEG-ADT, sulfur-fluorine (S-F) interactions have been proposed in the literature before as a significant intermolecular interaction that can influence the crystal packing.<sup>113</sup> In order to investigate these sulfur-fluorine (S-F) and hydrogen-fluorine (H-F) interactions, Dr. Karl J. Thorley preformed a pairwise interaction energy decomposition analysis<sup>120</sup> using the GAMESS software.<sup>121</sup> This analysis breaks down these intermolecular interactions into different stabilizing and destabilizing energy terms to underline the main effect S-F and H-F interactions have on
the molecule. Figure 3.3 illustrates the high stabilizing forces obtained with the HFHF orientation vs. SFSF, and HFSF.

Figure 3.3 Pairwise interaction energy decomposition analysis for in-plane interactions between the ends of diF-ADT dimers interacting through HFHF couplings, HFSF couplings, and SFSF couplings. The calculations were performed by Dr. Karl J. Thorley.

Figure 3.4 Probability of HFHF, HFSF, and SFSF interactions obtained from the percentage of the major and minor conformer percentages in the crystal structures of the 3-3 mix and 3-4 mix and its respective anti isomers (3-3a, and 3-4a).
Figure 3.4 presents HFHF as the major couplings present in the *anti* isomers crystal packing (3-3a and 3-4a). The probabilities were calculated for two neighboring ADT molecules of the same plane using the percent occupancies of sulfur extracted from their CIF files (Table 3.2). From these results we were able to conclude that the stabilizing effect of HFHF interactions, could be the reason behind the increased melting points reported for isomers 3-3a. The same observation cannot be made for molecule 3-4. The melting point of the mix is 10°C higher than 3-4a. I don’t have a good explanation as to why this is the case yet.

### 3.3 Device study

The device characteristics of the isolated isomers were studied and compared to their respective isomeric mixtures. Transistor devices were fabricated by Yaochuan Mei from Prof. Oana Jurchescu’s group at Wake Forest University. Ti/Au were deposited by e-beam evaporation over a SiO₂ substrate and used as the source and drain electrodes. The organic semiconductor was spin-coated from a 2-wt% solution in room-temperature chlorobenzene. Cytop dielectric was spin-cast from an undiluted solution on top of the organic semiconductor layer, followed by a curing step at 50 °C in a vacuum oven for 12 hours. Al gate electrodes were deposited by thermal evaporation to complete the devices. The channel lengths of the device, L, had values between 5 and 100 µm, and widths, W, of either 800 or 1000 µm.
Figure 3.5 Transfer characteristics of F-TES-ADT (3-3) and F-TEG-ADT (3-4) mix and their pure syn (3-3b, 3-4b) and anti (3-3a, 3-4a) isomers.

The transfer characteristics for both derivatives and their respective isomers are presented in Figure 3.5, and were taken in the saturation regime of the OFET (source drain voltage $V_{DS} = -40 \text{ V}$). All devices exhibit a very low threshold voltage ($V_{th}$), a sharp turn-on and a smooth linear relationship between (square root of the drain current) $\sqrt{I_D}$ and (gate-source voltage) $V_{GS}$. This is an indication of low contact resistance and minor trapping effects in the devices.

Table 3.3 Average mobilities of F-TES-ADT and F-TEG-ADT (mix, syn , and anti)

<table>
<thead>
<tr>
<th>Material</th>
<th>Avg. Mobility best 6 samples (cm$^2$/Vs)</th>
<th>Avg. Mobility all 20 samples (cm$^2$/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-3 (mix)</td>
<td>2.7±0.7</td>
<td>1.5±0.8</td>
</tr>
<tr>
<td>3-3b (syn)</td>
<td>3.0±0.4</td>
<td>1.9±0.9</td>
</tr>
<tr>
<td>3-3a (anti)</td>
<td>4.3±0.8</td>
<td>2.2±1.1</td>
</tr>
<tr>
<td>3-4 (mix)</td>
<td>2.4±0.3</td>
<td>1.7±0.6</td>
</tr>
<tr>
<td>3-4b (syn)</td>
<td>2.8±0.3</td>
<td>2.2±0.5</td>
</tr>
<tr>
<td>3-4a (anti)</td>
<td>6.2±0.4</td>
<td>3.4±1.6</td>
</tr>
</tbody>
</table>

Table 3.3 demonstrates the average field-effect mobility, $\mu$, of the best six samples studied, as well as the average mobility over all samples studied (> 20 for each type of ADT). For the TES compound the pure syn isomer displays a slight improvement ($\mu = 3 \pm$
0.4 cm²/ Vs) over its isomeric mixture (µ = 2.7 ± 0.7 cm²/ Vs). However, the anti isomer (3-3a) mobility has almost doubled (µ = 4.3 ± 0.8 cm²/ Vs). The same trend was obtained with 3-4a (µ = 6.2 ± 0.4 cm²/ Vs) where its mobility is double that of 3-4b (syn) (µ = 2.8 ± 0.3 cm²/ Vs) and the 3-4 (mix) (µ = 2.4 ± 0.3 cm²/ Vs). The performance of the anti isomer for both ADT molecules (anti F-TES-ADT and anti F-TEG-ADT) is significantly superior to that of its corresponding syn and mix ADTs.

Orbital overlap is a critical parameter in determining the charge mobility in the crystal. Therefore, the electronic coupling in these derivatives were studied and calculated using the crystal packing obtained with X-ray diffraction. To achieve this, Dr. Thorley used the localized monomer approach¹²² with Gaussian09,¹²³ using the B3LYP/6-31G(d) functional and basis set. As mentioned previously, F-TES-ADT and F-TEG-ADT pack in a 2-D fashion. Each ADT chromophore interacts with two other chromophores as demonstrated in Figure 3.1 and 3.2. Hence, the calculation was done on two sets of overlapping molecules, the minor orbital overlap (black circle), and the major orbital overlap (blue circle) acquired from the interaction between the three neighboring ADT chromophores (Figure 3.6).

<table>
<thead>
<tr>
<th>Material</th>
<th>Major overlap</th>
<th>Minor overlap</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-3 Mix</td>
<td>0.113 eV</td>
<td>0.026 eV</td>
</tr>
<tr>
<td>3-3a Anti</td>
<td>0.114 eV</td>
<td>0.022 eV</td>
</tr>
<tr>
<td>3-4 Mix</td>
<td>0.102 eV</td>
<td>0.030 eV</td>
</tr>
<tr>
<td>3-4a Anti</td>
<td>0.110 eV</td>
<td>0.027 eV</td>
</tr>
</tbody>
</table>

Figure 3.6 Major and minor orbital overlap presented in the blue and black ovals respectively. The electronic coupling of these overlaps for the F-TES-ADT and F-TEG-ADT mix derivatives, as well as their respective anti isomers, were calculated based on the refined crystal structures, and are shown in the table above.
The data in the table of Figure 3.6 suggest that the electronic couplings for the TES compound are very similar with a very slight increase (+0.001 eV) in the major overlap (blue circle) and a small decrease (-0.004 eV) in the minor overlap (black circle). In the TEG compound the electronic coupling of the anti isomer is 0.008 eV higher than that of its mixture, in the major overlap, and 0.003 eV lower in the minor overlap. However, the improved device characteristics were obtained for the anti isomers of both compounds (3-3a and 3-4a). This provides direct evidence that other variables, such as intermolecular forces, improved density and most importantly the existence of an inversion center, can be responsible for these documented improvements.

The improved intermolecular interaction as a result of the HF interaction in the anti isomer can have an impact on the molecule charge transfer characteristics. That was more noticeable with the anti isomer of the TEG compound (3-4a) where an increase in the crystal density was achieved. Moreover, the large intermolecular forces have lead to an increase in the melting point of 3-3a and 3-4a. Higher intermolecular forces induce higher unit cell density and improve orbital overlapping in the molecules, which leads to larger electronic coupling. This can explain the slight improvement in the electronic coupling seen with 3-3a and 3-4a.

Finally, the existence of an inversion centre, as mentioned previously, does have a major impact on the charge transport characteristics of ADT. The coordination between low degree of disorder for 3-3a and 3-4a, and improved charge transfer characteristics proves that disorder can have a detrimental effect on semiconductor performance. Mamada et al. also demonstrated that a limited disorder decreases the potential of charge carrier trapping, which should have a positive impact on mobility. Additionally, Mamada et al. also suggested that molecules with no permanent dipole (i.e., anti F-TES-ADT and anti F-TEG-ADT) tend to experience a smoother intermolecular relaxation that reduces trapping and increases mobility as a result of molecule reorientation. In a molecule with a permanent dipole moment, these reorientations are more relevant and need to be accounted for. The molecule with a permanent dipole adjacent to a charged molecule is required to go through energy reorganization to reorient itself in a favorable way before charge hopping occurs, resulting in a reduced charge carrier mobility.
3.4 Conclusion

I was able to develop a method that separates the syn and anti isomer, in functionalized ADT derivatives, by using the same method applied in chapter 2. The anti isomer in F-TES-ADT and F-TEG-ADT has proven to be the superior isomer outperforming its syn isomer counterpart, as well as its isomeric mixture. This is a result of strong intermolecular forces that create a denser molecular packing and stronger electronic coupling. Additionally, the existence of an inversion center along with the reduced disorder recorded in the anti isomers has proven to have major impact on the improved charge transfer capabilities. This is a result of a lack of permanent transition dipoles in these ADT derivatives, which facilitate charge transport in the crystal lattice and improves mobility.

3.5 Experimental

Solvents were purchased in bulk from Pharmco-Aaper. Tri-*iso*-butylsilylacetylene was prepared by literature methods.\textsuperscript{112} All other chemicals were used as supplied from Sigma-Aldrich. NMR spectra were measured on a Varian (Unity 400 MHz) spectrometer, chemical shifts reported in ppm relative to CDCl\textsubscript{3}.

\[
\text{Synthesis of 3-1(a-c):} \quad \text{To nitrogen purged round-bottom flask was added diethyl ether (15ml), followed by tri-*iso*-butylsilylacetylene (510 mg, 2.275 mmol). n-Butyllithium (1.6M in hexanes, 1.3 mL, 2.1mmol) was added dropwise at 0 \degree C and the mixture was stirred for 1 hour while allowing it to reach room temperature. F-ADT quinone\textsuperscript{113} (560 mg, 1.75mmol) was added to the flask followed by 40 mL of diethyl ether and the reaction was left to stir for 48 hours at room temperature. Ethynylmagnesium bromide (0.5M in THF, 6.8ml, 3.41 mmol) was added to the reaction mixture, which was stirred for another 2 hours. Deoxygenation preceded by the addition of 5 ml of 10\% aqueous H\textsubscript{2}SO\textsubscript{4}, and stannous chloride dihydrate (2 g, 8.75 mmol) and the mixture was stirred for 30 minutes. The mixture}
\]
was then quenched with water and extracted with ethyl acetate, then dried with magnesium sulfate. The solution was then filtered and the solvent was evaporated. The crude product was purified by chromatography on silica using hexanes as the eluent to yield 41% of isomers 3-1a, 3-1b, and 3-1c. The 3 isomers were recrystallized by slow evaporation from dichloromethane to yield red colored crystals. In general, these poorly stable materials were best kept in dilute solution under nitrogen in the dark.

3-1a (the molecule was not stable enough to obtain a reliable carbon or proton NMR): $^1$H NMR (400MHz, CDCl$_3$): $\delta$ 8.81 (s, 1H), 8.68 (s, 1H), 8.67 (s, 1H), 8.51 (s, 1H), 6.67 (s, 2H), 4.08 (s, 1H), 2.16 (m, 3H), 1.19 (d, $J= 6.94$ Hz, 6H), 0.95 (d, $J= 6.94$ Hz, 6H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 167.2, 167.2, 164.3, 164.2, 163.1, 136.4, 136.3, 136.2, 136.2, 133.7, 133.6, 129.6, 129.5, 129.4, 129.3, 129.2, 120.5, 120.4, 120.1, 120.0, 119.9, 119.7, 117.4, 115.1, 108.4, 103.4, 102.5, 102.4, 102.2, 90.1, 80.6, 67.9, 26.5, 25.3, 25.2 ppm.

3-1b (the molecule was not stable enough to obtain a reliable carbon or proton NMR): $^1$H NMR (400MHz, CDCl$_3$): $\delta$ 8.69 (s, 2H), 8.63 (s, 1H), 6.67 (s, 2H), 4.04 (s, 1H), 2.16 (m, 3H), 1.19 (d, $J= 6.61$ Hz, 18H), 0.95 (d, $J= 6.93$ Hz, 6H) ppm. $^{13}$C NMR (100 MHz,
CDCl₃): δ 167.3, 164.3, 163.1, 136.3, 136.2, 133.7, 129.8, 129.1, 129.1, 120.5, 120.4, 119.8, 114.5, 108.6, 103.6, 102.4, 102.3, 102.2, 102.1, 89.9, 80.5, 67.9, 26.5, 25.3 ppm.

3-1c (the molecule was not stable enough to obtain a reliable carbon or proton NMR): ¹H NMR (400MHz, CDCl₃): δ 8.88 (s, 2H), 8.70 (s, 2H), 6.75 (s, 2H), 4.17 (s, 1H), 2.13 (m, 3H), 1.16 (d, J= 6.61 Hz, 18H), 0.92 (d, J= 6.93 Hz, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 167.3, 164.3, 163.1, 136.3, 136.2, 133.6, 129.8, 129.1, 129.1, 120.4, 120.1, 120.1, 114.5, 108.6, 103.6, 102.4, 102.3, 102.2, 102.1, 89.9, 80.5, 67.9, 26.5, 25.3 ppm.

**General procedure for the synthesis of 3-2a:** in a 100ml round bottom flask 1a (290mg, 0.53 mmol) was dissolved in 5 ml THF and 10 ml methanol. 1ml of 15% KOH solution was added and the mixture was stirred for 2 hours until the solution turned into an orange suspension. The reaction mixture was then filtered and the solid washed with methanol, and dried under high vacuum to yield 160 mg 2a (80%) as an orange powder. The product was immediately taken to the next step without any further purification.
General procedure for the synthesis of anti diF-ADT (3-3a, and 3-4a): In a flame dried round bottom flask equipped with a stir bar, 160mg of 3-2a was dissolved in 10 ml of dry THF under nitrogen. LiHMDS (1M in hexane, 0.9ml, 0.9mmol) was added dropwise followed by chlorotriethyl silane or chlorotrigermyl silane (1.28 mmol) and the reaction was left to stir for 1 hour. After quenching with water and extraction with dichloromethane, the solution was dried (MgSO₄) and concentrated under vacuum. The crude product was then purified by silica gel chromatography with hexanes as the eluent, followed by recrystallization from hexanes to yield the pure ADT.

Anti diF TES ADT (3-3a): ¹H NMR (400MHz, CDCl₃): δ 8.92(s, 2H), 8.84(s, 2H), 6.80(d, JFH=2.51Hz, 2H), 1.22(t, J=15.71Hz, 18H), 0.87-0.93 (m, 12H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 167.3, 164.3, 163.1, 136.6, 136.5, 133.9, 130.1, 129.6, 129.5, 121.2, 120.8, 120.6, 120.4, 120.3, 117.5, 107.3, 103.2,102.7, 102.6, 7.9, 4.8 ppm. MS (EI 70 eV) m/z 602 (100%, M⁺). Elemental analysis calculated for C₃₂H₃₆S₂Si: %C 67.73, %H 6.02, %F 6.30, %S 10.63, Si 9.32. Found: %C 68.32, %H 6.39.
Anti diF TEG ADT (3-4a): $^1$H NMR (400MHz, CDCl$_3$): $\delta$ 8.95(s,2H), 8.87(s,2H), 6.79(d, $J_{HF}$=2.37Hz, 2H), 1.29-1.34(m, 18H), 1.11-1.17 (m, 12H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 167.5, 164.5, 163.4, 136.7, 136.6, 133.9, 130.2, 129.9, 129.8, 121.2, 120.8, 120.7, 120.6, 120.0, 117.4, 107.8, 102.9, 102.8, 102.7, 9.7, 6.6 ppm. MS (El 70 eV) m/z 692 (100%, M$^+$$)$. Elemental analysis calculated for C$_{32}$H$_{36}$S$_2$Si: %C 59.01, %H 5.24, %F 5.49, %S 9.27, %Ge 20.99. Found: %C 60.15, %H 5.31.

Syn diF TES ADT (3-3b): $^1$H NMR (400MHz, CDCl$_3$): $\delta$ 8.91(s,2H), 8.84(s,2H), 6.80(d, $J_{HF}$=2.51Hz, 2H), 1.23-1.18(m, 18H), 0.87-0.89 (m, 12H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 167.3, 164.3, 136.6, 136.4, 133.9, 133.7, 130.1, 129.6, 129.2, 121.2, 120.8, 120.3, 117.5, 116.2, 107.0, 106.9, 102.9, 102.6, 102.5, 7.74, 4.60 ppm. MS (El 70 eV) m/z 602 (100%, M$^+$$)$. Elemental analysis calculated for C$_{32}$H$_{36}$S$_2$Si: %C 67.73, %H 6.02, %F 6.30, %S 10.63, Si 9.32. Found: %C 68.10, %H 6.54.
Syn diF TEG ADT (3b): $^1$H NMR (400MHz, CDCl$_3$): $\delta$ 8.94(s, 2H), 8.84(s, 2H), 6.80(d, $J_{FH}=2.51$Hz, 2H), 1.29-1.34(m, 18H), 1.11-1.18 (m, 12H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 167.5, 164.5, 136.7, 136.6, 133.9, 130.4, 129.7, 129.6, 121.1, 121.0, 120.9, 118.1, 116.7, 108.0, 107.6, 103.1, 103.0, 102.9, 102.8, 9.6, 6.5 ppm. MS (EI 70 eV) m/z 692 (100%, M$^+\). Elemental analysis calculated for C$_{35}$H$_{38}$S$_2$Si: %C 59.01, %H 5.24, %F 5.49, %S 9.27, %Ge 20.99. Found: %C 60.10, %H 5.54.
Chapter 4 Small molecule donors and acceptors for binary and ternary BHJ

4.1 Cyano anthradithiophenes

Donor and acceptor materials are blended at different concentration ratios to make the active layer of Bulk Heterojunction (BHJ) solar cells. Here, I investigate small molecule/small molecule donor/acceptor blend systems as potential replacements for small molecule/polymer, and polymer/polymer donor/acceptor blends. The ease of tailoring the energy levels of ADTs by introducing electron withdrawing groups (EWG) and electron donating groups (EDG), along with the use of solubilizing groups to control the crystal packing, have made ADT an ideal candidate for this project. I hypothesize that by having two chemically similar molecules (same acene chromophore, differing frontier molecular orbital energy levels) acting as donors and acceptors in the active layer blend, the intermixing at the heterojunction can be controlled via annealing, and consequently charge transfer and exciton dissociation can be improved.

One of the advantages of employing cyano (CN) moieties as EWGs on the acene’s chromophore is the increase in the conjugation length. Such impact lowers the LUMO energy of the molecule, which decreases the band gap, and as a result improves the photon harvesting process. This was demonstrated with CN-pentacene derivatives. Cyano pentacene showed the ability to behave as an acceptor in BHJ solar cells because of their tuned electronic properties and their good charge transport abilities. The highest preforming cyano pentacene derivative showed a PCE of 1.5% compared to 3.5% exhibited by PC$_{61}$BM-based devices. Incorporating cyano groups into the ADT chromophore should have a similar effect on the electronic properties, which will allow us to study ADT derivatives in OPV.

Because crystal packing does have an impact on the molecule performance in BHJ photovoltaic, four derivatives with different solubilizing groups were synthesized in a similar fashion as described in Scheme 4.1. Synthesis begins with the protection of thiophene-3-carboxaldehyde (4-1) with ethylene glycol. Thiophene-3-acetal (4-2) was then deprotonated and reacted with dimethylformamide, followed by a deprotection to make thiophene-2,3-dialdehyde (4-4). 4-4 was then brominated to make the 5-bromothiophene-
2,3-dialdehyde (4-5) followed by an aldol condensation to generate the Br-ADT quinone (4-6). Addition of lithium alkylsilylacetylide to the Br-ADT quinone, followed by aromatization via deoxygenation with SnCl2/HCl gave (4-7). Finally, a palladium catalyzed cyanation reaction was performed to produce the final ADT derivatives (4-8).

Scheme 4.1 Synthetic outline of CN-ADT (4-8) derivatives.

It should be noted that the previous cyanation method used with pentacene was achieved using potassium cyanide and palladium (0) catalyst reaction with iodo halogenated pentacene. However, the same method was unsuccessful with ADT derivatives despite changing solvent and increasing temperatures. For instance, with 2,8-diiodo-bis(trialkylsilylethynyl) ADT derivatives, the reaction did not proceed at low temperature. Moreover, at 110 °C only one cyano group was successfully attached to the ADT chromophore while the other iodine was reduced to a proton. This can be explained by the dissociation of the Carbon-iodine bond via homolysis, followed by radical quenching that replaces the iodine atom with a hydrogen. To solve this problem I
substituted iodine for bromine, used Zn(CN)\(_2\) as a cyanide source, and DMF as a solvent along with Pd(PPh\(_3\))\(_4\) catalyst at 110°C.

It was reported by Takagi and co-workers\(^{125}\) that in a palladium catalyzed reaction there are two catalytic cycles. The first cycle is the classic palladium cross-coupling cycle with oxidative addition and reductive elimination steps, while the second, competing cycle consists of conversion of the catalyst to a palladium species that acts as a cyanide carrier. Thus, if we have an excess of cyanide, it will react with the catalyst to form an inactive palladium cyanide species that can not be reduced to the catalytically active palladium (0) species, and eventually inhibit the catalytic cycle. In order to control the concentration of cyanide in the reaction I used a solvent (DMF) that has a low Zn(CN)\(_2\) solubility. Also, the reaction has to be done in a dry environment, as the presence of water increases the solubility of zinc cyanide in DMF.

4.1.1 X-ray crystallography

Although 4-8a grows nice-looking crystals, the quality of these crystals was very poor. No diffraction pattern was observed on the X-ray diffractometer (Figure 4.1); instead we observed fuzzy streaks despite what solvent and which recrystallization method was used, whether it is slow evaporation from hexanes and ethyl acetate, or slow diffusion in chloroform and methanol.

![Image of X-ray diffraction pattern of 4-8a. The red circles indicate the fuzzy streaks.](image_url)

To obtain sharp diffraction spots the crystal must have long range ordering in all three dimensions. When the crystal has only one or two-dimensional ordering, the diffraction
spots start to stretch out creating fuzzy lines as seen in Figure 4.1. The presence of disorder increases charge trapping and reduces charge transport properties in bulk materials.

The isomeric mixture of ADTs (syn and anti), the usage of tri-sec-butylsilyl ethynyl solubilizing groups which contain chiral centers, and the thiophene disorder often observed in the ADT crystal structures, lead to large amounts of solid state disorder in molecule 4-8b. Despite that, we were able to obtain a partial refinement of the crystal packing. 4-8b packs in a 2-D fashion with the closest aromatic C-C distance of 3.37 Å. The existence of minimal interaction due to a poor stacking between the molecules is very evident in Figure 4.4b, predicting low charge transport capabilities. The crystal packing of molecule 4-8d shows 1-D slipped stacks with the closest aromatic C-C distance of 3.49 Å. Unfortunately 4-8c produce amorphous solid and failed to yield X-ray quality crystals when recrystallized in hexane, dichloroethane, toluene, and xylene.

![Figure 4.2 Thermal ellipsoid plot of 4-8b.](image-url)
Figure 4.3 Crystal packing of molecule 4-8b. The sec-butyl groups and protons are hidden for more clarity.

Figure 4.4 Crystal packing of molecule 4-8b. (a) Side view along the short axis of the molecule, (b) viewed perpendicular to the plane of the 4-8 ring system. The molecule exhibits close contact of 3.37 Å. It packs in 2-D stacks with a small orbital overlapping due to a slip in the crystal packing along the short axis. (sec-butyl groups and protons are hidden for more clarity).
Figure 4.5 Thermal ellipsoid plot of 4-8d

Figure 4.6 Crystal packing of 4-8d. Top view of the crystal packing showing a 1-D slip stacks (iso-propyl groups and protons are hidden for more clarity).
F-TES-ADT was selected to be blended with 4-8 due to their energy level compatibility as donor and acceptor materials.

F-TES-ADT displays high charge carrier mobility, energy level compatibility with 4-8 derivatives (Figure 4.7), high photoconductivity, and strong photoluminescence in solution-deposited films (Figure 4.9), which makes it an ideal donor candidate in blends with 4-8 (acceptor).

When blending 4-8 a-d with F-TES-ADT, the two materials did indeed co-crystallize as seen in Figure 4.8. However, the film uniformity was quite poor. Other donor/acceptor thin film blends were also fabricated at different concentration ratios of 4-8 a-d with F-TES-ADT, ethyl-TES-ADT, and ethylthienyl-TES-ADT. Similar observations were
recorded for these blends. Neither thermal annealing nor varying the concentration ratio in the film blend affected the film morphology or reduced the large amount of grain boundaries.

### 4.1.2 Organic binary BHJ

Small molecule BHJ solar cells were made with F-TES-ADT/4-8d blend, and were compared to other blends made with P3HT and PC_{61}BM as shown in Table 4.1. All blends showed low power conversion efficiency (PCE), despite a moderate open circuit voltage. This is related to very low short circuit currents, as a result of a mediocre photogenerated current or a very low charge transport characteristics.

Table 4.1 Solar cell characteristics for different blends.

<table>
<thead>
<tr>
<th>Blend</th>
<th>Concentration</th>
<th>(V_{OC}) (V)</th>
<th>(J_{SC}) (mA/cm²)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT/4-8d</td>
<td>1:1</td>
<td>0.8</td>
<td>0.016</td>
<td>0.16</td>
<td>0.0021</td>
</tr>
<tr>
<td>P3HT/ F TES ADT</td>
<td>1:1</td>
<td>0.46</td>
<td>0.016</td>
<td>0.22</td>
<td>0.0016</td>
</tr>
<tr>
<td>F TES ADT/4-8d</td>
<td>1:1</td>
<td>0.77</td>
<td>0.02</td>
<td>0.35</td>
<td>0.0048</td>
</tr>
<tr>
<td>F TES ADT/ PCBM</td>
<td>49:1</td>
<td>0.78</td>
<td>0.013</td>
<td>0.14</td>
<td>0.0015</td>
</tr>
<tr>
<td>F TES ADT/ PCBM</td>
<td>3:1</td>
<td>0.18</td>
<td>0.2</td>
<td>0.26</td>
<td>0.01</td>
</tr>
<tr>
<td>F TES ADT/ PCBM</td>
<td>1:1</td>
<td>0.15</td>
<td>0.52</td>
<td>0.28</td>
<td>0.024</td>
</tr>
</tbody>
</table>

Charge transfer and exciton dissociation are among the most obscure steps in photocurrent generation in OPV. Because it is very hard to control the morphology of the active layer film, it makes it impossible to follow the exciton behavior at the donor/acceptor interface. Charge transfer, for example, can proceed via different mechanisms. One such mechanism, Förster resonance energy transfer (FRET), is an energy transfer between two light sensitive molecules through non-radiative dipole-dipole interactions.\(^{126}\) Dexter electron exchange is another mechanism that involves fluorescence quenching where an excited electron is transferred from the excited molecule to the acceptor molecule\(^{127}\) and is usually dominant at distances shorter than 10 Å. Therefore, depending on the morphology of the film, one can expect one mechanism dominating the other, or even other mechanisms surfacing.
Dr Oksana Ostroverkhova and her group at Oregon St University have found that at very low concentration of added 4-8d to the F-TES-ADT film, the emission of F-TES-ADT aggregation (580, 625 nm) is the dominant photophysical process. However, upon increasing the concentration of 4-8d a new emission band (680 nm) appears that doesn’t correspond to the emission of F-TES-ADT or 4-8d, showing that when the donor and acceptor molecules are in direct contact, the majority of the electron transfer is happening via a new route. However, if we increase the concentration of 4-8d in the blend, that new emission band disappears and we only observe emission from F-TES-ADT aggregation (580, 625 nm) and 4-8d aggregation (750 nm). The new emission band (680nm) has an energy that matches the energy difference between the HOMO of the donor (F-TES-ADT) and the LUMO of the acceptor (4-8d). This new fluorescence peak can only be a result of a complex entity that is formed between donor and acceptor molecules in the active layer. Such complex species between an excited molecular entity (F-TES-ADT) with another molecular entity of different structure (4-8d) in the ground state is referred to as an exciplex. Hence, the fluorescence at 680 nm is a result of a F-TES-ADT/4-8d exciplex species.

When F-TES-ADT (D) and 4-8d (A) are blended with poly (methyl methacrylate) (PMMA), an inert spacer polymer, a limited and controlled direct contact between the donor and the acceptor molecules is obtained. By changing the concentration of PMMA in the blend, the distance that separates the donor and the acceptor molecules can be controlled. As a result, our collaborators were able to pinpoint the Förster resonance energy transfer and calculate the Förster radius to be 4.8 nm.

Table 4.2 Summary of photoluminescence spectra of F-TES-ADT/4-8 blend obtained under 355 nm excitation. The photoluminescence spectra showed that the majority of the emission is coming from a new band that correspond to an energy of 1.86 eV

<table>
<thead>
<tr>
<th>Donor in the blend</th>
<th>concentration added of 4-8 to the blend (M)</th>
<th>Wavelength (λ) of photoluminescence peaks (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pristine F TES ADT</td>
<td>0</td>
<td>580, 625</td>
</tr>
<tr>
<td>F TES ADT</td>
<td>3.6.10^{-4}</td>
<td>625, 680</td>
</tr>
<tr>
<td>F TES ADT</td>
<td>3.6.10^{-3}</td>
<td>680</td>
</tr>
<tr>
<td>F TES ADT</td>
<td>3.6.10^{-2}</td>
<td>680</td>
</tr>
<tr>
<td>- Pristine 4-8</td>
<td></td>
<td>750</td>
</tr>
</tbody>
</table>
Another promising direction in organic solar cell is organic ternary BHJs, in which an additional molecule with compatible energy levels is added to ordinary binary blends. Such additions have proven to be helpful in extending the absorbance of the blend, improving the PCE by as much as 35%, and increasing short-circuit currents ($J_{SC}$) due to additional charge transport pathways and enhanced charge photogeneration.

The HOMO/LUMO energies of 4-8d are compatible with that of P3HT and PC$_{60}$BM (Figure 4.9). Dr Ostroverkhova’s group anticipated that by adding 4-8d to the P3HT/PC$_{60}$BM system, they can create a cascading charge transfer states that can

<table>
<thead>
<tr>
<th>4-8d Concentration (M) wt%</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.6</td>
<td>7.1</td>
<td>0.51</td>
<td>2</td>
</tr>
<tr>
<td>1</td>
<td>0.55</td>
<td>5</td>
<td>0.52</td>
<td>1.5</td>
</tr>
<tr>
<td>2</td>
<td>0.54</td>
<td>4.8</td>
<td>0.53</td>
<td>1.4</td>
</tr>
<tr>
<td>5</td>
<td>0.52</td>
<td>2.9</td>
<td>0.54</td>
<td>0.75</td>
</tr>
</tbody>
</table>
theoretically improve charge transport and charge separation in OPV. However, when 4-8d was added to the P3HT/ PC_{61}BM system, an overall decrease in the cell function was achieved, mostly due to a reduced short circuit current (Table 4.3). In order to analyse the loss in performance (in P3HT/ PC_{61}BM system) and whether FRET or the exciplex formations have any effect on the cell performance, P3HT/F-TES-ADT/4-8d ternary blend was also studied.\textsuperscript{128}

Table 4.4 Summary of the figure of merits for P3HT: 4-8 (1:1) + n wt\% F-TES-ADT BHJ blends and the major peaks observed in their photoluminescence spectra.

<table>
<thead>
<tr>
<th>ADT-TES-F</th>
<th>Wavelength of different PL peaks</th>
<th>V_{OC} (V)</th>
<th>J_{SC} (10^{-2} mA)</th>
<th>FF</th>
<th>PCE (10^{-3} %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>900 (major) nm</td>
<td>0.8</td>
<td>1</td>
<td>0.16</td>
<td>1</td>
</tr>
<tr>
<td>2%</td>
<td>625, 700, 900 (major) nm</td>
<td>0.72</td>
<td>5</td>
<td>0.22</td>
<td>5.2</td>
</tr>
<tr>
<td>5%</td>
<td>580, 625, 900 (major) nm</td>
<td>0.72</td>
<td>2.7</td>
<td>0.22</td>
<td>4</td>
</tr>
<tr>
<td>10%</td>
<td>580 (major), 625, 900 (major) nm</td>
<td>0.75</td>
<td>5</td>
<td>0.21</td>
<td>7.2</td>
</tr>
<tr>
<td>20%</td>
<td>680 nm</td>
<td>0.52</td>
<td>5</td>
<td>0.26</td>
<td>7</td>
</tr>
</tbody>
</table>

The photoluminescence spectrum peaks of the ternary blend (P3HT: 4-8d: F-TES-ADT), summarized in Table 4.4, shows several different interactions in the active layer blend. At very low concentration of added F-TES-ADT (2 wt\%) the dominant photoluminescence (900 nm) matches the P3HT/4-8d exciplex energy. The J_{SC} for this blend is very low (0.05 mA) as well as the PCE (5.2 \times 10^{-3} \%). Upon increasing the concentration of F-TES-ADT to 5\% there was a quick decrease in the photogenerated current (0.027 mA) as well as the PCE (4 \times 10^{-3}\%) that accompanies the increase in the photoluminescence intensity of the P3HT/ F-TES-ADT exciplex (900 nm). By increasing the concentration of added F-TES-ADT we notice the decrease of the peak at 900 nm and the developing of the peak at 680 nm, which correspond to the F-TES-ADT/4-8d exciplex while J_{SC} and PCE remain almost constant. Therefore, our collaborators concluded that F-TES-ADT/4-8d, P3HT/4-8d exciplexes display a negative effect on the short circuit current as well as the PCE of binary and ternary BHJ solar cells, showing that these types of complexes are not conducive for efficient photo-induced charge separation.
Although 4-8d has shown high solubility, controlled crystal packing, and compatible HOMO/LUMO energies, the inability to form uniform thin films (low viscosity), along with their lack of charge separation and charge transport ability (due to exciplex formation) render these molecules unusable for BHJSC applications.

4.2 Dimerization of tetraceno thiophene derivatives

BHJ OPV Blends are usually spun casted to make the active layer. With small molecules, spin casting doesn’t usually give high film uniformity. This is due, to a high extent, to the low degree of viscosity that the solution of small molecular weight materials possesses. Polymers on the other hand make very good films when spin casted. However, their poor solubility in organic solvents and loss of mobility upon functionalization has motivated us to investigate new type of molecules as semiconductors. I hypothesized that by increasing the molecular weight of our small molecules I can change its physical properties in solution, which should lead to better films from spin casting. Different alkylsilyl ethynyl substituted tetraceno thiophene were employed to generate dimers via homo-coupling reactions resulting in materials with high intermolecular order, beneficial for good charge transport mobility.

It was very challenging to apply dimerization to ADT derivatives because of their highly active sites at the two and eight position in the ADT chromophore, which led to polymerization instead. Tetraceno thiophene derivatives (4-15) are isostructural and isoelectronic with ADTs with only one thiophene ring in the chromophore (one active site), making it an ideal candidate for homo-coupling reactions. The synthesis begins with the iodination of 4-4 in chloroform to yield 4-9, which was then reacted with 4-12 via aldol condensation leading to the quinone 4-13 in a 95% yield. 4-12 was obtained via a series of reduction reactions, beginning with 4-10 that was reduced using NaBH₄ and quenched with HCl in methanol to yield 87% of 4-11. Another reduction reaction was applied to 4-11 using sodium thiosulfate in dioxane and water to yield 98% of 4-12. Addition of lithiated silylacetylenes to 4-13, followed by deoxygenation with SnCl₂/ HCl gave 4-14. Homocoupling via a palladium catalyzed reaction employing stannous compounds was applied to 4-14, and generated the final product 4-15 in decent yields.
Scheme 4.2 Synthesis of tetracenothiophene (4-15) derivatives.

The crystal packing was only resolved for 4-15b which was recrystallized via slow evaporation technique using toluene as solvent. Unfortunately, the structure was not completely refined due to low crystal quality, but it did however give an idea about the crystal packing. Many attempts were applied to solve the crystal structure of the other 4-15 derivatives using slow evaporation technique from 1,2-dichloroethane, Toluene, chlorobenzene, and dichlorobenzene without any success.
Figure 4.10(a) crystal structure of 4-15b, the sec-butyl groups and protons of 4-15b are hidden for more clarity in b, c and d. (b) Shows the twisting in the silylacetylene portion of the molecule 2.41° twist (red circle), and 11.45° twist (blue circle). This could be a result of steric hindrance between the molecules of the same stack. (c) Side view along the long axis of the molecule with the blue arrow showing the steric interaction between the silylacetylene groups that could have potentially caused the twisting. (d) Side view along the short axis of the molecule showing another angle for the twist in the acetylene part of the molecule.
Figure 4.11 **4-15b** packs in a pseudo-sandwich herringbone look with the silylacetylene groups interacting with each other. As a result, orbital overlapping between molecules of different stacks is non-existent.

Figure 4.12 **4-15b** viewed perpendicular to the plane of the ring system, and shows the π-stacking with distances as close as 3.42Å.

Figure 4.13 Thin films optical microscopic pictures of **4-15** derivatives. **4-15b** shows some degree of uniformity compared to the other two derivatives. By Anna K. Hailey
TIPS-pentacene has been used before in BHJ solar cells as a donor material and showed PCE of 0.5% with PC$_{61}$BM (as the acceptor molecule). However, TIPS-pentacene reacts with PC$_{61}$BM (Figure 4.15) via Diels-Alder reaction creating a complex with very poor charge transfer properties that negatively affect its solar cell performance. 4-15 shows a little to no reaction with PC$_{61}$BM (Figure 4.15) while having energy levels that are compatible with PC$_{61}$BM (Figure 4.14) making it a suitable candidate to be studied as a donor molecule in 4-15/PC$_{61}$BM BHJ solar cell.
4.2.1 Device studies

Table 4.5 Summary of the figure of merits for conventional BHJ solar cell of 4-15b/ PC61BM at different concentration ratios.

<table>
<thead>
<tr>
<th>blend</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>PCE (%)</th>
<th>$R_s$ (Ω)</th>
<th>$R_p$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60:40</td>
<td>0.19</td>
<td>0.0001</td>
<td>0.26</td>
<td>0.0001</td>
<td>5900</td>
<td>50000</td>
</tr>
<tr>
<td>50:50</td>
<td>0.2</td>
<td>0.1</td>
<td>0.27</td>
<td>0.008</td>
<td>1900</td>
<td>14000</td>
</tr>
<tr>
<td>40:60</td>
<td>0.23</td>
<td>0.15</td>
<td>0.27</td>
<td>0.01</td>
<td>500</td>
<td>200</td>
</tr>
<tr>
<td>30:70</td>
<td>0.59</td>
<td>0.44</td>
<td>0.3</td>
<td>0.1</td>
<td>500</td>
<td>200</td>
</tr>
</tbody>
</table>

From the data summary in Table 4.5, obtained by Anna K. Hailey and the Loo group at Princeton University, we observe that concentration of 4-15b does affect the performance of the solar cell. The 30:70 4-15b/ PC61BM blend exhibits the best performance (0.1% PCE). Although, we notice a modest improvement in the $V_{OC}$ and the $J_{SC}$ of the device, the fill factor remained virtually constant. A high device series resistance and low shunt resistance could explain this observation. The high series resistance could be a result of bad film morphology for the 4-15b/PC61BM blend, due to high density of grain boundaries. Because the charge transport in small molecule BHJ is dominated by hopping, the amount of electronic overlap between the same chemically structured molecules (D/D, A/A) as well as the donor and the acceptor (D/A) molecules should have a major influence on the device fill factor (FF) and precisely the series resistance. The low shunt resistance can be explained by a current leakage due to bad exciton dissociation at the interface (geminate recombination), or the presence of traps leading to non-geminate charge recombination.

4.3 Conclusion

In conclusion, crystalline small molecules do not form uniform films because of their solution low viscosity. Addition of an inert polymer helps controlling the viscosity of the solution, but it can also affect the spacing between the molecules. However, the absence of a polymer spacer can lead to aggregation and hence bigger crystalline domains and that negatively affects the efficiency of exciton dissociation. Moreover, the distance that separates the donor and the acceptor molecules in the blend is critical. At very small distances the high intermolecular interaction facilitates exciplex formation. Exciplexes
have a negative influence on the solar cell performance because they do not dissociate easily and they tend to recombine. Additionally, increasing the molecular weight of small molecules does marginally improve the film morphology. However, the existence of the silylethynyl groups on the acene chromophore can hinder charge transfer between the donor and the acceptor molecules. In order to have a better understanding for this group of materials more studies have to be done on film morphology using electron microscopic methods. Molecular orientation on substrates is also very important since small molecules are known for their high ordering and strong orbital overlapping that leads to good charge transfer with high anisotropy, which makes controlling the molecule orientation on the substrate to be set to where the charge pathway matches the device architecture (vertical charge pathway) a necessity.

4.4 Experimental

Thiophene-2,3-dialdehyde (4-4): The procedure is d has been modified from what is reported in the previous reference. Flame dry a 250 ml round bottom flask equipped with a stir bar. To a solution of 4-2 (15.6 g, 100 mmol) in 100 ml of dry tetrahydrofurane (THF) at -78 °C, add BuLi (40 ml, 2.5M in hexane, 100 mmol) drop wise using an addition funnel. Wait 15 minutes after the addition and then add dimethylformamide (14.6g, 200 mmol) and let the reaction stir for 4 hours. The reaction was quenched with water and extracted 3 times with ethyl acetate then concentrated on high vacuum. The crude product (4-3) was taken to the next step without any further purification. In a 250 ml round bottom flask with a stir bar, mix 4-3 with 20 ml of THF and 20 ml of 10% aqueous HCl solution and let it stir while monitoring it via GCMS. After approximately 2 hours add 100ml of water to the reaction and extract three times with ethyl acetate. Dry with MgSO₄, filter, and then concentrate under high vacuum. Run a plug chromatography with 4:1 hexane/ethyl acetate. Recrystallize from (4:1) hexane: ethyl acetate to yield 78% of yellow fluffy crystals. The ¹H-NMR and ¹³C-NMR spectra were in agreement with literature data.
5-bromo-2,3-thiophenedialdehyde (4-5): 4-4 (2 g, 0.09 mmol) was dissolved in 60 mL chloroform then bromine (1.44 mL, 27.27 mmol) was added drop wise at room temperature, and the mixture was stirred overnight. Quench slowly with 5% solution of sodium thiosulfate until all bromine color is gone. Extract with dichloromethane 3 times. The mixture was dried, filtered and concentrated. The crude mixture was purified using silica chromatography with 4:1 hexane/EtOAc. Recrystallize from hexane/EtOAc mixture to get 2 g (64%) of yellow crystals 4-5. The 1H-NMR and 13C-NMR spectra were in agreement with published literature.

General procedure for making Br-ADT derivatives (4-7): Flame dry a 250 ml round bottom flask equipped with a stir bar. To a solution of 2.52g (11.24 mmol) trialkylsilylacetylene in 20 ml of heptane, add 4.38ml (2.5M in hexane, 10.96 mmol) BuLi drop wise at -78 °C and let the reaction stir. After one hour add 1g (2.81 mmol) 4-6 and then add another 50 ml of heptane and allow the reaction to stir overnight. The next day quench the reaction with water and extract with ethyl acetate, then dry with MgSO₄ and concentrate under high vacuum. Run the crude product through a silica gel plug using hexanes to get rid of the excess of the trialkylsilylacetylene then with 1:1 (hexane:DCM) to recover the dibromo-dialkylsilylethynylanthradithiophene diol intermediate. The diol was then dissolved in 200 ml of THF and 20 ml of 10% HCl solution containing 6g of SnCl₂·2H₂O and stir the solution for 30 minutes. Extract with hexanes (3 times), dry with MgSO₄, filter and concentrate. Run another fast plug chromatography with hexane to yield pink solid. 4-7 was used in the next step without recrystallization.
2,8-dibromo-5,12-bis(tri-iso-butylsilyl)anthra[2,3-b;6,7-b']dithiophene (4-7a): yield = 62%. MP: 240 °C. $^1$H NMR (400MHz, CDCl$_3$) $\delta$: 8.96 (s, 2H), 8.92(s, 2H), 7.38 (s, 2H), 2.07(m, 6H), 1.17(d, $J = 6.59$ Hz, 36H), 0.96(d, $J = 6.96$ Hz, 12H) ppm. $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 173.5, 141.2, 141.1, 140.3, 140.2, 130.7, 130.3, 130.2, 126.9, 120.9, 120.8, 120.2, 120.1, 119.8, 119.7, 118.4, 117.3, 109.9, 109.6, 109.3, 104.2, 104.1, 102.6, 26.9, 26.8, 25.9 ppm.

2,8-dibromo-5,12-bis(tri-sec-butylsilyl)anthra[2,3-b;6,7-b']dithiophene (4-7b): yield = 54%. MP 260°C. $^1$H NMR (400MHz, CDCl$_3$) $\delta$: 8.98(s, 2H), 8.95(s, 2H), 7.42 (s, 2H), 2.0 (m, 6H), 1.98 (m, 12H), 1.33 (d, $J = 7.32$ Hz, 18H), 1.13 (t, $J = 7.29$ Hz, 18H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 173.5, 141.2, 141.1, 140.2, 140.1, 130.7, 130.3, 126.8, 120.9, 120.8, 120.1, 120.0, 119.7, 119.6, 118.4, 117.3, 108.2, 107.9, 107.6, 104.4, 104.3, 104.2, 26.2, 19.8, 15.2, 14.3 ppm.
2,8-dibromo-5,12-bis(tricyclopentylsilyl)anthra[2,3-b;6,7-b’]dithiophene (4-7c): Yield = 37%. $^1$H NMR (400MHz, CDCl$_3$): $\delta$ 8.91(s, 2H), 8.90(s, 2H), 7.37 (s, 2H), 1.79(m, 6H), 1.115(m, 24H), 0.9(m, 24H) ppm. $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 169.5, 140.2, 139.1, 139, 138.7, 130.7, 129.8, 126.2, 120.3, 120.1, 120, 119.9, 119.7, 119, 118, 117.1, 107.9, 107.1, 107, 104.9, 104.1, 103.9, 29.1, 26.9, 23.5 ppm.

General procedure for making 2,8-dicyano-5,12-bis(trialkylsilylethynyl)anthra[2,3-b;6,7-b’]dithiophene CN-ADT derivatives (4-8): In a flame dry round bottom flask equipped with a stir bar, dissolve 4-7 (0.5g, 0.649 mmol) in dry DMF (1ml/0.1mmol). Add (0.304 g, 2.59 mmol) of Zn(CN)$_2$ to it and purge it with nitrogen (1min/ml), then add (75 mg, 0.0649 mmol) of Pd(PPh$_3$)$_4$ and purge for another 2 minutes before you place the flask in an oil bath and let it stir overnight at 110 °C. Take the flask out of the oil bath and let it cool down to room temperature then add water to it until the product crushes out. Filter with water. Run chromatography (plug) with 3/1 (hexane/DCM) as the eluent to separate the monocyano-substituted byproduct and other impurities. Concentrate and recrystallize from 1,2-dichloroethane to obtain pure violet solid compound (4-8).

2,8-dicyano-5,12-bis(tri-iso-butylsilylethynyl)anthra[2,3-b;6,7-b’]dithiophene (CN-TIBS-ADT) (4-8a): Yield = 68%. $^1$H NMR(400MHz, CDCl$_3$) $\delta$: 9.25(s, 2H), 9.24(s, 2H), 8.00(s, 2H), 2.12(m, 6H), 1.115(d, J= 6.96 Hz, 36H), 0.96 (d, J= 6.56Hz, 12H) ppm. $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 142.7, 140.3, 138.3, 138, 136.9, 132, 131.4, 131, 129.5, 125.9,
2,8-dicyano-5,12-bis(tri-sec-butyilsilyl)anthra[2,3-b;6,7-b’]dithiophene (4-8b): Yield = 52\%. MP 310°C. $^1$H NMR (400MHz, CDCl$_3$) $\delta$: 9.32 (s, 2H), 9.22 (s, 2H), 8.07 (s, 2H), 2.01 (m, 6H), 1.50 (m, 12H), 1.28 (d, $J = 7.32$ Hz, 18H), 1.13 (t, $J = 7.29$ Hz, 18H) ppm. $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 139.7, 139.3, 138.3, 138, 135.9, 131.9, 131.4, 131, 130.5, 125.5, 125.3, 121.6, 121.1, 120.9, 119.5, 117.5, 114.5, 113.6, 113.4, 110.5, 109.9, 109.3, 103.4, 103.5, 26.1, 19.6, 15.1, 14.3 ppm.

2,8-dicyano-5,12-bis(tricyclopentylsilyl)anthra[2,3-b;6,7-b’]dithiophene (4-8c): Yield = 33\%. $^1$H NMR (400MHz, CDCl$_3$) $\delta$: 9.36 (s, 2H), 9.28 (s, 2H), 8.10 (s, 2H), 2.01 (m, 12H), 1.72 (m, 36H), 1.29 (m, 6H) ppm. $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 140.2, 139.1, 138.1, 138, 136.2, 131.8, 131.4, 131, 129.9, 125.1, 124.7, 121.2, 121, 120.6, 119, 118.5, 114.1, 113.9, 113.4, 109.5, 109.3, 102.9, 102.5, 29.7, 26.7, 23.2 ppm.
5-iodo-2,3-thiophene dialdehyde (4-9): 4-9 was synthesized following the same procedure in ref.

1,4 Anthracenedione (4-11): In a 500 ml round bottom flask dissolve Quinizarin (4-10) (10g, 240 mmol) in 200 ml of methanol and cool it down to 0°C. Purge the solution with nitrogen for 30 minutes and start adding NaNH₄ (6.3g, 166.4 mmol) slowly. Let the reaction stir for an hour. Quench the solution slowly at 0°C with 120 ml of 6M HCl. Once done, filter the solid and wash it with water, and let it dry overnight. Purify using silica plug with DCM as the solvent. Evaporate the solvent to yield 87% of pure orange crystals. 

^1^H-NMR (400 MHz, CDCl₃): δ 8.64 (s, 2H) 8.08 (m, 2H), 7.71 (m, 2H), 7.08 (s, 2H), ppm. 

^13^C-NMR (100 MHz, CDCl₃): δ 184.7, 140.1, 134.8, 130.2, 129.6, 128.9, 128.3 ppm.

1,4-dihydroxyanthracene (4-12): Purge a solution of 50ml: 50ml dioxane: water with nitrogen for one hour than add 4-11 (2.6g, 12.5mmol), and Sodium dithionite (Na₂S₂O₄) (8.7g, 50mmol) and let the reaction stir overnight. Purge 300ml of water and 300ml of ether with nitrogen for one hour. Add to the reaction 100ml of water and 100ml of ether and transfer the solution to an extraction funnel. Extract with ether, dry with MgSO₄, Filter it out, and then concentrate under vacuum to yield 98% yellow solid, which was kept under vacuum. 

^1^H-NMR (400 MHz, DMSO-d₆): δ 9.56 (s, 2H), 8.67 (s, 2H), 8.08 (m, 2H), 7.46 (m, 2H), 6.62 (s, 2H), ppm. 

^13^C-NMR (100 MHz, DMSO-d₆): δ 145.3, 130.4, 128.3, 125.2, 120.6, 105.5 ppm.
2-iodotetraceno [2,3-b] thiophene-5, 12-dione (4-13): Dissolve 4-9 (1g, 3.76 mmol), and 4-12 (394.8g, 1.88 mmol) in 1:1 ethanol: THF (5ml: 5ml). Heat the flask up to make sure everything dissolved then add couple drops of 15% KOH and let the reaction stir for 30 minutes. Filter the solid using methanol, then wash it with ether to obtain 95% of 4-13 (yellow solid). (MALDI, TCNQ matrix) m/z 440 (100%, M⁺).

General procedure for making I-tetracenothiophene derivatives (4-14): Flame dry a 250 ml round bottom flask equipped with a stir bar. To a solution of (9.09 mmol) alkylsilylacetylene in 20 ml of heptane, add (3.54ml, 2.5M in hexane, 8.86 mmol) BuLi drop wise at -78 °C and let the reaction stir. After one hour add (1g, 2.27 mmol) 4-13 and then add another 50 ml of heptane and allow the reaction to go overnight. The next day Quench the reaction with water and extract with ethyl acetate, dry with MgSO₄ and concentrate under high vacuum. Run the crude product through a silica gel plug using hexane to get rid of the excess of the alkylsilylacetylene then with 1:1 (hexane:DCM) to recover the I-dialkylsilylethynyltetracenothiophene diol intermediate. The diol was then dissolve in 200 ml of THF and 20 ml of 10%HCl solution and 6g of SnCl₂.2H₂O and stir the solution for 30 minutes. Extract with hexanes (3 times), dry with MgSO₄, filter and concentrate. Run another fast plug chromatography with hexane.
2-iodotetraceno [2,3-b] thiophene-5, 12-tri-iso-butyldisilylethynyl (4-14a): Yield = 72%.
MP: 165 °C. $^1$H NMR (400MHz, CDCl$_3$) δ: 9.28 (s, 1H), 9.26 (s, 1H), 9.03 (s, 1H), 8.99
(s, 1H), 8.01 (m, 2H), 7.63 (s, 1H), 7.47 (d, J= 9.54 Hz, 2H), 2.12 (m, 6H), 1.115 (d, J=6.96
Hz, 36H), 0.96 (d, J=6.56Hz, 12H). $^{13}$C-NMR (100 MHz, CDCl$_3$): δ 143.3, 140.9, 133.6,
132.2, 132.1, 130.4, 130.3, 130.2, 130, 128.5, 128.4, 126.2, 126.1, 126, 125.9, 119.8, 118.9,
118.5, 117.5, 111.5, 109.6, 109.1, 104.2, 104.1, 84.17, 26.5, 26.4, 25.4 ppm.

![4-14a](image)

2-iodotetraceno [2,3-b] thiophene-5, 12-tri-sec-butyldisilylethynyl (4-14b): Yield = 68%.
MP: 200 °C. $^1$H NMR (400MHz, CDCl$_3$) δ: 9.33 (s, 1H), 9.31 (s, 1H), 9.06 (s, 1H), 9.03
(s, 1H), 8.02 (dd, J=5.88 Hz, J= 3.50 Hz, 2H), 7.66 (s, 1H), 7.48 (m, 2H), 2.04 (m, 6H),
1.48 (m, 12H), 1.32 (d, J = 7.29 Hz, 18H), 1.11 (t, J = 7.30 Hz, 18H) ppm. $^{13}$C-NMR (100
MHz, CDCl$_3$): δ 172.9, 143.3, 140.9, 133.7, 132.2, 132.1, 130.4, 130.3, 130, 128.5, 128.4,
126.2, 126.1, 126, 125.9, 119.8, 118.9, 118.5, 117.5, 111.5, 107.9, 107.5, 104.3, 104.2,
84.1, 25.7, 19.3, 14.7, 13.8 ppm.

![4-14b](image)

2-iodotetraceno [2,3-b] thiophene-5, 12-tri-cyclopentylsilyldisilylethynyl (4-14c): Yield = 55%.
$^1$H NMR (400MHz, CDCl$_3$) δ: 9.31 (s, 1H), 9.22 (s, 1H), 8.99 (s, 1H), 8.99 (s, 1H), 8.99
(s, 1H), 8.04
(dd, J=5.81 Hz, J= 3.39 Hz, 2H), 7.61 (s, 1H), 7.51 (m, 2H), 2.03 (m, 12H), 1.78 (m, 36H), 1.35 (m, 6H) ppm. $^{13}$C-NMR (100 MHz, CDCl$_3$): δ 172.1, 143.8, 140.5, 133.4, 132.6, 132.3, 130.9, 130.1, 129.9, 128.2, 128.4, 126.2, 126.1, 126, 125.9, 119.8, 118.9, 118.5, 117.5, 111.5, 107.9, 107.5, 104.3, 104.2, 84.1, 29.6, 26.8, 23.5 ppm.

5, 12-triisobutylsilyylethynyl Tetraceno [2,3-b] thiophene dimer (4-15a): In a flame dried 100 ml round bottom flask equipped with a stir bar, dissolve 4-14a (300mg, 0.351mmol) in 10 ml of dry toluene. Purge the solution for 15 minutes then add Pd(PPh$_3$)$_4$ (40 mg, 0.0351mmol), hexamethylditin (38mg, 0.117 mmol), and the solution was stirred at 100 °C overnight using a condenser. Evaporate the solvent then run a silica gel plug using 150 ml of hexane to get rid of excess hexamethylditin. The product was then eluted with 3:1 hexane:DCM to obtain the pure product which was recrystallized in 1,2 dichloroethane to yield 65% green powder. The same procedure was followed to make 4-15b, and 4-15c.

4-15a: Yield 65%. MS (MALDI, DHB matrix) m/z 1455 (M$^+$). $^1$H NMR (400MHz, CDCl$_3$): δ 9.27 (d, J= 3.50 Hz, 2H), 9.05 (s, 1H), 9.01 (s, 1H), 7.97 (dd, J = 4.41-2.37, 2H), 7.52 (s, 1H), 7.36 (dd, J = 6.71-2.70, 2H), 2.25 (m, 6H), 1.23 (d, J = 6.54 Hz, 36H), 1.15 (d, J = 6.56 Hz, 12H) ppm. 141.3, 140.2, 139.9, 133, 132.9, 131.6, 131.5, 131.1, 131,
4-15b: Yield 60%. MS (MALDI, DHB matrix) m/z 1256 (M+). \(^1\)H NMR (400MHz, CDCl\(_3\)): \(\delta\) 9.29 (d, J = 3.50 Hz, 2H), 9.06 (s, 1H), 9.01 (s, 1H), 7.98 (dd, J = 4.71Hz, J= 2.30 Hz, 2H), 7.60 (s, 1H), 7.43 (dd, J = 5.71Hz, 2.90 Hz, 2H), 2.02 (m, 6H), 1.56 (m, 12H), 1.35 (t, J = 6.74 Hz, 18H), 1.16 (d, J= 7.25 Hz, 18H) ppm. \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) 140.5, 139.4, 139.1, 133.5, 132.2, 132.1, 130.9, 130.7, 130.6, 130.3, 130.2, 128.5, 128.4, 126.3, 126.2, 126.1, 126.0, 122.6, 122.1, 120.1, 119.6, 107.3, 104.4, 104.3, 25.7, 19.3, 14.7, 13.9 ppm.

4-15c: Yield 45%. \(^1\)H NMR (400MHz, CDCl\(_3\)): \(\delta\) 9.31 (d, J= 3.50 Hz, 2H), 9.12 (s, 1H), 9.06 (s, 1H), 7.95 (dd, J = 4.71 Hz, J= 2.30 Hz, 2H), 7.55 (s, 1H), 7.41 (dd, J = 5.71Hz, J= 2.90 Hz, 2H), 2.01 (m, 12H), 1.79 (m, 36H), 1.38 (m, 6H) ppm. \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) 141.5, 139.9, 139.1, 133.7, 131.8, 132.2, 130.6, 130.3, 130.1, 130, 129.1, 128.5,
128.1, 126.5, 126.1, 125.9, 125.7, 122.3, 122.1, 120.5, 119.2, 106.9, 104.8, 104.1, 29.5, 26.3, 23.6 ppm.
Chapter 5 Singlet fission in anthradithiophene derivatives

5.1 Singlet fission in TES-ADT & F-TES-ADT

Singlet fission (SF) has gained a lot of attention recently as a potential phenomenon that can be exploited in organic photovoltaics.\textsuperscript{134, 135} It is a mechanism that generates multiple electrons from one absorbed photon. Acenes have been frequently reported to demonstrate such abilities, mainly due to their triplet energy level laying half way between that of the ground state and the singlet excited state, as stated in chapter one. Anthradithiophenes (ADT) are isoelectronic and isostructural analogues of pentacene. Previous studies have demonstrated that sulfur atoms can improve orbital overlap due to a d-\(\pi\) wave function overlap between sulfur and carbon atoms.\textsuperscript{37, 38} Additionally, TES-ADT and F-TES-ADT (Figure 5.1) crystallize in a 2-D \(\pi\)-stacking motif with high degree of orbital overlap, and strong electronic couplings.\textsuperscript{51} Since intermolecular forces are believed to have an impact on SF, studying such correlations using ADT derivatives that possess different crystal packing styles, can offer some insights on SF’s poorly understood mechanism.

![Top view of crystal packing of F-TES-ADT (top left) with its normalized absorbance spectra: in solution (blue)/ thin film (grey) (bottom left). Top view of TES-ADT crystal packing (top right) with its normalized absorbance spectra: in solution (blue)/ in thin film (grey) (bottom right).](image)

Figure 5.1
The F-TES-ADT crystal structure reveals intermolecular contacts as close as 3.38Å and a plane-to-plane distance of 3.04Å. TES-ADT on the other hand, displays a close intermolecular contact of 3.21 Å and a plane-to-plane distance of 2.89Å. These numbers suggest that TES-ADT molecules acquire stronger orbital overlap than F-TES-ADT. As a result, the absorbance spectra of F-TES-ADT display a 733 cm⁻¹ redshift between solution absorbance spectrum in toluene and thin film absorbance spectrum (Figure 5.1). Similarly, TES-ADT reveals an even larger redshift of 752 cm⁻¹ (Figure 5.1) between its solution absorbance spectrum in toluene and thin film absorbance spectrum.

To test singlet fission in TES-ADT and F-TES-ADT, our collaborators, Dr. Chaw Keong Yong from the Cavendish Laboratory at the University of Cambridge, applied transient absorption (TA) measurements on thin films of TES-ADT and F-TES-ADT. TA, also known as flash spectroscopy, is a pulse-probe measurement applied on organic semiconductor thin films. The thin film gets irradiated with a short pulse (femtosecond) of high intensity laser light, which excites a molecule from its ground state to an excited (higher energy) state. This is followed by a probing light source that measures the absorption spectra of the molecule, while in the excited state, at various times after the excitation. Overall, TA is the observation of short-lived species in the absorption spectra of an excited molecule at different times following the excitation. TA measurements were completed on spin casted (SC), and zone casted (ZC) thin films of F-TES-ADT, and zone casted (ZC), spin casted (SC), and drop casted (DC) films of TES-ADT (Figure 5.2). These films were excited at wavelength between 800-1020 nm followed by monitoring the population of triplets in their transient absorption spectra (Figure 5.2).

It was demonstrated that by using solvents with different polarities we could control the morphology and the type of polymorphs generated in TES-ADT thin films. For instance spin casting TES-ADT from non polar solvents like toluene, and hexane will generate selectively the β-phase polymorph.¹³⁶ However, spin casting or drop casting TES-ADT from polar solvents, suchlike tetrahydrofuran, will generate the α-phase polymorphs.¹³⁶ As illustrated in Figure 5.2, the β-phase polymorph exhibits higher singlet fission rate than α-phase polymorph. This indicates certain correlation between film morphology and singlet fission rate. Additionally, recent efforts by Prof. Stingelin at Imperial College demonstrate
that the α-phase of TES-ADT retains a close intermolecular contact of 3.38 Å compared to close intermolecular contact of 3.21 Å calculated for TES-ADT (single crystal). The α-phase also exhibits a smaller slip along the long axis (3.08 Å for the α-phase vs. 3.23 Å for TES-ADT single crystal), as well as a smaller short axis slip (1.73 Å for the α-phase vs. 1.99 Å for TES-ADT single crystal).\textsuperscript{137} Unfortunately, the β-phase intermolecular distances and geometry in the unit cell are still unknown, however we know that the β-phase has a triclinic unit cell (just like the single crystal and the α-phase unit cell) with a density similar to that of the TES-ADT single crystal.\textsuperscript{137} Additionally, the β-phase polymorph of TES-ADT demonstrates the highest charge transport capability (mobility of 0.22 cm\(^2\)/Vs for the β-phase vs. 0.06 cm\(^2\)/Vs for the α-phase).\textsuperscript{136} Close intermolecular contacts, as well as high charge transfer proficiency suggest the existence of stronger orbital overlapping in the β-phase polymorph compared to other TES-ADT polymorphs.\textsuperscript{137} Considering the β-phase TES-ADT polymorph displays a higher singlet fission rate than that of the α-phase TES-ADT and F-TES-ADT films, we hypothesized that closer π-π overlapping expedites higher ordered molecular aggregation that could have a decisive impact on improving singlet fission rate.\textsuperscript{138}

Figure 5.2 Transient absorption summary diagram that illustrates the different singlet fission rate of the studied molecules (TES-ADT, F-TES-ADT, and F2-EHT-ADT or 5-4) extracted at wavelength between 800 and 1020 nm. Figure made by Chaw Keong (University of Cambridge).
As reported by literature, high intermolecular forces have proven to be crucial in guaranteeing higher long-range order in crystal packing.\textsuperscript{138} Such forces can potentially lead to better exciton delocalization, which is accredited as a potential cause for enhanced singlet fission rate (Figure 5.2).\textsuperscript{138} Furthermore, to prove the relationship between thin film morphology and singlet fission rate, Dr. Keong fabricated different F-TES-ADT films using different methods (zone casting and spin casting). Zone casted F-TES-ADT films produced Nano-ribbon films (Figure 5.3), while the spin casted F-TES-ADT produced small crystallites (Figure 5.3).

\textbf{Nano-ribbons (ZC) \hspace{1cm} Crystallites (SC)}

![Nano-ribbons](image1) \hspace{1cm} ![Crystallites](image2)

Figure 5.3 Optical microscopic figures of nano-ribbons F-TES-ADT thin film obtained via zone casting vs. crystallites F-TES-ADT thin film obtained via spin casting. Figures taken by Chaw Keong (University of Cambridge).

As expected, zone casted F-TES-ADT thin film demonstrates higher triplet generation rate as a result of high ordering obtained with nano-ribbon thin films (Figure 5.4). High ordered films facilitate charge transfer, which lead to higher exciton delocalization and thus improves singlet fission rate. On the other hand, small crystallites in spin casted F-TES-ADT films generate high amount of grain boundaries (Figure 5.3) that hinders exciton delocalization, and as a result the singlet fission rate is reduced (Figure 5.4).
Figure 5.4 Temporal evolutions of singlet and triplet photoinduced absorption features for nano-ribbons F-TES-ADT (ZC) and crystallites F-TES-ADT (SC). These data were taken as the mean over the wavelengths 740 to 760 nm and 965 to 975 nm for the triplet and singlet photoinduced absorption, respectively and at a longer time delay than figure 5.2. Data collected and figure made by Chaw Keong (University of Cambridge).

5.2 Difluoro ethylhexylthienyl ADT

The electronic coupling and the intermolecular interaction of ADTs with an alkyl thiophene at the 5 and 11 position, as well as its impact on singlet fission rate was examined in molecule 5-4.

Scheme 5.1 Synthesis of F2EHT-ADT (5-4).
The synthesis of 5-4 is presented in Scheme 1 and it starts with the addition of the alkylated thiophene (5-2) to the F-ADT quinone (2-5). The isolated intermediate diol (5-3) was deoxygenated using a mixture of sodium hypophosphite and sodium iodide in acetic acid. The reaction was refluxed for an hour and the precipitate was dissolved and extracted in dichloromethane. The crude product was purified via chromatography in 95:5 (hexane: dichloromethane) and recrystallized in 1,2-dichloroethane to generate 62\% orange needle shaped crystals.

5-4 packs in a 1-D herringbone motif (Figure 5.5a) with a close intermolecular contact of 3.58 Å and a plane-to-plane distance of 3.56Å. As a result, 5-4 generates a less dense unit cell in comparison to F-TES-ADT and TES-ADT, despite the smaller slip in the molecule long axis (Figure 5.5d). The reduced aggregation was detected in 5-4 with a small red shift between its solution and thin film absorption spectra (Figure 5.6).

Figure 5.5 Crystal packing of molecule 5-4. (a) A side view along the long axis of the molecule exhibiting the herringbone motif. (b and d) A top view along the long axis displaying the crystal packing between the molecule of the same column stacks (long axis slip of 3.67 Å and 0.07 Å short axis slip). (c) HF interaction between the hydrogen of the ethylhexyl thienyl moiety and the fluorine atom.
5-4 displays slower singlet fission rate (nanosecond scale) (Figure 5.2), which harmonizes with our hypothesis and demonstrates that stronger orbital overlap has significant impact on singlet fission rate.

![Figure 5.6 Absorption spectra of molecule 5-4 (solution blue)/thin film (grey).](image)

**5.3 Alkylsilylethynyl acetylene F-ADT**

As demonstrated in Chapter 3, using halogens, more specifically fluorine, does impact the intermolecular forces of ADT molecules. This observation is also reported in literature where halogenation has proven to be an effective technique to enhance intermolecular electronic couplings and charge transport.\(^{113}\) Our group has synthesized fluorinated ADT derivatives with good solubility, and established a technique that allows us to tune the crystal packing of these derivatives by simply modifying the size of the alkylsilyl groups attached to the ADT backbone.

As mentioned previously, singlet fission depends highly on the arrangement of molecules in solid state, where the molecule orientation and displacement in the crystal packing can have a huge impact on the singlet fission mechanism.\(^{91,139}\) Therefore, in this section I attempt to investigate and understand the relationship between intermolecular interaction / crystal packing motifs/electronic coupling, and the rate of singlet fission by synthesizing a series of F-ADT derivatives with different alkylsilyl solubilizing groups, and monitor the impact of these changes on aggregation, and predominantly on singlet fission rate.
Scheme 5.2 Synthetic schemes of fluorinated F-ADT derivatives

The majority of the derivatives shown in Scheme 5.2 pack in a similar fashion (2-D stacks), which allow us to monitor and compare the effect of long and short axis slips, as well as the variations in the intermolecular contacts, on the rate of singlet fission, and deliver a more accurate understanding of the correlation between molecular ordering in the solid state, and singlet fission.

For instance 5-5 illustrates a 2-D packing motif, just like with F-TES-ADT, but with weaker orbital overlap due to a slip in the molecule packing along the long axis (7.38 Å for major overlap, see Figure 5.7, and 9.51 Å slip for the minor overlap) and the short axis (3.25 and 3.04 Å for the major and minor overlap respectively), leading to a plane-to-plane distance of 3 Å (major orbital overlap, blue circle), and 3.65 Å (minor overlap, purple circle), along with a close intermolecular contact of 3.2 Å. The thin film absorbance spectrum of molecule 5-5 displays no redshift, which can be explained by the weak intermolecular forces detected in the crystal structure (Figure 5.7).
Derivative 5-6 presents a different crystal packing, 1D sandwich herringbone motif, with less orbital overlap than F-TES-ADT. A distance of 3.27 Å separate the two adjacent planes, and a close intermolecular contact of 3.48 Å with a long axis slip of 3.67 Å and a short axis slip of 0.07. This amount of orbital overlapping was enough to generate a 138 cm⁻¹ red shift in the absorbance spectra of molecule 5-6 (Figure 5.8).
5-7 packs similar to 5-5 but with stronger orbital overlapping (Figure 5.8) overall, and a shift of 7.2 Å in the long axis and 2.1 Å short axis slip. A close intermolecular contact of 3.3 Å, and a plane-to-plane distance of 3.5 Å indicate a twist in the molecule backbone. However, a small redshift (138 cm⁻¹) in the thin film absorbance spectra of molecule 5-3 was recorded (Figure 5.9).

Figure 5.9 Top view of the crystal packing of molecule 5-7 (top left). Side view of the crystal packing of molecule 5.7 (bottom left). Absorption spectra of molecule 5-7 in solution (blue) and thin film (grey). Alkylsilyl group was deleted for more clarity.

Unfortunately I wasn’t able to get the crystal packing of molecule 5-8. However, judging by its absorbance spectra, 5-8 does not offer strong aggregation with a red shift of 242 cm⁻¹ recorded (Figure 5.10).

Table 5.1 Long and short axis slips of major and minor overlap in different ADT derivatives extracted from solved crystal structures.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Major overlap</th>
<th></th>
<th>Minor overlap</th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Long axis slip (Å)</td>
<td>Short axis slip (Å)</td>
<td>Long axis slip (Å)</td>
<td>Short axis slip (Å)</td>
</tr>
<tr>
<td>TES-ADT</td>
<td>7.84</td>
<td>1.99</td>
<td>4.79</td>
<td>3.00</td>
</tr>
<tr>
<td>F-TES-ADT</td>
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<td>1.86</td>
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<td>3.00</td>
</tr>
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<td>5-4</td>
<td>3.67</td>
<td>0.07</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5-5</td>
<td>7.38</td>
<td>3.25</td>
<td>9.51</td>
<td>3.04</td>
</tr>
<tr>
<td>5-6</td>
<td>7.20</td>
<td>2.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5-7</td>
<td>6.85</td>
<td>3.30</td>
<td>9.12</td>
<td>1.43</td>
</tr>
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</table>
Figure 5.10 Absorption spectra of molecule 5-8 in solution (blue) and thin film (grey). Alkylsilyl group was deleted for more clarity.

No singlet fission studies have been completed yet on this series of ADT derivatives.

5.4 Singlet fission in F-TES-ADT/ PC$_{71}$BM blends for OPV

Dr. Keong tested singlet fission in photovoltaics and studied the potential to harvest the generated triplets by manufacturing BHJ OPV cell of F-TES-ADT/ PC$_{71}$BM (Figure 5.11).

Figure 5.11 Representation of the energy bands presenting the energy levels of the singlet and triplet states in F-TES-ADT and the singlet state energy levels of PC$_{71}$BM.
The transient absorption spectrum expresses the triplet dissociation into free charges (Figure 5.12b). That was also confirmed with an internal quantum efficiency (IQE) of 120%. Quantum efficiency in solar cells indicates the amount of current generated upon irradiation of the cell by photons. Internal quantum efficiency however, is the ratio of the current generated to the number of photons absorbed by the cell. However, upon increasing the concentration of PC\textsubscript{71}BM the triplet dissociation decreases in the system, which could be an indication of the importance of F-TES-ADT aggregation to preserve and assure more efficient singlet fission.

Figure 5.12 (a) External quantum efficiency (EQE), and internal quantum efficiency (IQE) of F-TES-ADT/PC\textsubscript{71}BM photovoltaic cell. (b) Transient absorption measurements illustrating the relationship between the conversion of triplet population into charges (singlets) in the F-TES-ADT/PC\textsubscript{71}BM photovoltaic cell, a proof of singlet fission. Data collected and figures made by Chaw Keong (University of Cambridge).

F-TES-ADT/PC\textsubscript{71}BM cell demonstrates a PCE of 0.98% with a V\textsubscript{OC} of 0.7V and a J\textsubscript{SC} 0.3 mA. This demonstrates the successful usage of singlet fission and proves that SF can be a useful tool to improve OPV efficiency (Figure 5.13).
Figure 5.13 I-V curve of F-TES-ADT/ PC71BM photovoltaic cell. Chaw Keong (University of Cambridge).

5.5 ADT dimers for intramolecular singlet fission

Most singlet fission studies are done in solid state where intermolecular forces have the major impact on SF.\textsuperscript{93} For efficient SF the singlet excited state of a photoexcited chromophore must be able to share its energy with a neighboring ground-state chromophore. Friend and coworkers were able to demonstrate, with a pentacene derivative, that SF can also occur in solution.\textsuperscript{140} Moreover, Tykwinski and coworkers demonstrated singlet fission reaching a triplet quantum yields as high as 156\% using pentacene dimers in solution.\textsuperscript{141} In an attempt to apply the same principle on ADT derivatives, I synthesized a new series of ADT dimers, with different linkages, to be investigated for intamolecular (solution) singlet fission.

The synthesis is straightforward starting with the intermediate 3-1 formed in chapter 3 (Scheme 5.3). Via nucleophilic substitution reactions, I synthesized different ADT dimers with different alkysilyl linkages. Molecule 5-9 for instance was formed using LiHMDS as a base and 1,2-bis (chlorodimethylsilyl) ethane as the linkage. The product
was purified via chromatography using 3:1 Hexane: DCM eluent. The solid was recrystallized in acetone to produce 60% needle shaped dark red crystals.

Scheme 5.3 Synthetic schemes of 5-9 and 5-10 dimers

Molecule 5-9 displays a high degree of freedom around the akylsilyl linkage (1,2-bis (chlorodimethylsilyl) ethane), allowing the monomer in molecule 5-9 to fold on itself generating some electronic couplings between the monomers of the same molecule (Figure 5.14). Although dimers possess a poor charge transfer characteristics as a result of charge trapping in the solid state,142 5-9 exhibits a good long range electronic coupling in the crystal packing with intermolecular close contact of 3.2Å between the monomers of the same molecule and 3.3Å between adjacent molecules of the same stacks (Figure 5.14).
Figure 5.14 Crystal packing of molecule 5-9 exhibiting a 2-D packing motif as seen in the side view along the long axis of the molecule (bottom left). The top view along the long axis illustrates the orbital overlapping of molecule 5-9. Ellipsoid plot of 5-9 is on the right side of the figure.

Molecule 5-10 was synthesized by reacting 3-1 with dichlorodiisopropylsilane using LiHMDS as a base (Scheme 5.3). The crude product was purified using chromatography to yield 65% orange powder. 5-10 is a much more strained molecule as a result of a fixed tetrahedral angle (approximately 109°) at the alkylsilyl linkage. Unfortunately we weren’t able to solve the crystal structure of this molecule. However, the different angle between the two monomers should give us a new data point that can be helpful while examining the correlation between the angle of the monomers and intramolecular singlet fission.

Scheme 5.4 Synthesis of molecule 5-11 via Hay-coupling.
Molecule **5-11** was synthesized using Glaser-Hay coupling with monomer **3-1** (Scheme 5.4). The crude product was purified via chromatography using hexane as the eluent followed with recrystallization from 1,2-dichloroethane to yield 50% blue thin needle shaped crystals.

![Image](image.png)

**Figure 5.15** Crystal packing of molecule **5-11**. A side view along the short axis of the molecule presents the 1-D packing motif that **5-11** possesses (top left). A top view along the short axis of **5-11** displays the orbital overlapping between the molecules. Ellipsoid plot of molecule **5-11** is also given (right).

X-ray crystallography of molecule **5-11** reveals isolated pair stacking with strong orbital overlap between the monomers (Figure 5.15). **5-11** presents another unique geometry with 0° angle between the monomers, which produces a flat molecule.

Although, all three dimers are made with the same monomer, the different linkages give us different angles within the dimers, which allow us to observe the effect of these angles on singlet fission (in solution). At this point none of these dimers have been studied for singlet fission.
5.6 Experimental

2-Ethylhexylthiophene (5-2): In a 500 ml flame dried round bottom flask equipped with a stir bar, dissolve thiophene (5-1) (20g, 238mmol) in 200 ml of dry THF. Cool the reaction down to -78°C. Add the n-BuLi (31ml, 77.35 mmol) drop wise using a dried addition funnel. Let the reaction stir at -78°C for 30 minutes then let it warm up to room temperature for 30 minutes before adding 2-ethylhexylbromide (13.8g, 71.4 mmol) and heat the reaction up at reflux overnight. Quench with water, extract with hexane, dry it out using MgSO4, and concentrate under high vacuum. The crude product was distilled under vacuum at 80°C to yield 68% of colorless oil (5-2). GC-MS (EI) m/z 196 [M+]. Characterization for the compound has been published.143

5-3: Dissolve ethylhexylthiophene (5-2) (566mg, 3.37 mmol) in 20 ml of dry ether in a 250 ml flame dried round bottom flask equipped with a stir bar. Cool the flask down to 0°C and add n-BuLi (1.3ml, 3.26mmol) drop wise. Let the solution warm up to room temperature before placing it in an oil bath at 50°C for 2 hours. The F-ADT quinone (2-5) was then added with 200ml of dry ether. The reaction was then stirred overnight until all is clear. Quench the reaction with water and extract with ether. MgSO4 was then added as a drying agent. The solution was then filtered and the solvent was removed under vacuum. The crude product was purified using chromatography with dichloromethane as the eluent to yield 75% of a white solid (5-3). The product was used in the next step without any further purification.
2,8-difluoro-5,12-bis(2-ethylhexylthienyl)anthra[2,3-b;6,7-b']dithiophene (5-4): 5-3 was dissolved in 20 ml of acetic acid, NaI (2g, 13.33mmol), and NaH2PO2.XH2O (2g, 22.73 mmol) were added and the reaction was stirred at reflux for 1 hour. The reaction was cooled down to room temperature then filtered using water and washed with methanol. The crude product was then purified via chromatography using 95:5 (Hexanes: Dichloromethane) as the eluent to yield 42% of orange powder (8). Recrystallization was accomplished in 1,2-dichloroethane to yield 60% of orange needle shaped crystals. MP 170 °C. MS (MALDI, DHB matrix) m/z 714 (M+). ¹H NMR (400MHz, CDCl₃): δ 8.96 (d, JHF = 7.86 Hz, 1H), 8.88 (s, 1H), 8.85 (s, 1H), 7.85 (d, J = 11.71 Hz, 2H), 7.74 (d, J = 11.7 Hz, 2H), 7.34 (s, 2H), 3.65 (m, 1H), 3.20 (m, 1H), 2.29 (m, 1H), 2.09 (m, 7H), 1.89 (m, 2H), 1.64 (m, 5H) ppm. ¹³C-NMR (100 MHz, CDCl₃): δ 166.9, 166.8, 163.9, 146.6, 145.6, 143.1, 137.2, 137.1, 136.9, 136.4, 136.2, 136.1, 135.5, 135.4, 135.3, 132.7, 129.7, 129.6, 129, 126.4, 125.2, 120, 119.7, 117.3, 116.7, 102.4, 41.5, 34.4, 32.5, 32.1, 31, 30.5, 30.16, 28.9, 25.9, 23.11, 23, 14.2, 14, 1, 14, 12.9, 10.9 ppm.

General procedure for the synthesis of compound 5-1,2,3,4: Flame dry a 250 ml round bottom flask equipped with a stir bar. To a solution of 11.24 mmol trialkylsilylecetylene in 20 ml of heptane, add 4.38ml (2.5M in hexane, 10.96 mmol) BuLi drop wise at -78 °C and let the reaction stir. After one hour add (1g, 2.81 mmol) of 4-6 followed with 50 ml of heptane and allow the reaction to stir overnight. The next day quench the reaction with
water and extract with ethyl acetate, then dry with MgSO4 and concentrate under high vacuum. The crude product was purified using chromatography with 9:1 hexane: DCM.

![Tricyclohexylsilylacetylene](image)

Tricyclohexylsilylacetylene was synthesized following the literature procedure.\textsuperscript{112}

![Tert-butyldiphenylsilylacetylene](image)

Tert-butyldiphenylsilylacetylene was synthesized following literature procedure.\textsuperscript{144}

\begin{align*}
2,8\text{-difluoro-5,12-bis(tricyclohexylsilylethynyl)anthra[2,3-b;6,7-b']dithiophene (5-5):} & \\
\text{recrystallized from 1,2-dichloroethane to produce 50% of orange crystals. MS (MALDI,} & \\
\text{DHB matrix) m/z 926 (M\textsuperscript{+}).} & \\
\text{\textsuperscript{1}H NMR (400MHz, CDCl3/CS2 (1:3)):} & \\
\delta & 8.92 \text{ (s, 2H), 8.84 (s, 2H), 6.74 (s, 2H), 2.04 (m, 12H), 1.86 (m, 18H), 1.35 (m, 12H), 1.19 (m, 18), 1.12 (m,} & \\
\text{6H ppm.} & \\
\text{\textsuperscript{13}C-NMR (100 MHz, CDCl3/CS2 (1:3)):} & \\
\delta & 167.5, 167.4, 164.5, 148.7, 136.6, 136.5, 133.9, 130.3, 130.07, 129.8, 129.5, 129, 125.1, 121.1, 120.9, 120.7, 120.6, 117.4, 106.4, 104.1, 102.7, 102.6, 29.2, 28.8, 27.5, 23.7 ppm.}
\end{align*}
2,8-difluoro-5,12-bis(triphenylsilylethynyl)anthra[2,3-b;6,7-b’]dithiophene (5-6): recrystallized from toluene to produce 45% orange/red crystals. MS (MALDI, DHB matrix) m/z 890 (M+). $^1$H NMR (400MHz, CDCl$_3$/CS$_2$ (1:3)): δ 8.89 (s, 2H), 8.81 (s, 2H), 7.82 (m, 12H), 7.48 (m, 18H), 6.67 (s, 2H) ppm. $^{13}$C-NMR (100 MHz, CDCl$_3$/CS$_2$ (1:3)): δ 167.7, 164.7, 137, 135.7, 134.5, 133.2, 133.1, 133, 130.5, 130.3, 130.2, 128.2, 122.7, 120.8, 120.7, 120.6, 120.5, 112.1, 111.1, 110.7, 106.7, 106.4, 104.9, 104.8, 102.7, 102.6 ppm.

2,8-difluoro-5,12-bis(tert-butyl-diphenylsilylethynyl)anthra[2,3-b;6,7-b’]dithiophene (5-7): Recrystallized from 1,2-dichloroethane to yield 50% red crystals. MS (MALDI, DHB matrix) m/z 850 (M+). $^1$H NMR (400MHz, CDCl$_3$/CS$_2$ (1:3)): δ 8.98 (s, 2H), 8.91 (s, 2H), 7.99 (m, 8H), 7.45 (m, 12H), 6.72 (s, 2H), 13.34 (s, 18H) ppm. $^{13}$C-NMR (100 MHz, CDCl$_3$/CS$_2$ (1:3)): δ 165.2, 163.2, 136.9, 135.8, 133, 132.9, 129.9, 128.1, 128, 125.7, 120.9, 120.6, 120.5, 119.9, 105.9, 105.2, 105.1, 102.7, 102.6, 27.4, 26.1 ppm.
2,8-difluoro-5,12-bis(tri-n-hexylsilylene)anthra[2,3-b:6,7-b’]dithiophene 5-8:
Recrystallized from hexane to yield 65% fibrous crystals. MP 55 °C. $^1$H NMR (400MHz, CDCl3): $\delta$ 8.93 (s, 2H), 8.84 (s, 2H), 6.80 (s, 2H), 1.62 (m, 12H), 1.48 (m, 14H), 1.34 (m, 24H), 0.9 (m, 28H) ppm. $^{13}$C-NMR (100 MHz, CDCl3): $\delta$ 167.3, 164.3, 136.5, 136.4, 130.1, 129.9, 129.6, 129.4, 129.3, 120.8, 120.7, 120.5, 120.4, 117.7, 117, 116.4, 107.9, 107.7, 107.5, 103, 102.9, 102.8, 102.6, 102.5, 102.4, 33.2, 31.7, 24.3, 22.6, 14.1, 13.5 ppm.

5-9: In a flame dried round bottom flask equipped with a stir bar, dissolve 3-1(200mg, 0.340 mmol) in 15 ml of dry THF. At room temperature, add LiHMDS (0.340ml, 1M solution in Hexane, 0.340 mmol), and 1,2-Bis(chlorodimethylsilyl)ethane (39 mg, 0.170mmol) to the solution and let the reaction stir at room temperature. After 1 hour, quench the reaction with water and extract with ethyl acetate. Dry the solution using MgSO4, filter, and concentrate. The crude product was purified using chromatography in 95:5 (hexane: DCM) eluent. The pure product was recrystallized in acetone to produce 60% red crystals. MP 198 °C. MS (MALDI, DHB matrix) m/z 1287 (M-CH$_3$)$^+$, $^1$H NMR (400MHz, CDCl3): $\delta$ 9.31 (m, 4H), 9.16 (m, 4H), 7.87 (m, 1H), 7.03 (m, 3H), 2.75 (m, 6H), 1.79 (m, 40H), 1.56 (m, 12H), 1.13 (m, 12H) ppm. $^{13}$C-NMR (100 MHz, CDCl3): $\delta$ 184.3, 182.5, 167.2, 164.2, 157.8, 154.1, 142.1, 136.5, 136.4, 133.6, 129.9, 129.2, 124.9, 120.4, 120.3, 120.2, 117.1, 116.7, 108.4, 103.6, 102.9, 102.6, 102.9, 26.8, 25.6, 25.5, 9.6 ppm.
**5-10:** In a flame dried round bottom flask equipped with a stir bar, dissolve **3-1** (200 mg, 0.340 mmol) in 15 ml of dry THF. At room temperature, add LiHMDS (0.340 ml, 1 M solution in Hexane, 0.340 mmol), and dichloro di-iso-propylsilane (31.47 mg, 0.170 mmol) to the solution and let the reaction stir at room temperature. After 1 hour, quench the reaction with water and extract with ethyl acetate. Dry the solution using MgSO₄, filter, and concentrate. The crude product was purified using chromatography in 95:5 (hexane: DCM) eluent. The pure product was recrystallized in 1,2 dichloroethane to produce 45% orange powder. MP 220 °C. MS (MALDI, DHB matrix) m/z 1256 (M⁺). ¹H NMR (400 MHz, CDCl₃): δ 9.02 (s, 3H), 8.96 (s, 1H), 8.93 (s, 1H), 8.88 (s, 3H), 7.25 (s, 1H), 6.75 (s, 3H), 2.13 (m, 6H), 1.53 (m, 12H), 1.15 (d, J = 6.56 Hz, 38H), 0.92 (d, J = 6.56 Hz, 12H) ppm. ¹³C-NMR (100 MHz, CDCl₃): δ 167.5, 165.3, 164.5, 136.8, 136.7, 134.4, 130.5, 130.3, 130.1, 130, 129.9, 120.9, 120.8, 120.6, 120.3, 118.8, 104.9, 103.7, 102.7, 102.5, 95.5, 80.1 ppm.

**5-11:** In a 100 ml round bottom flask, dissolve **3-1** (200 mg, 0.340 mmol) in 15 ml of THF, (36 mg, 0.051 mmol) Pd(PPh₃)₂Cl₂, and 0.5 ml triethylamine and let the reaction stir at 45 °C overnight. The reaction was quenched with water the next day, and extracted with ethyl acetate. The solution was dried out using MgSO₄ and the solvent was evaporated to yield a blue solid. The crude product was purified using chromatography in 95:5 (hexane: DCM), and recrystallized in 1,2 dichloroethane to yield 50% blue thin crystals. ¹H NMR (400 MHz, CDCl₃): δ 8.90 (s, 1H), 8.81 (s, 2H), 8.72 (m, 3H), 8.66 (m, 1H), 7.24 (s, 2H),
6.74 (s, 2H), 6.65 (s, 1H), 2.13 (m, 6H), 1.17 (d, J = 6.52 Hz, 36H), 0.94 (d, J = 6.85 Hz, 12H) ppm. $^{13}$C-NMR (100 MHz, CDCl3): $\delta$ 170.4, 167.7, 137.1, 136.8, 134.5, 134.1, 130.9, 130.3, 130.2, 130.1, 129.3, 121.1, 121, 120.9, 120.8, 120.2, 120.1, 120, 103.5, 102.7, 102.6 ppm.
Chapter 6 Conclusion

6.1 Summary of my work

Anthradithiophene (ADT) is a versatile molecule that can be tailored to fit different types of electronic applications. ADTs are synthesized as an isomeric mixture due to a nonregioselective aldol condensation that generates the ADT quinone; a precursor in the ADT formation. I demonstrated in chapter 2 that desymmetrizing ADT molecules create a permanent dipole that helps separating the ADT isomers chromatographically. Isomer 2-3c demonstrated mobility four orders of magnitude higher than its isomeric mixture. This result further stresses the impact of isomeric purity on charge transport and how an isomer performance can be masked when mixed with other underperforming isomers. Furthermore, I demonstrated in chapter 3 the ability to use the same approach used in chapter 2 to produce an ADT molecule with a dipole moment as well as an open edge that allows separation via chromatography. I illustrated the importance of isomeric purity by showing the anti isomers of F-TES-ADT and F-TEG-ADT almost doubling the mobility recorded for their respective mixtures. I hypothesized that the lack of transition dipole in the anti isomers, and the presence of an inversion centre of symmetry plays a crucial role in facilitating charge transports in the crystal, and improving mobility.

In chapter 4 I tested the idea of small molecules donor/ small molecules acceptor blends for organic photovoltaics. The idea was to create a better intermixing at the donor acceptor interface as well as controlling the co-crystallization process via annealing. Unfortunately the tendency of ADT derivatives to aggregate made it hard to create uniform thin films with small domains that assure the right distance for exciton diffusion. Additionally, cyano ADT molecules were tested in binary and ternary photovoltaic systems with very small to no success. Our collaborators demonstrated that excimer formation between CN-ADT and F-TES-ADT as well as CN- ADT and P3HT have a negative effect on exciton dissociation and power conversion efficiency, and therefore it needs to be avoided.

Finally in chapter 5, I illustrated the correlation between film morphology and singlet fission rate. TES-ADT acquires the ability to generate thin film with different polymorphs.
The β-phase polymorph is believed to have the stronger electronic coupling and displays the largest singlet fission rate. Moreover, F-TES-ADT exhibits the same type of correlations with crystalline nano-ribbons film, demonstrating greater singlet fission abilities than crystallites F-TES-ADT film. This is a result of better electronic couplings and stronger intermolecular forces that improve long-range order in the molecules inducing exciton delocalization, which leads to enhance singlet fission rate. Our collaborators also showed the capability of taking advantage of singlet fission process in organic photovoltaics where F-TES-ADT showed a PCE of 0.98% and IQE of 120%.

6.2 Future work

Separating the isomers for mjölnir F-ADT derivatives and monitoring the difference in the crystal packing between the isomers should provide additional insight on the role of fluorine in crystal packing. H-F interactions are strong interactions but are not enough to influence the crystal packing in the presence of the alkylsilyl functionalizing groups. H-F also shows no effect on crystal packing in bare F-ADT, due probably to the domination of edge to face interaction in the herringbone-packing motif.

Unfortunately, all ADT molecules that I synthesized for organic photovoltaic applications do not seem to preform that well in the blend. Part of the problem is the morphology as I demonstrated in this thesis. Introducing long alkyl chains to the ADT chromophore can improve the viscosity as well as solubility of ADTs in solution. However, the solubilizing groups must not act as an insulator that inhibits charge transport between ADTs and the donor or acceptor molecules used in the blend. Instead I need to synthesize ADT derivatives with electron bridging group at the 5 and 11 position, that are conjugated with the ADT chromophore, to facilitate charge transport, while inserting the solubilizing groups at the 2 and 8 position of the ADT to provide the necessary solubility, and viscosity. Finally more ADT derivatives need to be made in order to develop a library of F-ADT derivatives with different crystal packing, orbital overlapping and electronic coupling in order to prove the existence of the relationship between electronic couplings and singlet fission.
References


133 M. L. Grimminger, 2011, paper 850.


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Publications


