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PERIODIC TRENDS IN STRUCTURE FUNCTION RELATIONSHIP OF ORGANIC HETEROACENES

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Dr. John Anthony, Director of Graduate Studies
PERIODIC TRENDS
IN STRUCTURE FUNCTION RELATIONSHIP
OF ORGANIC HETEROACENES

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
Marsha (Loth) Grimminger
Lexington, Kentucky

Director: Dr. John Anthony, Professor of Chemistry
Lexington, Kentucky

2011

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ABSTRACT OF DISSERTATION

PERIODIC TRENDS
IN STRUCTURE FUNCTION RELATIONSHIP
OF ORGANIC HETEROACENES

Our group has previously shown that small changes to molecular structure result in large changes to device properties and stability in organic electronic applications. By functionalizing aromatic heteroacenes with group 14 and group 16 elements, it is possible to control morphology and improve stability for a variety of applications such as thin film transistors and solar cells. Functionalization within the heteroacene core led to changes in electronic structure as observed by electrochemistry and light absorption. By substituting down the periodic table, the carbon heteroatom bond length increased, leading to subtle changes in crystal packing. Absorption maxima were red-shifted and stability to light decreased. Substitution of group 14 elements to the solubilizing ethynyl groups attached to the heteroacene also had an effect on crystallization and stability. Substitution of silicon with carbon decreased solubility as well as stability to light. Substitution with germanium also decreased stability to light, but close contacts within the crystal structure and solubility in nonpolar organic solvents increased.
KEYWORDS:

Organic Semiconductors, Acenes,
Organic Thin Film Transistors, HOMO
Energy Levels, Solution Processing

Marsha (Loth) Grimminger

12/5/2011
Date
PERIODIC TRENDS
IN STRUCTURE FUNCTION RELATIONSHIP
OF ORGANIC HETEROACENES

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### LIST OF SYMBOLS AND ABBREVIATIONS

- **(tert-butyl)ethynyl**  
  t-Bu
- **(triethylgermyl)ethynyl**  
  TEG
- **(triethylsilyl)ethynyl anthradithiophene**  
  TES ADT
- **[1]benzoseleno[3,2-b][1]-benzoselenophene**  
  DPh-BSBS
- **[1]benzothioino[3,2-b][1]-benzothiophene**  
  BTBT
- **[n]Thienoacenes**  
  [n]TAc
- **acenedithiophenes**  
  ATs
- **acetic acid**  
  AcOH
- **all-syn thiophenes isomer of DBTDT**  
  BBTT
- **anthradifuran**  
  ADF
- **anthradithiophene**  
  ADT
- **atomic force microscopy**  
  AFM
- **bandgap**  
  $E_g$
- **benzene-thiophene alternating molecules**  
  BTAs
- **benzo[1,2-b:4,5-b′]bis[b]benzothiophene**  
  BBBT
- **benzodithiophene**  
  BDT
- **capacitance per unit area**  
  $C_i$
- **channel conductance**  
  $g_o$
- **channel length**  
  $L$
- **channel width**  
  $W$
- **diacene-fused thienothiophenes**  
  DAcTTs
- **dianthra[2,3-b:2′,3′-f]thieno[3,2-b]thiophene**  
  DATT
- **dibenzo[b,b′] thieno[2,3-f:5,4-f′]bis[1]benzothiophene**  
  DBTBT
- **dibenzo[d,d′] thieno[3,2-b;4,5-b′]dithiophene**  
  DBTDT
- **dichloromethane**  
  DCM
- **differential pulse voltammetry**  
  DPV
- **differential scanning calorimetry**  
  DSC
- **dinaphtho[2,3-b:2′,3′-f]seleno[3,2-b]selenophene**  
  DNSS
- **dinaphtho[2,3-b:2′,3′-f]thieno[3,2-b]thiophene**  
  DNTT
- **diphenyl benzoditellurophene**  
  DPh-BDTe
- **diphenyl benzodithiophene**  
  DPh-BDT
- **diphenyl benzoditselenophene**  
  DPh-BDS
- **diphenyl-benzothieno-benzothiophene**  
  DPh-BTBT
- **dithieno [2,3-d;2′,3′-d′]benzo[1,2-b;4,5-b′]dithiophene**  
  DTBDT
- **drain Voltage**  
  $V_D$
- **drain-source voltage**  
  $V_{DS}$
- **dual gate thin film transistor**  
  DG
- **ethyl acetate**  
  EtOAc
- **ethanol**  
  EtOH
- **field effect mobility**  
  $\mu_{FET}$
- **field effect transistor**  
  FET
- **gate-source voltage**  
  $V_{GS}$
- **grazing incidence X-ray diffraction**  
  GIXD
- **hexamethyldisilazane**  
  HMDS
highest occupied molecular orbital

HOMO

hours

hr

hydrobromic acid

HBr

hydrochloric acid

HCl

lowest unoccupied molecular orbital

LUMO

magnitude of the sheet density charge

$|\mathcal{Q}|$

mass spectrometry

MS

matrix-assisted laser desorption ionization

MALDI

metal-oxide-semiconductor field effect transistor

MOSFET

methanol

MeOH

minutes

min

mobility

$\mu$

$N$-bromosuccinimide

NBS

n-butyllithium

n-BuLi

$N$-chlorosuccinimide

NCS

$N$-fluorobenzenesulfonylimide

NFSI

$N$-formylmorpholine

NFM

napthadithiophene

NDT

nuclear magnetic resonance

NMR

octadecyltrichlorosilane

OTS

octafluoro ethynyl functionalized pentacene

F8 Pn

on/off current ratio

$I_{\text{on/off}}$

one-dimensional $\pi-\pi$ stacking

1-D $\pi$-stack

pentacene

Pn

pentadithiophene

PDT

pentafluorobenzene thiol

PFBT

permittivity of free space

$\varepsilon_o$

photoluminescence

PL

photoluminescence microscopy

PLM

photosensitive polyimide

PSPI

poly($\alpha$-methylstyrene)

P$\alpha$MS

poly(methyl methacrylate)

PMMA

poly(triarylamine)

PTAA

potassium hydroxide

KOH

proportionality constant

$g_d$

relative permittivity

$\varepsilon$ or $k$

rotations per minute

RPM

Siemens

S

seconds

s

self-assembled monolayer

SAM

silicon dioxide, silica

$\text{SiO}_2$

single molecule fluorescence spectroscopy

SMFS

sodium hydroxide

NaOH

solvent vapor annealing

SVA

space charge limited current

SCLC
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<td>$\sqrt{I_D}$</td>
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<td>stannous chloride dihydrate</td>
<td>SnCl$_2$</td>
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<td>subthreshold slope or swing</td>
<td>$S$</td>
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<td>tetrathioindene</td>
<td>TDT</td>
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<td>tetrafluoro ethynyl functionalized pentacene</td>
<td>F$_4$Pn</td>
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<td>tetrahydrofuran</td>
<td>THF</td>
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<tr>
<td>triisopropylsilyl</td>
<td>TIPS</td>
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<td>two-dimensional $\pi-\pi$ stacking</td>
<td>2-D $\pi$-stack</td>
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Chapter 1: Introduction

1.1 Electronic Materials and Devices

Our group has been focused on the synthesis and characterization of organic semiconductors for electronic devices. All materials are classified into metals, insulators, and semiconductors by their conductivity ($\sigma$) in Siemens (S) per meter (m), or reciprocal ohm meter ($\Omega^{-1}m^{-1}$). An ohm is the unit that denotes resistance (R) for a resistor. The resistance, a constant, is current, in amps (A) divided by voltage in volts (V).

$$S = \frac{1}{\Omega} = \frac{A}{V} = \frac{1}{R}$$

Siemens represent the slope for a resistor according to Ohms law. Ohms law states that current ($I$) is proportional to voltage ($V$) (Figure 1.1).

$$I = \frac{V}{R}$$

Ohms law means that for a resistor with a conductance of 1 S, there will be a 1 A increase in current for every 1 V increase in voltage applied.

Figure 1.1

\[ current \ vs. \ voltage \ (IV) \ plot \ of \ Ohm's \ law \]

Conductivity is also the inverse of resistivity ($\rho$) in ohm meters (\(\Omega m\)), which is the magnitude of an applied electric field (E) divided by the current density ($J$) in Am$^{-2}$.

$$\sigma(S/m) = \frac{1}{\rho(\Omega m)} = \frac{J}{E}$$

Thus, conductivity is the result of applying an electric field to a sample with a defined area. Materials that have high conductivity (>10$^4$S/m) are classified as
metals and allow fast movement of electric charge through the material with low resistivity. Materials with low conductivity (<10^{-6} S/m) are insulators with high resistivity and resist the flow of electric charge. Semiconductors are the materials that lie in the middle and can conduct electron charges (n-type) or hole charges (p-type).

For inorganic p-type materials, the actual movement of charge is still from an electron, but it moves to fill a defect vacancy or trap within the crystal structure rather than moving from high concentration to low as an n-type (Figure 1.2). Charge transport takes place by thermally induced lattice deformations known as phonons, so charge transport decreases with lower temperatures.

![Figure 1.2](image)

**Figure 1.2**

*N-type (a) and P-type (b) charge migration within a doped silicon crystal lattice*

Organic materials do not show the same temperature dependence. In materials with low conductivity, charge transfer occurs by hopping through a polaron, or charge separation within a conjugated system.

![Structure of polythiophene polaron, as interpreted from UV-Vis spectroscopy](image)

*Structure of polythiophene polaron, as interpreted from UV-Vis spectroscopy*

Mobility (\(\mu\), in cm^2/Vs) is a measure of the velocity of charge migration within a unit area under an applied electric field. Though organics have lower mobility than traditional inorganic semiconductors, they are of interest due to their ease of purification and large-scale, lower temperature solution processing combined with flexible applications.

Mobility can be measured by time of flight (TOF), space-charge limited current (SCLC) and field effect transistors (FET). TOF and SCLC measurements require the use of a sufficiently thick single crystal, while FET measured from the thin film
transistor (TFT) architecture would be utilized in commercial devices. TOF and SCLC are more common for inorganic semiconductors, but they are restricted to transport in one direction for most organics. That direction may not correspond to the most suitable for charge transport in the crystal structure so FET mobilities will be compared in this volume.

My project specifically has been focused on synthesizing organic materials for TFTs. Transistors act as a switch that allows current to pass through when the device on. Organic materials are usually p-type due to their low conductivity and the location of the energy levels where charge transfer occurs known as the bandgap (E_g) or difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). Organic TFTs usually operate as an accumulation layer in metal-oxide-semiconductor field-effect transistors (MOSFET) leading to lower mobilities than doped inorganic materials like silicon, which operate in an inversion layer.

The FET device structure for p-types materials usually consists of an n-doped gate electrode covered with an insulating dielectric (Figure 1.3). A semiconductor with source and drain conducting electrodes is put in contact with the dielectric and voltage is applied from gate to source. This voltage induces charge migration in the dielectric, which results in the accumulation of charges at the dielectric/semiconductor interface. If enough voltage is applied to the gate to overcome the threshold voltage (V_T), drain current (I_D) can be measured. If the threshold voltage is not overcome, the current measured is the leakage current (I_{leakage}) resulting from carrier tunneling through the insulating dielectric (typically <10^{-12} A for organics).

**Figure 1.3**

FET representation in the off and on state interpreted from Horowitz

1.2 Transistor Output

Using Ohm’s law, it is possible to calculate the parameters V_T, on/off current ratio (I_{on/off}), subthreshold slope (S), and field effect mobility (\mu_{FET}) for a TFT device.
\[ I_D = g_d V_{DS} \]

A transistor that is on has a voltage passing from source to drain (\(V_{DS}\)) and \(I_D\). The proportionality constant (\(g_d\)) for Ohm’s law is defined as the drain conductance as the gate-source voltage (\(V_{GS}\)) goes to zero. Since it cannot literally be calculated, the channel conductance (\(g_o\)) is used.

\[ g_o = \frac{W}{L} \mu |Q| \]

The value \(g_o\) is determined by the channel width (\(W\)) and length (\(L\)), the field-effect mobility of the charge carriers (\(\mu_{FET}\)), and the magnitude of the sheet density of the accumulation layer charge (\(|Q|\)).

\[ |Q| = C_i (V_{GS} - V_T) \]

\(|Q|\) is related to the capacitance per unit area (\(C_i\)) of the dielectric insulator (in the absence of traps), the applied \(V_{GS}\), and \(V_T\).

\[ C_i = \frac{\varepsilon \varepsilon_o}{t_i} \]

Capacitance is inversely proportional to thickness. The constant of proportionality is the product of the known constant permittivity of free space (\(\varepsilon_o\)) in vacuum times the value of the relative permittivity (\(\varepsilon\)) of the gate insulator. This constant is divided by the thickness (\(t_i\)) of the dielectric insulator to obtain \(C_i\).

\[ I_D = \frac{W \mu C_i}{2L} (V_{GS} - V_T)^2 \]

By substituting back to Ohm’s Law, a relationship can be made between the input \(V_{GS}\) and output \(I_D\) to \(\mu_{FET}\), and \(V_T\) with respect to the channel area and \(C_i\).

Transistors have two characteristic output graphs that are used to obtain key parameters \(\mu_{FET}\), \(V_T\), \(I_{on/off}\), and \(S\). The transfer characteristics (Figure 1.4) are plotted as the drain current in A vs. the applied gate-source voltage in V. The square-root of drain current (\(\sqrt{I_D}\)) is also plotted vs. \(V_{GS}\).
Figure 1.4

**Transfer characteristics for solution processed bottom contact OTFT with dielectric and gold surface treatment.**

The threshold voltage can be found by extrapolating the x-intercept for the linear region of the blue curve $\sqrt{I_D}$ vs. $V_G$. For this system the threshold voltage was +6 V. The threshold voltage is the voltage at which the transistor turns on when all traps are filled, so ideally it should be as close to but not equal to zero to decrease operation energy. Mobility is also calculated from the slope of this line by rearranging the equation:

$$\mu = \frac{2L}{WC_i} \left( \frac{\partial \sqrt{I_D}}{\partial V_{GS}} \right)^2$$

When the values $L = 5 \, \mu m$ and $W = 5 \, \mu m$ are substituted and the slope squared, the mobility is $7.34 \times 10^{-3} \text{cm}^2/\text{Vs}$.

The on/off current ratio and subthreshold slope are calculated from the $I_D$ vs. $V_G$ plot, which is the red curve. Subthreshold slope is calculated by taking the inverse slope at its steepest point. Subthreshold slope gives an idea of the on/off switching speed for the device and should be less than 1 for a good display. The subthreshold slope for this system is 13 V/decade. The on/off current ratio is the maximum current in the on state divided by the leakage current in the off state. It should be $>10^5$ to show a significant change from off to on. For this system a very low on/off current ratio of 5 was calculated since the current was measured at the lowest sensitivity for this parameter analyzer. Conventional silicon MOSFETs have an on/off current ratio of $>10^9$ due to their increased on current values compared to organics.

The mobility can also be calculated from the output characteristics (Figure 1.5), which are a plot of $V_{DS}$ vs. $I_D$. 


The drain-source voltage is varied at a constant gate-source voltage for several different steps. The saturation mobility is calculated using a very small drain-source voltage where it is less than the gate-source voltage minus the threshold voltage.

$$V_{DS} < V_{GS} - V_T$$

For this example $V_{DS}$ it is about -1V and the mobility can be found from a new relationship using the slope.

$$\left( \frac{\partial I_D}{\partial V_{GS}} \right)_{V_{DS}} = \frac{W \mu C_i}{L} V_{DS}$$

$$\mu = \frac{L}{V_{DS} W C_i} \left( \frac{\partial I_D}{\partial V_{GS}} \right)_{V_{DS}}$$

The saturation mobility calculated for this system was $7.3 \times 10^{-3}$ cm$^2$/Vs. It is important to note that the mobilities calculated using the linear and saturation methods may not be the same. This difference is a property of contact effects since the mobility is dependent on the gate-source bias that is related to the sheet carrier density in the accumulation layer.

1.3 Acenes

Acenes are linearly fused aromatic rings commonly used as organic semiconductors. Synthetic complexity increases with increasing number rings ($n$) since solubility
decreases. Small molecule semiconductors, including acenes, typically have higher mobilities due to their increased crystallinity compared to polymers. In general, high mobility compounds result from well-ordered films within the first 3 monolayers of the channel region.

1.3.1 Pentacene

![Figure 1.6](image)

Pentacene (Pn, 1) is one of the most studied organic semiconductors. It adopts a herringbone structure (Figure 1.6) in the solid state to minimize electron repulsion from the more electron dense central ring.

The SCLC mobility for ultra pure single crystals of 1 has been calculated to be as high as 35 cm²/Vs. Initially, TFT devices resulted in a mobility of 2 × 10⁻³ cm²/Vs from evaporation, but improvements were made with the use of self-assembled monolayers (SAMs) to tune surface energy and morphology.

Pentacene orients on silicon dioxide (SiO₂) dielectric with the long axis perpendicular to the substrate (Figure 1.10) as measured by grazing incidence X-ray diffraction (GIXD). For UV/ozone cleaned SiO₂, a high surface energy is measured using the contact angle for a water droplet (Figure 1.7). The lower the contact angle, the higher the surface energy since water is polar and will spread out on a hydrophilic surface.
Pentacene forms islands on a high surface area dielectric rather than finished monolayers since many nucleation sites are started at the surface\textsuperscript{7}. This discontinuous film decreases mobility. Other organics form “coffee stain” rings on high surface energy substrates since drying forms crystalline regions on the outside of the droplet (Figure 1.8)\textsuperscript{8}.

Similarly, a high contact angle denotes low surface energy. The hydrophobic surface causes the water droplet to bead up, also known as dewetting (Figure 1.9)\textsuperscript{7}.

The biggest morphology challenge is at the triple interface between the acene, electrodes, and dielectric on a bottom contact device\textsuperscript{7}. Most acenes orient differently on the gold electrodes than silica dielectric due to surface hydroxyl groups. For pentacene, orbital overlap is in the plane of charge transport from crystals nucleated on the dielectric, but not for those nucleated on the electrodes\textsuperscript{7}. 

\textit{depiction of contact angle measurement using deionized water (DI water) recreated from Gamota et al.\textsuperscript{7}}

\textit{cartoon of droplet on high surface energy interpreted from Deegan et al.\textsuperscript{8} with resulting “coffee stain” ring from Dr. Brad Conrad, NIST}

\textit{cartoon of dewetting caused by low surface area substrate recreated from Professor Thomas Jackson, Penn State University}
depiction of alignment on high surface energy UV/ozone treated gold electrode/silicon dioxide dielectric interpreted from Lee et al.17

SAM surface modifications can be used to tune crystal orientation. By using hydrophobic alkylsilyl derivative such as octadecyltrichlorosilane (OTS) or hexamethyldisilazane (HMDS), a low surface energy substrate can be made. For 1, the same perpendicular orientation as silica results, but other acenes discussed in chapter 2 align differently on SAM treatment than SiO2. OTS SAM treatment improved film uniformity and mobility for 1 by directing complete monolayer formation rather than islands17.

By using alkyl or aromatic thiols such as pentafluorobenzene thiol (PFBT) on the source and drain electrodes, a low surface energy electrode is made. The orientation of 1 is the same as on the dielectric creating a more uniform morphology (Figure 1.11)17.

depiction of pentacene orientation on low surface energy benzenethiol treated Au electrodes and alkylsilane treated silica dielectric interpreted from Lee et al.17
Device results confirm the improved morphology with a doubling of mobility and decrease in subthreshold slope and threshold voltages.\(^{21}\)

SAM treatment on the electrodes have the added benefit of improving charge injection into the acene HOMO by varying the electrode work function.\(^{22}\) Gold has a work function of 5.2 eV while 1 has a HOMO of 5.1 eV. Charge injection can be improved by increasing the work function of gold in a p-type device using different aromatic thiols. Less expensive silver can also be used as an electrode, though its work function of 4.7 eV is not well suited for most organics. When treated with thiol SAMs a maximum work function of 5.35 eV was achieved.\(^{23}\)

Varying the dielectric can also lead to improved device mobilities. The use of polymeric gate dielectrics improved the mobility of 1 to 3.0 cm\(^2/\)Vs and a photosensitive polyimide (PSPI) to 6 cm\(^2/\)Vs.\(^{26}\)

The current highest TFT mobility 6.4 cm\(^2/\)Vs for 1 was achieved by using a trilayer low surface area silica dielectric fabricated by sol/gel on a flexible polymeric substrate.\(^{27}\) This method afforded decreased dielectric surface roughness as measured by atomic force microscopy (AFM) and low surface energy as measured by a contact angle of 78°. They also found that mobility decreased as permittivity (k) increased. This relationship is surprising since the dielectric acts as a capacitor and capacitance is proportional to k value at a constant thickness.

\[
C_i = \frac{k \varepsilon_0}{t_i}
\]

1 itself has the disadvantages of low stability and solubility. Solution processed pentacene devices have also been fabricated using a soluble precursor, but only with mobilities as high as 3 \(\times\) 10\(^{-2}\) cm\(^2/\)Vs.\(^{28}\)

Pentacene forms symmetric and butterfly dimers (2a, 2b) in light and degrades by endo peroxide formation (3) in the presence of oxygen.\(^{5}\)

Stability can be improved by making changes to the molecular structure. By decreasing the HOMO level using a phenanthrene-like structure (Table 1.2)\(^{29}\), it is possible to generate the air-stable isomer picene (4).\(^{30}\) In air, the mobility was found to be >3 cm\(^2/\)Vs and >5 cm\(^2/\)Vs when exposed to 500 Torr oxygen.\(^{32}\)
1.3.1.1 Perfluoropentacene

Stability can also be increased by functionalization on the acene core. Complete fluorination of pentacene (perfluoropentacene, 5) resulted in n-type behavior with an electron mobility of 0.22 cm²/Vs and a reduction potential close to that of C₆₀.

1.3.1.2 6,13-diethynylpentacenes

To improve solubility, trialkylsilylethynyl pentacene derivatives were functionalized at the central ring (6).

By using triisopropylsilyl (TIPS) ethynyl pentacene (TIPS Pn, 6a) high mobility two-dimensional (2-D) \( \pi-\pi \) stacking (\( \pi \)-stack) was achieved in the solid state (Figure 1.12).
molecular and crystal structure for 6a TIPS Pn (alkyl groups are removed for clarity)

Again, initially a modest mobility (0.4 cm²/Vs) was found with vapor deposited films\textsuperscript{36}, but the introduction of solution processing\textsuperscript{37} with the added improved morphology through surface modifications mobilities reached 1.8 cm²/Vs\textsuperscript{38}.

When triethylsilyl (TES, 6b) groups were used instead, a one-dimensional (1-D) π-stack (Figure 1.13) resulted with a maximum mobility of $1 \times 10^{-4}$ cm²/Vs\textsuperscript{5}.

A roadmap for obtaining 2-D π-stacking was developed for linear acenes (Figure 1.14)\textsuperscript{39}. When the diameter of the spherical silyl derivative is half that of the acene backbone, 2-D π-stacking can be achieved. When the diameter is less or greater
than half, 1-D π-stacking will result. When the diameter is much greater than half, herringbone interactions will result with only alkyl-alkyl interactions. This method of obtaining 2-D π-stacking has been supported by other linear acenes and heteroacenes.

Figure 1.14

*cartoon for obtaining 2-D π-stacking where green is the spherical trialkylsilane diameter and red is the acene backbone length*

When alkynyl chains were used instead of silyl derivatives on functionalized pentacenes, no 2-D π-stacking was found. For larger alkyl chains (octyl and decyl) crystals decomposed into orange chromophores after an hour in light and air.

1.3.1.3 Partially fluorinated 6,13-diethynylpentacenes

Improved stability for functionalized pentacenes has been demonstrated by partial fluorination, which also lowered the HOMO (Table 1.2). For tetrafluoro (F4 Pn, 9) and octafluoro (F8 Pn, 10) functionalized pentacenes, the solution stability doubled or tripled depending on the ethynylsilyl derivative.

The mobility, however, decreased to 0.12 cm²/Vs and 1 x 10⁻⁵ cm²/Vs for solution processed F4 TIPS Pn (9a) and F8 TIPS Pn (10a) respectively. While the former device has a higher mobility than vacuum deposited films, the latter displayed poor morphology corresponding to the low mobility.
1.4 Heteroacenes

Another way to decrease the HOMO level is to introduce periodic table group 16 element-containing heteroacenes furan, thiophene, or selenophene. This wide variety of compounds can be broken into 4 molecular classes.

1.4.1 \([n]\)Thienoacenes ([n]TAc)

Thienoacenes (TAc) are fused or ladder-type oligothiophenes with low-lying HOMO levels around 5.5 eV. TAc are “phenacenes” rather than “acenes” since they adopt similar electronic structure to phenanthrene (scheme 1.1). TAc typically exhibit low solubility for unfunctionalized derivatives so vapor deposition is the best method for thin film formation. The highest mobility for this class is 1.8 cm²/Vs for a single crystal and 0.5 for vapor deposited TFTs using OTS surface treatment.

The planar pentathienoacene dithieno[2,3-d:2’,3’-d’]thieno[3,2-b:4,5-b’]dithiophene ([5]TAc, 11) adopts a 1-D π-stack in the solid state with blue fluorescence. Top contact TFTs were fabricated with a mobility of 0.045 cm²/Vs. Higher number of fused rings have been synthesized but TFT results were not published. [7]TAc, 12 also adopts a 1-D π-stack in the solid state and has a red-shifted absorption compared to 11. Both fused derivatives had similar absorption
spectra to the corresponding non-fused oligothiophene, but the emission spectra are blue-shifted[57]

The addition of external benzene rings improved mobility to the group maximum 1.8 cm²/Vs for solution deposited single crystals of dibenzo[d,d’]thieno[3,2-b;4,5-b’]dithiophene (DBTDT), 13a[44] and 0.51 cm²/Vs for vapor deposited TFTs on OTS treated dielectric[45]. Solution deposited single crystals for the isomer 13b (BBTT) had a mobility of 0.6 cm²/Vs[46]. Group 16 functionalization could also be done to make a mixed thiophene and selenophene-containing derivative 14b with a higher mobility of 1.1 cm²/Vs and lower bandgap (Table 1.2) compared to 0.5 cm²/Vs for the all-thiophene analogue 14a[48].

1.4.2 Benzene-thiophene alternating molecules (BTAs)

BTAs are also a ladder-type phenacenes that can be vacuum or solution processed[43]. The highest mobility (1.7 cm²/Vs) from this class comes from dip-coating a functionalized heteroacene[50].

The thieno[f/f’]bis[1]benzo-thiophene isomers 15a and 15b had mobilities of 0.011 cm²/Vs and 0.12 cm²/Vs respectively showing that even small changes to the molecular structure can lead to orders of magnitude difference in device performance[51]. Both adopt a 1-D π-stack in the solid state.

Dibenzo[b,b’] thieno[2,3-f:5,4-f’]bis[1]benzothiophene (DBTBT) was synthesized as a mixture of isomers and as the pure isomer 16. The mobility decreased from 0.15 cm²/Vs to <0.03 cm²/Vs from the pure compound to mixture[52].
Using functionalized dithieno [2,3-d;2',3'-d']benzo[1,2-b;4,5-b']dithiophene (DTBDT, 17a, 17b), solution processing was possible. A high mobility of 1.7 cm²/Vs was obtained from dip coating using 17b, while the mobility dropped to 1.2 cm²/Vs from spin-coating.

1.4.3 Acenedithiophenes (ATs)

Acenedithiophenes benzodithiophene (BDT, 18), napthadithiophene (NDT, 19), and anthradithiophene (ADT, 20) are isoelectronic with acenes. Synthesis of pure isomers have been reported, but only 18 and 19 have published TFT results for comparison.

1.4.3.1 Benzodithiophenes (BDTs)

2,6-diphenylbenzo[1,2-b:4,5-b']dichalcogenophenes derivatives Diphenylbenzodithiophene (DPh-BDT, 18a) with its selenium (DPh-BDS, 18b) and tellurium (DPh-BDTe, 18c) derivatives have shown maximum mobilities of 8.1 x 10⁻², 0.17, and 7.3 x 10⁻³ cm²/Vs respectively with excellent light stability. The syn isomers exhibited mobilities an order of magnitude lower (3 x 10⁻³ and 0.02 cm²/Vs for 18a' and 18b' respectively).
1.4.3.2 Naphthadithiophenes (NDTs)

Functionalized NDT isomers with acene {naphtho[2,3-b:6,7-b']dithiophenes (19) and naphtho[2,3-b:7,6-b']dithiophenes (19')} and phenacene {[naphtho[1,2-b:5,6-b']dithiophenes (21) and naphtho[2,1-b:6,5-b']dithiophenes (21')} structures were synthesized. The acenes showed a HOMO of 5.09 eV, while the phenacenes had much lower HOMOs that ranged from 5.66 eV to 5.52 eV (Table 1.2). The absorption for 23b was redshifted from 23b' by about 30 nm. The highest mobility was obtained from 23b of 1.5 cm²/Vs with dramatically improved stability compared to tetracene. The isomers again showed differing mobilities under the same fabrication conditions.

<table>
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<th>Compound</th>
<th>( \mu_{\text{FET}} ) (cm²/Vs)</th>
</tr>
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<tbody>
<tr>
<td>19b</td>
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<tr>
<td>19b'</td>
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<td>21b</td>
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<tr>
<td>21b'</td>
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</table>

Table 1.1: mobilities for DPh-NDTs

1.4.3.3 Anthradithiophenes (ADTs)

Anthra[2,3-b:6,7-b']dithiophene (ADT, 20) was initially synthesized as a mixture with its isomer anthra[2,3-b:7,6-b']dithiophene with a maximum mobility of 0.15 cm²/Vs with alkyl substitution (20b). Mobility was low partially due to the mixture of isomers, which may cause disordered films. Synthesis of alkyl funtionalized anti ADT (20c, 20d) has been synthesized, but without device results.
1.4.3.4 Silyl ethynyl acenedithiophenes

Ethynyl substituted ADTs bis(trialkysilylethynyl)anthra[2,3-b;6,7-b']dithiophene (ethynyl ADTs, 21) and higher acenes tetradiithiophene (TDI, 22) and pentadiithiophene (PDT, 23) were synthesized as a mixture of isomers from quinones with varying silylethynyl groups for solubility and crystal packing.\[60\] 2-D π-stacking was induced for ADT using TES functionalization (21a), while 1-D π-stacking was found for TIPS ADT (21b) and TIPS TDT (22a). Only the anti isomer will be shown for clarity, but isomerically pure ethynyl ADTs functionalized at the thiophene 2-position have been reported.\[61\]

By using a bulkier tri(tert-butyl)silyl (TTBS) group it was possible to prevent dimerization in the 7-fused ring system PDT (23a), while TIPS PDT (23b) fully dimerized within hours in solution.

Their absorption spectra corresponded with that of an acene with one less ring. TIPS TDT absorption is similar to 1 while the higher acenedithiophenes increase maximum absorption by 100 nm with each additional ring. Derivatives of 21 will be discussed in more detail in chapter 2.
1.4.3.5 Acene monothiophenes

![Acene monothiophenes](image)

The monothiophene acenes anthra[2,3-b]thiophene (24) and tetraceno[2,3-b]thiophene (25) had a mobility from vacuum deposition of 0.15 cm²/Vs and 0.31 cm²/Vs respectively, though dithiophenes are more commonly reported.62

1.4.4 Diacene-fused thienothiophenes (DAcTTs)

![Diacene-fused thienothiophenes](image)

The compound [1]benzothieno[3,2-b][1]-benzothiophene (BTBT, 26) is the most well studied of this class. Numerous derivatives as well as heteroacene substitution has been performed.

![Derivatives of BTBT](image)

Mobilities in the range of pentacene (2.0 cm²/Vs) have been reported from phenyl functionalized BTBT (DPh-BTBT, 26a), which are stable in air and moisture for months. By functionalizing with octyl groups (26b) the mobility increased to 16.4 cm²/Vs for inkjet printed single crystals. Solution processed TFTs for 26b also showed a high mobility of 5 cm²/Vs and mobilities >3 cm²/Vs were reported for longer chains (26c). The selenium analogue [1]benzoseleneno[3,2-b][1]-benzoselenophene (DPh-BSBS, 27) had a mobility of 0.3 cm²/Vs.

![Derivatives of BTBT](image)

Using dithiophene as the central rings resulted in a mobility for this hexacene analogue dinaphtho[2,3-b:2',3'-f]thieno[3,2-b]thiophene (DNTT, 28) of 2.9 cm²/Vs still with a lower HOMO and air stability than the corresponding acene. The single
crystal mobility was 8.3 \( \text{cm}^2/\text{Vs} \). By functionalizing with decyl groups (28a), the mobility was increased to 12 \( \text{cm}^2/\text{Vs} \) from solution deposited single crystals and 7.9 \( \text{cm}^2/\text{Vs} \) from vapor deposited films. The selenium analogue (DNSS, 29) had a maximum mobility of 1.9 \( \text{cm}^2/\text{Vs} \).  

Even the 8-fused ring derivative dianthra[2,3-b:2',3'-f]thieno[3,2-b]thiophene (DATTe, 30) shows good stability to air and a high mobility of 3.0 \( \text{cm}^2/\text{Vs} \).  

### 1.5 HOMO summary

<table>
<thead>
<tr>
<th>Compound</th>
<th>HOMO (eV)</th>
<th>( E_g ) (eV)</th>
<th>Reference</th>
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<tr>
<td>BSBS 27</td>
<td>5.46</td>
<td>4.20</td>
<td>69</td>
</tr>
<tr>
<td>DNTT 28</td>
<td>5.44</td>
<td>3.0</td>
<td>70</td>
</tr>
<tr>
<td>DNSS 29</td>
<td>5.38</td>
<td>2.9</td>
<td>70</td>
</tr>
<tr>
<td>DATT 30</td>
<td>4.88</td>
<td>2.66</td>
<td>43</td>
</tr>
</tbody>
</table>

*Table 1.2: HOMO levels for various acenes and heteroacenes*
1.6 Thin film deposition

Vacuum deposition can be used for small molecules as a method of obtaining crystalline films, but polymers usually decompose before sublimation. Solution processing is a cost-effective method for large area deposition that is one of the drawing points of organic semiconductors. Simple processing techniques such as dip-coating, screen printing, inkjet printing, and spraying can be used, but with decreased mobilities. Spin coating is more often used to allow fast evaporation or drop casting for slower evaporation. Spin coating methods must often be optimized for speed (RPM), solvent, and annealing temperature for each semiconductor on a specific substrate. Drop casting can be performed in closed containers to retain a solvent-rich atmosphere or uncovered for faster evaporation. Films can also be grown using the Langmuir-Blodgett technique, but semiconductors must be insoluble in water and be functionalized for self-assembly on the substrate. Single crystals can also be solution processed when deposited from suspension to yield high mobility devices.

1.7 Goals for new materials

Functionalization to known and new heteroacenes will be discussed in detail pertaining to light stability, electronics, and device results. By using periodic functionalization at the solubilizing X and heteroatom Y, it is hoped that a trend for stability can be discussed relating to the HOMO level. Halogenation will be applied to Z to further improve stability.

Figure 1.15

![General heteroacene functionalization](image)

Chapter 2 discusses the functionalization of ethynyl ADT (21) with group 14 containing groups as well as halogenated derivatives. Chapter 3 will discuss the periodic substitution to the heteroatom and Chapter 4 will discuss the effect of heteroatom location on HOMO-LUMO energy levels.
Chapter 2: R group functionalization on anthradithiophenes.

2.1: ADT

As discussed in chapter 1, heteroacenes are of interest for electronic materials since they more resistant to dimerization and oxygen degradation due to an increased HOMO level\(^{43}\). Ethynl functionalized ADTs (21) did not dimerize and the desired 2-D \(\pi\)-stacking (Figure 2.3) was achieved with bis(triethysilylethynyl)anthra[2,3-b;6,7-b']dithiophene (TES ADT, 21a) synthesized in an isomeric mixture\(^{77}\). TFT mobilities on the same order of magnitude as pentacene were reported (1 cm\(^2\)/Vs) from solution processing. Though spin cast films are amorphous, large crystal grains can be induced by solvent-vapor annealing (SVA)\(^{78}\).

Decomposition by endoperoxide formation is still prevalent in these derivatives and TES ADT has a half-life in thin film form of just 14 minutes compared to several hours for TIPS pentacene, 6a. Payne \textit{et al}\(^{77}\) have already shown that functionalizing the anthradithiophene backbone with alternative silylethynyl derivatives has an effect on the crystal packing as well as device properties, but my approach was to substitute the silicon atom with other group 14 elements. This substitution had an effect on the electronic properties and processability as well as photostability.
2.1.1 Synthesis of group 14 functionalized ADT

Figure 2.1

*Functionalization target for ADT where X represents group 14 elements C, Si, Ge, and Sn.*

Derivatives were synthesized from ADT quinone\(^7^9\) as reported by Payne and coworkers (Scheme 2.1)\(^7^7\).

Scheme 2.1

The hydrocarbon alkyne \(33\),-diethyl-1-pentyne was not readily available so commercially available 3,3-dimethylbutyne (t-Bu acetylene) was used in its place. The smaller diameter of this substituent compared to triethylsilyl may not induce 2-D \(\pi\)-stacking as predicted from the roadmap discussed in chapter 1\(^9^9\).
The alkyl derivative adamantly ADT (21d) (Figure 2.2) has also been synthesized and characterized by Sankar Subramanian, but shows none of the π-stacking needed for good charge transfer and uniform thin films.

Synthesis of the triethylstannyl acetylene was successful, but the tin functionalized acene was not stable enough for characterization. There is a decrease in stability to light going down group 14 from silicon to germanium (Table 2.1) so it is possible that the tin derivative is not stable enough for purification in the presence of light and oxygen.

X-ray analysis of the t-Bu (21b) and triethylgermyl (TEG) (21c) derivative crystals has not been obtained.
2.1.2 Electronic characteristics of group 14 functionalized ADT

The optical absorption spectra for ADTs (Figure 2.4) was red shifted from carbon to silicon, but only slightly red-shifted from silicon to germanium. This difference is due to the greater difference in electronegativity from carbon to silicon than silicon to germanium.

The red shift observed (Table 2.1) for thin films of these materials compared to their solution spectra was small and similar for all derivatives since solution processed
ADT films do not readily crystallize without annealing. Functionalizing down group 14 resulted in a decreased bandgap as estimated by differential pulse voltammetry (DPV).

<table>
<thead>
<tr>
<th>Acene</th>
<th>Solution $\lambda_{\text{max}}$ (nm)</th>
<th>Film $\lambda_{\text{max}}$ (nm)</th>
<th>Shift (nm)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>$E_g$ (eV)</th>
<th>Film $t_{1/2}$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-Bu ADT</td>
<td>543</td>
<td>547</td>
<td>4</td>
<td>5.21</td>
<td>3.01</td>
<td>2.21</td>
<td>7.8</td>
</tr>
<tr>
<td>TES ADT</td>
<td>554</td>
<td>560</td>
<td>6</td>
<td>5.22</td>
<td>3.05</td>
<td>2.17</td>
<td>14.2</td>
</tr>
<tr>
<td>TEG ADT</td>
<td>553</td>
<td>557</td>
<td>4</td>
<td>5.28</td>
<td>3.14</td>
<td>2.13</td>
<td>9.5</td>
</tr>
</tbody>
</table>

Table 2.1: electronic characteristics for group 14 ethynyl functionalized ADT derivatives 21a-c

Solubility in the non-polar solvents increases down group 14 with the carbon derivative being only slightly soluble at room temperature. I also found that thin film stability to light was highest with silicon but there is not a clear trend down the group. This stability is surprising since TEG ADT has the lowest HOMO, though the values may not be different enough to show improved stability. It was difficult to fabricate uniform films from drop casting for the t-Bu derivative, but none of the films exhibited crystallinity, which might improve stability.

2.1.3 Thermal characteristics of group 14 functionalized ADT

There was also a noticeable change in thermal characteristics between the derivatives altered at the alkyne substituent. The differential scanning calorimetry (DSC) showed two exothermic phase transitions for clean TES ADT (Figure 2.5, black).

![Figure 2.5](image)

*DSC for pure TES ADT (black), light exposed TES ADT (blue), and TES ADT heated to 200 °C (red)*

The lower temperature phase transition of pure TES ADT occurs at 137.04°C only for samples that have not been exposed to light. This peak can be used as a tool to
determine purity. When exposed to light, only one transition at 137.10°C can be found that corresponds to melting (blue). Decomposition due to endoperoxide (35) formation disrupts the π-stacking and decreases intermolecular attraction causing a decrease in the melting point.

![Diagram of molecule 35](image)

The endoperoxide 35 can easily be seen in the aromatic region of the proton NMR for samples with one transition (Figure 2.6). For pristine samples with two transitions, the melting point occurs at 154.72°C.

**Figure 2.6**

![Proton NMR spectra](image)

proton NMR in CDCl₃ for (a) clean TES ADT and (b) 17 hr light exposed TES ADT

When a sample of TES ADT is heated above its melting point (Figure 2.5, red), cooled, and heated again the melting point broadens and shifts to a lower temperature 128.00 °C. The endothermic peak is recrystallization during the cooling cycle. Since some decomposition occurs in the melt, impurities are again introduced which disrupt π-stacking upon crystallization.

X-ray analysis of crystals of TES ADT acquired at room temperature was attempted, but no new polymorph was found. Work was done to isolate the higher
temperature form in crystals suitable for x-ray analysis by heating crystals under nitrogen. The resulting crystals behaved more like a powder under X-ray diffraction (Figure 2.7) so no packing structure could be extracted.

Figure 2.7

*room temperature X-ray diffraction frame of TES ADT crystals heated under nitrogen*

![Image of X-ray diffraction frame]

Figure 2.8

*DSC comparison for t-Bu ADT (black), TES ADT (teal), and TEG ADT (purple)*

The DSC for t-Bu ADT, 21b (Figure 2.8) shows only one transition at 114.88 °C, though the sample does not appear to have endoperoxide peaks in the NMR. TEG ADT, 21c has three phase transitions at 124.05 °C, 142.40 °C, and 151.45 °C with the latter being the melting point slightly lower than TES ADT.

2.1.4 Improved light stability from TES ADT blends

High mobilities for small molecules are usually obtained from bottom-contact devices made from silicon/silicon dioxide patterned by lithography with ultra high purity material and ultra clean substrate surface. Since organic molecules cannot compete with crystalline silicon for high performance devices, ease of device fabrication and low cost processing have been major selling points for organic
In general, polymers have lower mobilities than small molecules, but they yield more uniform large area films from solution processing.

Bottom gate, top contact devices on silicon/silicon dioxide using a small molecule semiconductor blend with insulating polymers have been analyzed as a step towards fabrication of all-solution processed devices. For these studies TIPS Pn (8a) and TES ADT (26a) were blended with semi-crystalline, low permittivity dielectric constant poly(α-methylstyrene) (PaMS). The polymer and semiconductor impurities were more soluble than TES ADT, so vertical phase separation occurred forming high purity acene crystals at the interfaces. The higher density of the acene can explain crystal formation at the surface interface, but crystals also form at the top air interface. The endoperoxide remains in solution since it adopts a bent structure, which does not readily crystallize from solution.

Time dependent thin film DSC measurements for devices made from light exposed solutions showed the elimination of the first phase transition and a shift to a lower melting point after less than 10 minutes of irradiation. The DSC images for light exposed PaMS blends required 30 minutes of irradiation for complete elimination of the first transition.

Device results for these light exposed blends showed similar characteristics to those fabricated from freshly prepared TES ADT (Table 2.2). The UV exposed TES ADT films exhibited no transistor performance, but blends incorporating these impure materials continued to exhibit transistor performance even after the disappearance of the second peak on the DSC.

<table>
<thead>
<tr>
<th>Film/UV exposure (min)</th>
<th>$\mu_{\text{average}}$ (cm$^2$/Vs)</th>
<th>$V_T$ (V)</th>
<th>$I_{\text{on/off}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TES ADT/0</td>
<td>0.0053 ± 0.0024</td>
<td>1.7 ± 1.3</td>
<td>3.0 x 10$^4$</td>
</tr>
<tr>
<td>TES ADT/10</td>
<td>$&lt;10^{-5}$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Blend/0</td>
<td>0.038 ± 0.009</td>
<td>1.5 ± 0.8</td>
<td>9.8 x 10$^4$</td>
</tr>
<tr>
<td>Blend/10</td>
<td>0.040 ± 0.011</td>
<td>1.0 ± 0.5</td>
<td>3.0 x 10$^6$</td>
</tr>
<tr>
<td>Blend/20</td>
<td>0.037 ± 0.014</td>
<td>1.1 ± 0.9</td>
<td>1.2 x 10$^6$</td>
</tr>
<tr>
<td>Blend/30</td>
<td>0.034 ± 0.013</td>
<td>1.0 ± 0.6</td>
<td>2.7 x 10$^5$</td>
</tr>
</tbody>
</table>

Table 2.2 TFT data for TES ADT and TES ADT/ PaMS blends

These values suggest that polymer blends not only improve light stability, but also increase overall mobility by removing other impurities from the active charge transport zone.

### 2.1.5 Synthesis of halogenated ADTs

Our collaborators Stephanie Lee and Professor Lynn Loo at Princeton have been working on improving device performance and solution-processability of TES ADT by making blends with ADT derivatives functionalized at the thiophene 2-position.
Halogenated derivatives, especially difluorinated derivatives, have shown dramatically improved light stability according to Subramanian et al. (Table 2.3).

Scheme 2.2

Synthesis of these derivatives required the protection of thiophene dialdehyde (33), lithiation, halogenation, deprotection, and condensation to synthesize the desired dihalo ADT quiones (Scheme 2.2). Lithiated acetylenes were added and deoxygenated with tin chloride to form the desired heteroacenes.

Though my yields for halogenation of thiophene-2,3-diacetal were improved (Scheme 2.3), bromine (Scheme 2.4) and iodine (Scheme 2.5) substituents could be added from thiophene-2,3-dialdehyde directly, removing the need for an aldehyde protecting group.

Scheme 2.3

improved yields for synthesis of 5-fluoro and 5-chloro thiophene dialdehyde 37 and 38
Bromination of thiophene dialdehyde was achieved following the procedure reported by Okamoto et al.\textsuperscript{86} using an excess of bromine in the presence of iodine catalyst.

\[
\text{Scheme 2.4}
\]

\[
\text{synthesis of 5-bromothiophene dialdehyde, 39 without protection}
\]

Iodination was achieved following the procedure outlined by D’Auria and coworkers\textsuperscript{87} using hypervalent iodine in the form of the reagent [bis(trifluoroacetoxy)iodo]benzene.

\[
\text{Scheme 2.5}
\]

\[
\text{synthesis of 5-iodothiophene dialdehyde, 40 without protection}
\]

The corresponding dihalo ADT quinones and final acenes were prepared by condensation similar to Subramanian (Scheme 2.6)\textsuperscript{40}

\[
\text{Scheme 2.6}
\]

\[
\text{improved yields for synthesis of halogenated TES ADT derivatives 45a-48}
\]

<table>
<thead>
<tr>
<th>Acene</th>
<th>Film t(_{1/2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>TES ADT</td>
<td>14.2 minutes</td>
</tr>
<tr>
<td>F TES ADT</td>
<td>74.2 days</td>
</tr>
</tbody>
</table>

Table 2.3 functionalized F ADT Photostability comparison
2.1.6 Functionalized ADT/TES ADT blends

By using F TES ADT 45a as a nucleation site for TES ADT 21a in blends, crystal grain size could be controlled88. F TES ADT crystallizes first due to decreased solubility creating nucleation sites for TES ADT which grows larger crystals. Work with Cl TES ADT (46)/TES ADT blends have been studied in more detail using GIXD to probe the entire 100 nm thick film for Cl TES ADT reflections and crystal orientation. Spin cast and drop cast TFTs were prepared from a variety of blended solutions (Figure 2.9).

![Figure 2.9](image)

*Figure 2.9*

*mobility comparison for spin cast Cl TES ADT/TES ADT blend TFTs from 0.7 wt.% at 1500 RPM for 60s; and drop cast TFTs from 0.5 wt.% in toluene onto 95°C substrate*

A similar trend was found for both casting processes, where the maximum mobility was reached with 62.5% Cl TES ADT. This percentage showed the most uniform crystallinity in AFM images (Figure 2.11). The minimum mobility occurred at 50% Cl TES ADT, which showed completely phase-separated crystalline Cl TES ADT and amorphous TES ADT. This phase separation means isolated Cl TES ADT crystals were formed within the amorphous TES ADT film without uniform crystallinity through the device. Dropcast films were much rougher than spin cast making it more difficult to get a good contact for transistor curves.
Comparing the output characteristics (Figure 2.10), the current is highest for 62.5% Cl TES ADT and lowest for 50% due to improved film uniformity of the more crystalline 62.5% Cl TES ADT films.

**Figure 2.11**

AFM images of the channel region for Cl TES ADT/TES ADT spin cast TFTs.
AFM images (Figure 2.11) show that blends with less than 30% Cl TES ADT are mostly amorphous, while those with more than 50% Cl TES ADT are crystalline. Films at 37.5% Cl TES ADT appear crystalline in the AFM, but GIXD patterns (Figure 2.12) suggest a lower degree of crystallinity than 87.5%. This result means TES ADT is not being nucleated for low percentages of Cl TES ADT and Cl TES ADT itself is dispersed so that it cannot crystallize as well. Films with 50% Cl TES ADT have phase separated, which can be seen by the crystal embedded in the amorphous film. This morphology leads to the lowest current due to poor uniformity and crystalline coverage across the channel.

**Figure 2.12**

![GIXD patterns of Cl TES ADT/TES ADT spin cast films](image)

For films with less than 50% Cl TES ADT, the GIXD pattern (Figure 2.12) of Cl TES ADT is present, but very weak suggesting a lower degree of crystallinity. At 50%, the pattern is stronger that that of 62.5%, which suggests phase separation and leading to isolated Cl TES ADT crystals that show stronger reflections.

Solution grown single crystals for X-ray analysis were made from the optimal blend 62.5% Cl TES ADT/TES ADT. The results showed TES ADT as the nucleation site for Cl TES ADT needles. The crystals were separated and analysis showed no Cl TES ADT within the TES ADT block-like crystals. Here, the increased solubility of Cl TES ADT in hexane means TES ADT crystals precipitated first which nucleated Cl TES ADT needles. For thin films, Cl TES ADT crystals act as the nucleation site because better solvents for TES ADT are used like toluene.
DSC of 62.5% Cl TES ADT/TES ADT solution grown crystals (black) compared to TES ADT (red), and Cl TES ADT (green).

DSC measurements were also done to the same crystal blend, which showed the expected peaks for both compounds (Figure 2.13). The melting points for both compounds were decreased in the blended crystals suggesting some disruption of π-stacking. The phase transition for TES ADT increased since TES ADT crystals were insulated with Cl TES ADT needles that did not conduct heat as efficiently as the metal pan.

Other functionalized TES ADTs were used and characterized by AFM/GIXD (Figure 2.14).
Dihalogenated ADTs F, Cl, and Br form well ordered crystals in 1:1 blends with TES ADT as seen by strong reflections in GIXD images. I TES ADT blends show less intense reflection due to randomly oriented crystals. I TES ADT itself does not grown crystalline films like the other halogenated derivatives. Ethyl TES ADT/E/TES ADT blends form completely amorphous films with no visible reflections in GIXD.

Figure 2.15

Halogenated derivatives F, Cl, and Br follow a similar trend, where grain size decreases with increasing concentration of additive (Figure 2.15). These derivatives aggregate well in the solid state so it is proposed that they seed TES ADT crystal growth. I and Et derivatives are much larger and therefore aggregation in decreased. Also, Et TES ADT is more soluble in toluene than TES ADT and much more soluble than halogenated derivatives by a factor of 3 or more so is less likely to crystallize first.

The grain size vs. mol % additive curve flattens out for all halogenated derivatives because eventually the maximum number of nucleation sites are formed and an increase in additive cannot increase nucleation. Et TES ADT/TES ADT blends do not follow this trend since Et TES ADT is not acting as a nucleation site and increased amounts simply disrupt TES ADT aggregation to decrease grain size.

2.2: F ADTs

F TES ADT itself has shown high thin film mobilities and dramatically improved stability to light compared to TES ADT. This compound has the added benefit of increased volatility, which means that high purity vapor grown single crystals (VGSC) can be formed that give a better representation of the intrinsic mobility.
A similar R group functionalization approach was applied to silylethynyl substituted F ADTs for analysis of crystal packing, vapor grown single crystal formation and light stability.

**2.2.1 Vapor grown single crystal devices**

Small symmetric (trimethylsilyl, TMS, 45b) and branched (tert-butylidimethylsilyl, TBDMS, 45c) silyl containing derivatives yielded vapor grown single crystals (VGSCs).

**Scheme 2.7**

*Synthesis of VGSC yielded F ADT derivatives F TMS ADT, 45b and F TBDMS ADT, 45c*

Both new derivatives yielded single crystals with an interesting twisted 1-D π-stack (Figures 2.16 and 2.17). This stacking has not been observed in other acenes, though a similar cruciform packing has been found for some substituted pentacenes[^3].
This stacking would suggest less overlap and therefore lower mobilities, which was confirmed by device analysis at NIST by Professor Oana Jurchescu and Brad Conrad. Both ADTs had single crystal mobilities on the order of a 1-D π-stack but their thin film mobilities differed by 4 orders of magnitude (Table 2.4). Thin film formation was not optimized and poor coverage was observed for F TMS ADT. VGSCs for 2-D π-stacking F TES and F TIPS ADT have been previously reported by Jurchescu et al.\textsuperscript{94}.
<table>
<thead>
<tr>
<th></th>
<th>Acene</th>
<th>Single Crystal μFET (cm²/Vs)</th>
<th>Ion/off</th>
<th>Thin film μFET (cm²/Vs)</th>
<th>Ion/off</th>
</tr>
</thead>
<tbody>
<tr>
<td>F TES ADT</td>
<td>6</td>
<td>1 x 10⁸</td>
<td>1.5</td>
<td>1 x 10⁷</td>
<td></td>
</tr>
<tr>
<td>F TIPS ADT</td>
<td>1.5</td>
<td>N/A</td>
<td>1.0 x 10⁻⁷</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>F TMS ADT</td>
<td>3 x 10⁻³</td>
<td>N/A</td>
<td>3.2 x 10⁻⁶</td>
<td>N/A</td>
<td></td>
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<tr>
<td>F TBDMS ADT</td>
<td>7 x 10⁻²</td>
<td>1 x 10⁸</td>
<td>6 x 10⁻²</td>
<td>1 x 10⁷</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.4 VGSC and TFT mobilities for F ADTs 45a-c

2.2.1.1 F TMS ADT TFT optimization

Transistors were made from VGSCs of F TMS ADT, 45b. SAM treatment optimization was applied resulting in the highest mobilities from OTS treatment of the dielectric (Figure 2.18).

![Figure 2.18](image)

Figure 2.18

Transfer (a) and output (b) characteristics for VGSC devices of F TMS ADT 45b

Solution processing requires more optimization before an accurate mobility determination can be made. The solvent from which the films are cast must have a high enough boiling point to allow self-assembly, but must also completely evaporate. The semiconductor must also be soluble in the chosen solvent. SAM optimization must also be performed.

![Figure 2.19](image)

Figure 2.19

Thin film morphology for spin cast of F TMS ADT, 45b from chlorobenzene (a) and chloroform (b); drop cast films from chlorobenzene (c) and chloroform (d).

Thin films of F TMS ADT (Figure 2.19) were deposited from solution from various solvents by spin casting and drop casting. More uniform thin films were obtained from chloroform, but the coverage was not completely uniform from spin casting in any solvent. OTS treatment of the dielectric again yielded the best results. PFBT
treatment of gold source and drain electrodes did not significantly improve mobility data for this derivative.

Figure 2.20

![Graphs showing transfer and output characteristics for TFTs of F TMS ADT, 45b spin cast (a) and drop cast (b) from chloroform onto OTS treated dielectric.]

The device results for spin casting and drop casting from chloroform are similar (Figure 2.20), with spin cast devices resulting in a slightly higher mobility despite non-uniform coverage.

2.2.1.2 F TBDMS ADT TFT optimization

PFBT electrode treatment yielded the highest mobility for solution processed F TBDMS ADT, 45c TFTs from Conrad et al.

Figure 2.21

![Images showing spin cast (a), and drop cast (b) films of F TBDMS ADT, 45b]
Drop cast films gave very low mobilities ($\mu_{\text{FET}} < 1 \times 10^{-6}$ cm$^2$/Vs) due to dewetting on the surface. An amorphous film resulted with isolated “coffee stain rings” of high crystallinity leading to non-uniform coverage across the channel (Figure 2.21).

Spin cast devices; however, had much better film formation and mobilities almost as high as vapor grown single crystals were found (Table 2.4).

### 2.2.2 Group 14 functionalized F ADT

![Functionalization target for F ADTs](image)

*Functionalization target for F ADTs where X represents group 14 elements C, Si, Ge, and Sn and R represents methyl or ethyl.*

Functionalization with group 14 elements on F ADT derivatives was used to determine if the silicon is necessary for vapor grown single crystals.

![Scheme](image)

*synthesis of group 14 ethynyl F ADTs 45a, 45d-e*

Again, the tin derivative was not stable enough for characterization.

#### 2.2.2.1 Crystal packing

Functionalization down group 14 showed a change in crystal packing with t-Bu ADT, 45d adopting a 1-D π-stack (Figure 2.23) while F TES ADT (45a) (Figure 2.24) and F TEG ADT (45e) (Figure 2.25) exhibited 2-D π-stacking.
Figure 2.23

Crystal structure for F t-Bu ADT, 45d

Figure 2.24

Crystal structure for F TES ADT, 45a
2.2.2.2 Electronic characteristics

The electronic differences between carbon, silicon, and germanium derivatives were explored using absorption spectroscopy in solution and thin film (Figure 2.26) as well as electrochemically (Table 2.5).

solution and thin film absorption spectra for functionalized F ADT derivatives 45a, 45d-e
We observe an increased red shift for all F ADT derivatives compared to ADT, but this shift is much larger for the TES and TEG derivatives meaning more aggregation in the solid state.

Thin film photostability analysis yielded almost a three-fold decrease in half-life for F TEG ADT compared to F TES ADT (Table 2.5). This decreased stability was also found for TEG ADT compared to TES ADT. For F TEG ADT, there is a decrease in the HOMO level compared to F TES ADT which may be the reason for its decreased light stability.

<table>
<thead>
<tr>
<th>Acene</th>
<th>Solution $\lambda_{\text{max}}$ (nm)</th>
<th>Film $\lambda_{\text{max}}$ (nm)</th>
<th>Shift (nm)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>$E_g$ (eV)</th>
<th>Film $t_{1/2}$ (days)</th>
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</thead>
<tbody>
<tr>
<td>F t-Bu ADT</td>
<td>515</td>
<td>529</td>
<td>14</td>
<td>5.35</td>
<td>3.09</td>
<td>2.26</td>
<td>-</td>
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<tr>
<td>F TES ADT</td>
<td>527</td>
<td>554</td>
<td>27</td>
<td>5.35</td>
<td>3.05</td>
<td>2.30</td>
<td>74.2</td>
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<tr>
<td>F TEG ADT</td>
<td>523</td>
<td>548</td>
<td>25</td>
<td>5.24</td>
<td>3.17</td>
<td>2.25</td>
<td>26.3</td>
</tr>
</tbody>
</table>

Table 2.5 electronic characteristics for group 14 ethynyl functionalized F ADTs 5a, 45d-e

There is also an increase in solubility in nonpolar solvents down group 14 with the t-Bu derivative being sparingly soluble and F TEG ADT being more soluble than F TES ADT.

2.2.2.3 Thermal characteristics

F TES ADT has two phase transitions near room temperature that make obtaining consistent devices difficult (Figure 2.27). F TEG ADT does not appear to have these transitions, though it has a pristine NMR. As noted with ADT derivatives, similar molecular structures do not necessarily mean similar thermal properties. Improved
film formation for F TEG ADT has been suggested by Professor Oana Jurchescu at Wake Forest University, which may correspond to the lack of room temperature phase transition.

### 2.2.2.4 F t-Bu ADT TFT optimization

Solution processed devices for F t-Bu and F TEG ADT were fabricated by Professor Oana Jurchescu (formerly at NIST, currently at Wake Forest University) (Table 2.6). Efforts to prepare vapor grown single crystals for t-Bu and TEG substituted F ADTs are still ongoing.

<table>
<thead>
<tr>
<th>Acene</th>
<th>Crystal packing</th>
<th>Thin film μFET (cm²/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F t-Bu ADT</td>
<td>1-D slipped stack</td>
<td>8.0 x 10⁻⁴</td>
</tr>
<tr>
<td>F TES ADT ⁴₅</td>
<td>2-D brickwork</td>
<td>1.5</td>
</tr>
<tr>
<td>F TEG ADT ²</td>
<td>2-D brickwork</td>
<td>3.25</td>
</tr>
</tbody>
</table>

Table 2.6 crystal packing and mobility comparison for group 14 ethynyl functionalized F ADTs ⁴₅a, ⁴₅d-e

The lower mobility for F t-Bu ADT reinforces the trend that 1-D π-stacking grows less uniform horizontal films, which are necessary for good transistor coverage. It was also difficult to grow uniform thin films for light stability studies for F t-Bu ADT due to its decreased solubility.

**Figure 2.28**

*a, b, c* solution processed F t-Bu ADT, ⁴₅d TFTs spin cast from chlorobenzene (a-b) and chloroform (c). Figure (b) is the magnification of film (a), which showed the highest mobility though all had discontinuous coverage.

Small F t-Bu ADT crystal nucleation occurs in the channel region rather than on the electrodes leading to discontinuous films (Figure 2.28). For high performing F TES ADT, nucleation occurs on PFBT treated electrodes that grow across the channel.
2.2.2.5 F TES ADT TFT optimization

F TES ADT shows much improved device characteristics with average mobilities higher than 1 cm²/Vs.

As mentioned before the coverage across the channel is much more uniform for F TES ADT than F t-Bu ADT since nucleation starts at the PFBT treated electrode and grows large grains (around 10 μm) into the channel region. For devices with a small channel length (5 μm), the grain size is on the same order of magnitude as the channel width so a single grain can grow across the channel with no grain boundary as observed by combining scanning Kelvin probe microscopy (SKPM) with AFM topography.

As channel length increases above the typical grain size (20 μm), crystal nucleation starts from both sides of the channel and the growing crystals meet in the middle of the channel causing a ridge. For devices with an even larger channel length (80 μm) some nucleation occurs on the dielectric surface within the channel leading to a dramatic change in molecular orientation (Figure 2.30).
Crystals that nucleate on PFBT treated electrodes are oriented such that the π-stacking direction is the same as the direction of charge transport which leads to the best performance. Crystals that nucleate on untreated dielectric form a mixture of small crystals of the desired orientation mixed with crystals oriented perpendicular to them shown in the representation.

### 2.2.2.5.1 Inkjet printed F TES ADT TFTs

Ink-Jet printed F TES ADT films were investigated by the Professor Thomas Jackson and Ph. D. student Yuan Yuan Li at Penn State. The previously published spin cast high mobility processing method using toluene with low surface energy substrate resulted in amorphous films by inkjet printing due to dewetting (Figure 2.31).
When a high surface energy substrate was used along with a higher boiling solvent, improved wetting was observed, but with non-uniform crystallinity. “Coffee-stain” rings discussed in chapter 1 were formed due to a pinned contact line and outward convective flow, which is common with high surface energy substrates (Figure 2.32).

(a) OM images for F TES ADT, 45a inkjet printed from toluene onto PFBT/Au and HMDS/SiO2, contact angle measurements for (b) SiO2 dielectric and (c) gold electrodes reprinted with permission from Professor Thomas Jackson at Penn State University

Figure 2.32

(a) OM images for F TES ADT, 45a inkjet printed from chlorobenzene onto UV/ozone cleaned Au and SiO2, contact angle measurements for (b) SiO2 dielectric and (c) gold electrodes and (d) droplet evaporation representation reprinted with permission from Professor Thomas Jackson at Penn State University
When an even higher boiling point solvent was used to try to avoid an outward evaporation, large grain sizes resulted, but without wetting the treated surface (Figure 2.33).

The droplet moved across the low surface energy substrate while drying, which would lead to inconsistent device results in a commercial application (Figure 2.34).

By using a 1:1 mixture of chlorobenzene and 1,2,4-trichlorobenzene similarly to the approach used for inkjet printed TIPS Pn films\textsuperscript{102} or polystyrene\textsuperscript{103} large crystal grains were achieved. Chlorobenzene allowed wetting of the substrate while the Marangoni and convective flows were balanced from the mixed solvents with different vapor pressures (Figure 2.35)\textsuperscript{104}.
The Marangoni effect controls droplet spreading using a mixed solvent system\textsuperscript{104}. By using a mixture where the minor component has a higher boiling point, but lower surface tension, it is possible to induce a surface tension gradient\textsuperscript{102}. This gradient generates a flow that is perpendicular to the convective, outward flow seen in high surface energy surfaces that causes “coffee-stain” rings (Figure 2.35). When these two flows are balanced, uniform evaporation can occur preventing the aggregation of crystalline material around the outside of the droplet while wetting of the surface.

A maximum mobility of 0.42 cm\textsuperscript{2}/Vs with a threshold voltage of 3 V, subthreshold slope of less than 1 V/decade and on/off current ratio of 10\textsuperscript{7} were obtained from the mixed solvents (Figure 2.36). While these results are promising, the device-to-device uniformity was not good so SAM optimization is being done to improve and obtain reproducible morphology (Figure 2.37).
2.2.2.5.2 Spray-coated F TES ADT TFTs

Ease of fabrication was again improved with optimization for spray-coating. F TES ADT was sprayed from solution onto Si/SiO₂ bottom contact devices varying spraying distance, gas pressure, and solvent to optimize crystal growth. The best devices were obtained from with a mobility of 0.3 cm²/Vs and on/off current ratio of 10⁷. The measured mobilities for chlorobenzene, toluene, and 1,2-dichlorobenzene were 0.3, 0.1 and 0.01 cm²/Vs respectively. These values correspond to solvent evaporation due to differences in vapor pressures. Toluene has the highest vapor pressure, so evaporation takes place faster than chlorobenzene resulting in less time for crystals to orient on the film. Vapor pressure is not the only factor since 1,2-dichlorobenzene has the lowest vapor pressure, but also the lowest mobilities. Films from dichlorobenzene were not continuous resulting in “coffee stain” crystalline areas isolated within amorphous regions.

The pressure of the spraying gas also had an affect on crystal morphology and mobility (Table 2.7). Argon gas was used as the spraying gas to prevent oxidation of the semiconductor. The most uniform crystal size was obtained from lower carrier gas pressures. The mobilities correspond well with this result. As the pressure increases, the solution is blown off of the substrate leading to less uniform coverage. At higher pressures, the crystal size continues to decrease, but crystal density increases in the channel as does the mobility.
<table>
<thead>
<tr>
<th>Ar pressure (psi)</th>
<th>5</th>
<th>9</th>
<th>10</th>
<th>18</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{FET}$ (cm²/Vs)</td>
<td>0.15</td>
<td>0.030</td>
<td>0.040</td>
<td>0.05</td>
<td>0.08</td>
</tr>
<tr>
<td>± 0.05</td>
<td>± 0.007</td>
<td>± 0.008</td>
<td>± 0.02</td>
<td>± 0.02</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.7 average mobilities for spray-coated F TES ADT, 45a TFTs

Spraying distance had an effect on the mobility with a maximum being reached with the nozzle being 13 cm from the surface. When the nozzle is too close, a similar result as high gas pressure is observed. When the distance is too far, evaporation of the solvent takes place before reaching the substrate so film crystallinity and uniformity decrease.

2.2.2.6 F TEG ADT TFT optimization

F TEG ADT, 45e also showed promising results with uniform crystal growth and high mobilities. This compound also readily grows uniform films from spin casting in low wt. % solution of chlorobenzene with crystallization on PFBT treated gold electrodes (Figure 2.38). Very uniform films with even larger crystal grains result from solvent-vapor annealing.

![Figure 2.38](image)

_F TEG ADT, 45e thin films deposited onto PFBT treated gold contacts from (a) 2 wt.% solution in chlorobenzene (b) 2 wt.% solution in chlorobenzene solvent-vapor annealed, and (c) 0.25 wt.% in chlorobenzene from Professor Oana Jurchescu at Wake Forest University_

Films spin cast from 2 wt.% solution in chlorobenzene showed mobilities of 1.35 cm²/Vs, but a decrease in concentration more than doubled mobility as fabricated by Oana Jurchescu at Wake Forest University (Figure 2.39). As seen in Figure 2.38, the lower concentration solution formed larger grain size, but with still good uniformity. Films cast from 0.25 wt.% had a mobility of 3.25 cm²/Vs.
Figure 2.39

transfer (a) and output (b) characteristics for F TEG ADT 45e spin cast from 0.25 wt.% solution in chlorobenzene onto bottom contact PFBT treated transistors from Professor Oana Jurchescu at Wake Forest University

Figure 2.40

F TEG ADT 45e TFT spin cast from 0.25 wt.% solution in chlorobenzene onto bottom contact PFBT treated electrodes (a) mobility vs. channel length plot (b) OM and (c) zoom of channel region morphology from Professor Oana Jurchescu at Wake Forest University

There is still a channel width dependence for F TEG ADT, like F TES ADT, suggesting grain sizes within the tens of micrometers and nucleation on PFBT treated electrodes (Figure 2.40). The maximum mobility is still higher than that of F TES ADT under the same conditions.
Figure 2.41

mobility spread for 28 F TEG ADT 45e TFT devices studied from Professor Oana Jurchescu at Wake Forest University

Device mobility varied from device to device, but more than a third of the devices had a mobility over 1 cm²/Vs while only one showed no transistor characteristics (Figure 2.41).

2.2.2.7 Blend device performance

As previously discussed in section 2.1.4, work has been done to combine the higher mobility of small molecules with the ease of polymer fabrication by blending small molecule semiconductors with insulating polymers. Semiconducting polymers can also be used to generate ambipolar devices which should better compete with amorphous silicon.80-83

Professor Thomas Anthopoulos and his research group at Imperial College, London use semiconductor/polymer blends that exhibit vertical phase separation82 to fabricate dual gate (DG) and top gate (TG) structured TFTs (Figure 2.42).106 This method takes advantage of the fact that the semiconductor is concentrated at the top and bottom of the blend, as measured by dynamic secondary ion mass spectrometry (DSIMS) with Cs ion bombardment.
Amorphous p-type semiconducting polymer poly(triarylamine) (PTAA) was blended with high mobility small molecules to improve device-to-device uniformity for large area applications. F TES ADT/PTAA blend devices with large grain sizes and an average mobility of >2 cm²/Vs were measured and stored in air that showed no decrease in mobility over a four week study. The off current, increased steadily which decreased the on/off current ratio over time, though off currents were improved by annealing aged films.

Work has also been done with 1:1 F TEG ADT/PTAA blends to determine the differences in processing and mobility in the group 14 functionalized F ADTs. The Anthopoulos group analyzed spin coated film morphology on glass with polarized light microscopy (PLM) and AFM to determine what annealing conditions led to the best film morphology (Figure 2.43). They then fabricated top gate TFTs with CYTOP dielectric and Al gate to test for mobility.
PLM figures (scale μm) for TEG ADT, 45e/PTAA blend spin coated from tetralin at 500 RPM for 10 s then 2000 RPM for 20 s on glass (a) annealed at 100°C for 5 min; (b) slow dried for 6 min at RT then annealed at 100°C for 5 min; (c) annealed at 140°C for 5 min; (d) Sample C further annealed at 140°C for 1 hr from Professor Thomas Anthopoulos at Imperial College, London

The most uniform films came from annealing at 100°C for 5 min, but there may be smaller crystals within the visible large domains. PLM is used to measure the average crystal grain size (Figure 2.44). Though crystals of F TEG ADT appear to be larger than F TES ADT with less birefringence the mobility is lower which would suggest poorer morphology or non-uniform crystal size.
Top gate TFTs with CYTOP dielectric and Al gate were prepared at Imperial College, London on top of the above F TEG ADT/PTAA films on glass in air, under nitrogen, and in air at higher annealing temperatures. The slow dried devices showed large leakage current due to high surface roughness from large crystal grain, similar to F TES ADT blends. Devices fabricated under nitrogen had the highest mobilities (Figure 2.45). Higher temperature annealing moved the threshold voltage closer to zero, but decreased mobility (Table 2.8).
Table 2.8 average mobilities for F TEG ADT 45e/PTAA blend TG TFTs from Professor Thomas Anthopoulos at Imperial College, London

Overall, mobilities for F TEG ADT/PTAA blends are lower than those of F TES ADT/PTAA blends, though grain size appears larger. The improved mobilities upon fabrication under nitrogen may correspond to the almost 3-fold decrease in stability to light and air for F TEG ADT compared to F TES ADT (Table 2.5).

2.3 Summary

These results show that improvements are being made to processing and stability of organic small molecules like TES ADT and F TES ADT for TFTs. Functionalization with group 14 elements on the solubilizing ethynyl groups decreases stability to light, but also changes the bandgap. The lower bandgap combined with improved mobility and processability for F TEG ADT make it an interesting target for studying solution processing and crystal growth, as has been done extensively with F TES ADT. New large-scale solution processing techniques were also optimized as an attempt to push towards commercial devices.

2.4 Experimental

Bulk solvents (methylene chloride (DCM), chloroform, pentane, hexane, heptane, ethyl acetate (EtOAc), toluene, isopropanol, absolute ethanol, 95% ethanol, methanol, diethyl ether, tetrahydrofuran (THF), glacial acetic acid (AcOH)) were purchased from Pharmco Aaper. Unless specified, organic phases were dried using anhydrous magnesium sulfate 99.5% purchased from Alfa Aesar. N-formylmorpholine 99+% was purchased from TCI America. 1,4-cyclohexanedione 98% and bromine 99.8% were purchased from Acros Organics. Thiophene-3-carboxaldehyde 96%, anhydrous potassium carbonate 99%, sodium thiosulfate pentahydrate 99+, reagent grade stannous chloride (SnCl2) dihydrate, and [bis(trifluoroacetoxy)iodo]benzene 97% were purchased from Alfa Aesar. Chloroform-D 99.8% was purchased from Cambridge isotope labs Inc. Benzene ACS grade, ACS grade concentrated hydrochloric acid (HCl), and ACS grade sodium hydroxide (NaOH) were purchased from VWR. (Trimethylsilyl)acetylene (TMSA) 97%, (triethylsilyl)acetylene (TESA) 97%, (triisopropylsilyl)acetylene (TIPS) 97%, tert-butyldimethylsilylacetylene (TBDMSA) 98% and 3,3-dimethyl-1-butyne (t-buA) 98% were purchased from GFS chemicals. Triethylgermylchloride and camphor sulfonic acid >98% were purchased from Fisher. N-fluorobenzenesulfonylimide (NFSI) 98% was purchased from Matrix Scientific. Ethylene glycol 99+%,
chlorosuccinimide (NCS) 98%, iodine >99.8%, carbon tetrachloride 99.9%, anhydrous THF ≥99.9% inhibitor free, 2.5 M n-butyllithium solution (n-BuLi) in hexanes, and 0.5 M ethynylmagnesium bromide solution in THF were purchased from Sigma Aldrich.

Flash chromatography was performed using 60 Å pore size, 230 x 400 mesh silica gel purchased from Sorbent technologies. Nuclear magnetic resonance (NMR) spectra were measured on Varian instruments (Gemini 200 MHz / Unity 400 MHz) spectrometer. Chemical shifts were reported in ppm relative to CDCl₃ or C₃D₆O as internal standard. Absorption spectra were measured on a UV-2501PC Shimadzu instrument or an Evolution 300 BB UV-Visible spectrometer from Thermo Scientific. Mass spectroscopy was analyzed in EI mode at 70 eV on a JEOL (JMS-700T) Mass Spectrometer and Bruker Daltonics MALDI-TOFMS in the positive ion mode with no matrix or TCNQ matrix. Cyclic voltammetry was carried out on a BAS CV-50W and BASInc. EpsilonEC potentiostat, with ferrocene as the internal standard in a 1M Bu₄NPF₆ solution in DCM.

**Thiophene-3-aldehyde ethylene acetal (32)**

The starting material, 3-thiophenecarboxaldehyde, 31 was purified by flash chromatography with dichloromethane. A 500 mL round bottom flask was charged with 50 g (446 mmol) thiophene-3-carboxaldehyde dissolved in 250 mL of benzene. 31 mL of ethylene glycol (558 mmol) was added along with a catalytic amount of camphor sulfonic acid. The reaction mixture was heated at 111°C overnight, with water collected in a Dean-Stark apparatus. After cooling to room temperature, the mixture was poured into 200 mL of saturated sodium bicarbonate solution and stirred at room temperature for 10 minutes. It was extracted with ether, dried and concentrated under reduced pressure to give 68.95 g (99%) of 32 as a brown oil. ¹H NMR (200 MHz, CDCl₃) δ: 3.935 (m, 4H); 5.883 (s, 1H); 7.177 (d, J = 5.2 Hz, 1H); 7.275 (d, J = 4.6 Hz, 1H); 7.402 (s, 1H) ppm. ¹³C NMR (50 MHz, CDCl₃) δ: 64.912, 100.394, 123.575, 125.760, 126.185, 140.375 ppm. MS (EI 70 eV) m/z 156 (M⁺), 84 (M⁺-C₃H₅O₂).

**Thiophene-2,3-dicarboxaldehyde (33)**

A mass of 15.6 g (100 mmol) 32 was dissolved in 100 mL anhydrous THF in a flame dried 250 mL round bottom flask under nitrogen atmosphere. The reaction mixture was cooled to -75°C and 40 mL (100 mmol) 2.5 M n-BuLi solution in hexanes was added slowly. The mixture was allowed to stir for 15 minutes at -75°C, after which 22 mL (215 mmol) N-formylmorpholine was added. The solution was allowed to warm to room temperature while stirring overnight. After quenching with water, the reaction mixture was extracted with ether, dried, and concentrated. A quick silica gel plug using 2:1 hexane/ethyl acetate removed most of the lower impurities. The crude product was concentrated and then dissolved in 100 mL 80% acetic acid. This mixture was heated to 60°C overnight or room temperature over the weekend. After cooling to room temperature, the mixture was diluted with 400 mL water and
100 mL ethyl acetate was added. After separation, the organic layer was washed twice with water, dried, and concentrated. Silica gel chromatography using 5:1 hexane/ethyl acetate was used to isolate the crude product. After recrystallization from hexane, 9.52 g (68%) fluffy yellow crystals 33 were isolated. $^1$H NMR (200 MHz, CDCl$_3$) $\delta$: 7.648 (d, $J$ = 5.2 Hz, 1H); 7.749 (d, $J$ = 5.0 Hz, 1H); 10.387 (s, 1H); 10.495 (s, 1H) ppm. $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta$: 130.307, 134.101, 182.967, 185.001 ppm. MS (El 70 eV) $m/z$ 140 (M$^+$), 111 (M$^+$-CHO).

**Thiophene-2,3-dialdehyde ethylene diacetal (36)**

A mass of 7.0 g (50 mmol) 33 dissolved in 100 mL benzene with 6.96 mL (125 mmol) ethylene glycol and a catalytic amount of camphor sulfonic acid was heated at 111°C overnight in a Dean-Stark apparatus. After cooling to room temperature, the mixture was poured into about 200 mL of saturated sodium bicarbonate solution and stirred at room temperature for 30 minutes. It was then extracted with ether, dried and concentrated under reduced pressure to give 11.29 g (99%) dark brown oil 36. $^1$H NMR (200 MHz, CDCl$_3$) $\delta$: 3.866 (m, 4H); 3.961 (m, 4H); 5.938 (s, 1H); 6.245 (s, 1H); 7.024 (d, $J$ = 5.2 Hz, 1H); 7.163 (d, $J$ = 5.2 Hz, 1H) ppm. $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta$: 64.672, 64.831, 98.123, 98.659, 124.792, 126.491, 137.425, 139.785 ppm. MS (El 70 eV) $m/z$ 228 (M$^+$).

**5-fluorothiophene-2,3-dialdehyde (37)**

To a flame dried 250 mL round bottom flask under nitrogen atmosphere, 7.30 g (32 mmol) 36 dissolved in 30 mL dry THF was cooled to -78°C. 12.8 mL (32 mmol) of 2.5 M n-BuLi solution in hexanes was added slowly. After stirring for 15 minutes at -78°C, 21.68 g (69 mmol) N-fluorobenzene sulfonamide (NFSI) dissolved in 70 mL dry THF was added dropwise via addition funnel. The cold bath was removed and the reaction allowed to stir overnight at room temperature. After quenching with water, the reaction mixture was diluted with ether, washed with brine, dried, and concentrated. The crude product was purified by silica column chromatography using a mixture of 9:1 hexane/DCM ramping to 1:1 to remove the sulfonate byproduct. The product was eluted in 1:1 hexane/EtOAc. After deprotection in 100 mL 80% aqueous acetic acid at 60°C overnight, the mixture was diluted with water and extracted with ether. After being dried and concentrated, the product was purified using silica chromatography with a 5:1 mixture of hexane/EtOAc followed by a second silica column using 1:1 hexane/DCM. After recrystallization from hexane, 2.78 g (55%) light yellow crystals 37 were isolated. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 6.994 (d, $J$ = 1.1 Hz, 1H); 12.240 (d, $J$ = 1.5 Hz, 1H); 10.373 (d, $J$ = 2.9 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 110.564, 139.778 (d, $J$ = 222 Hz), 168.392, 174.439, 182.012, 183.682 ppm. MS (El 70 eV) $m/z$ 156 (M$^+$), 127 (M$^+$-CHO).

**5-chlorothiophene-2,3-dialdehyde (38)**

A mass of 1.31 g (6 mmol) 36 was dissolved in 6 mL dry THF in a 100 mL flame dried round bottom flask. The solution was cooled to -78°C then 2.76 mL of 2.5M n-
BuLi in hexane (6.9 mmol) was added slowly. After stirring for 20 minutes, 1.15 g (8.6 mmol) N-chlorosuccinimide was added in small portions. The mixture was allowed to warm slowly to room temperature while stirring overnight. After quenching with water, the mixture was extracted with ether, dried and concentrated. Silica chromatography using a 2:1 mixture of hexane and ethyl acetate afforded a mixture of the chlorinated diacetal and starting material. After deprotection in 50 mL 80% acetic acid at 60°C overnight, the mixture was diluted with water and extracted with ether. After being dried and concentrated, the product was purified using silica chromatography with a 5:1 mixture of hexane and ethyl acetate to yield 0.63 g (63%) pale yellow powder 38. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.400 (s, 1H); 10.212 (s, 1H); 10.333 (s, 1H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 128.773, 140.964, 143.181, 145.815, 181.660, 183.641 ppm. MS (EI 70eV) \(m/z\) 174, 176 (3:1, M\(^+\)), 145, 147 (3:1, M\(^+\) - CHO).

5-bromothiophene-2,3-dialdehyde (39)

33 (1.4 g, 10 mmol) was dissolved in 20 mL chloroform with 1 crystal iodine. Bromine (1.54 mL, 30 mmol) was added dropwise at room temperatures, and the mixture was stirred overnight. After extracting with sodium carbonate and sodium thiosulfate solutions, the mixture was dried, filtered and concentrated. The crude mixture was purified using silica chromatography with 5:1 hexane/EtOAc then 1:1 hexane/CH\(_2\)Cl\(_2\). After recrystallization from hexane 1.80 g (82%) yellow crystals 39 were isolated. \(^1\)H NMR (200 MHz, CDCl\(_3\)) \(\delta\): 7.590 (s, 1H), 10.258 (s, 1H), 10.370 (s, 1H) ppm. \(^{13}\)C (50 MHz, CDCl\(_3\)) \(\delta\): 124.086, 132.637, 143.943, 148.739, 181.595, 183.530 ppm. MS (EI 70eV) \(m/z\) 218, 220 (1:1, M\(^+\)), 189, 191 (1:1, M\(^+\)-CHO).

5-iodothiophene-2,3-dialdehyde (40)

A mass of 2.80 g (20 mmol) 33 and 3.05 g (12 mmol) iodine was dissolved in 30 mL carbon tetrachloride. The reagent [bis(trifluoroacetoxy)jodo]benzene (5.16 g, 12 mmol) was added last and the reaction mixture was allowed to stir at room temperature overnight. After washing with sodium thiosulfate solution and extraction with ether, the product was dried, filtered and purified by silica chromatography with hexane followed by 1:1 hexane/DCM. After recrystallization from hexane 3.03 g (57%) yellow crystals 40 were obtained. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 6.721 (s, 1H); 9.698 (s, 1H); 9.794 (s, 1H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 86.511, 139.590, 144.561, 152.849, 181.333, 183.307 ppm. MS (EI 70eV) \(m/z\) 266 (M\(^+\)), 237 (M\(^+\)-CHO).

anthra[2,3-b;6,7-b']dithiophene-5,11-dione and anthra[2,3-b;7,6-b']dithiophene-5,11-dione (ADT quinone, 34)

A mass of 3.5 g 33 (25 mmol) and 1.4 g (12.5 mmol) cyclohexanedione were dissolved in 40 mL absolute ethanol in a 250 mL Erlenmeyer flask. 6 drops of 15% KOH solution in water were added and the reaction mixture was allowed to stir for 1 hour after washing down the sides with methanol. The precipitate was filtered,
washed with methanol and ether, and dried. A mass of 3.48 g (87%) clumpy tan-
mustard powder 34 was obtained. (MALDI, TCNQ matrix) m/z 320 (100%, M+).

2,8-difluoroanthra[2,3-b;6,7-b']dithiophene-5,11-dione and 2,8-
difluoroanthra[2,3-b;7,6-b']dithiophene-5,11-dione (F ADT quinone, 41)

0.5000 g (3.2 mmol) freshly recrystallized 37 and 0.1795 g (1.6 mmol) cyclohexanone were dissolved in 10 mL absolute ethanol in a 50 mL Erlenmeyer flask. 2 drops of 15% KOH solution in water were added and the reaction mixture was stirred for 30 minutes after washing down the sides with methanol. After filtration, the precipitate was washed with methanol and ether and dried to give 0.3594 g (63%) tan static-prone powder 41. (MALDI, TCNQ matrix) m/z 356 (100%, M+).

2,8-dichloroanthra[2,3-b;6,7-b']dithiophene-5,11-dione and 2,8-
dichloroanthra[2,3-b;7,6-b']dithiophene-5,11-dione (Cl ADT quinone, 42)

1.000 g (5.7 mmol) 38 and 0.3218 g (2.9 mmol) cyclohexanone were dissolved in 10 mL absolute ethanol in a 50 mL Erlenmeyer flask. 2 drops of 15% KOH solution in water were added and the reaction mixture was stirred for 1 hour after washing down the sides with methanol. After filtration, the precipitate was washed with methanol and ether and dried to give 0.6260 g (56%) tan powder 42. (MALDI, TCNQ matrix) m/z 389 (100%, M+).

2,8-dibromoanthra[2,3-b;6,7-b']dithiophene-5,11-dione and 2,8-
dibromoanthra[2,3-b;7,6-b']dithiophene-5,11-dione (Br ADT quinone, 43)

2.2046 g (10 mmol) 39 and 0.5612 g (5 mmol) cyclohexanone were dissolved in 10 mL absolute ethanol in a 250 mL Erlenmeyer flask. 2 drops of 15% KOH solution in water were added and the reaction mixture was stirred for 1 hour after washing down the sides with methanol. After filtration, the precipitate was washed with methanol and ether and dried to give 1.1446 g (48%) mustard tan powder 43. (MALDI, TCNQ matrix) m/z 478 (100%, M+).

2,8-diiodoanthra[2,3-b;6,7-b']dithiophene-5,11-dione and 2,8-
diiodoanthra[2,3-b;7,6-b']dithiophene-5,11-dione (I ADT quinone, 44)

2.000 g (7.5 mmol) 40 and 0.4210 g (3.8 mmol) cyclohexanone were dissolved in 20 mL absolute ethanol in a 50 mL Erlenmeyer flask. 4 drops of 15% KOH solution in water were added and the reaction mixture was stirred for 1 hour after washing down the sides with methanol. After filtration, the precipitate was washed with methanol and ether and dried to give 1.1612 g (54%) tan powder 44. (MALDI, TCNQ matrix) m/z 572 (100%, M+).

5,12-bis(triethylsilyl-ethyl)anthra[2,3-b;6,7-b']dithiophene and 5,12-
bis(triethylsilyl-ethyl)anthra[2,3-b;7,6-b']dithiophene (TES ADT, 21a)
(general procedure for making ADT derivatives)

Into a flame dried round bottom flask, 2.23 mL (12.5 mmol) triethylsilyl acetylene dissolved in 10 mL of heptane was added. The vessel was cooled to 0°C and 4.38 mL (10.9 mmol) 2.5 M n-BuLi was added. After stirring at room temperature for 1 hour the quinone, 34 (1 g, 3.1 mmol) along with 90 mL heptane and 10 mL dry THF was added and the mixture was stirred at room temperature overnight. After quenching with water the crude diol was dissolved in THF and 2.82 g (12.5 mmol) tin chloride with 100 mL 10% HCl was added. The mixture was allowed to stir at room temperature for 1 hour after which it was extracted with hexane, washed with water, dried, and concentrated. The product was purified using silica column chromatography in hexane to give 1.4150 g (80%) dark purple solid. The solid was recrystallized from hexane to give 1.3089 g (74%) dark purple crystals 21a. $^1$H NMR (400 MHz, CDCl$_3$) δ: 0.905 (quart, $J = 7.995$ Hz, 12H); 1.233 (t, $J = 7.861$ Hz, 18H); 7.436 (d, $J = 5.596$ Hz, 2 H); 7.538 (d, $J = 5.596$ Hz, 2H); 9.101 (s, 2H); 9.150 (s, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 4.948, 8.030, 120.203, 121.455, 121.508, 123.953, 130.010, 130.102, 155.099 ppm. MS (MALDI-TOF, no matrix) m/z 566 (100%, M$^+$).

5,12-bis(tert-butylethynyl)anthra[2,3-b;6,7-b']dithiophene and 5,12-bis(tert-butylethynyl)anthra[2,3-b;7,6-b']dithiophene (t-Bu ADT, 21b)

47% dark purple needles 21b. $^1$H NMR (400 MHz, CDCl$_3$) δ: 1.619 (s, 18H); 7.442 (d, $J = 5.27$ Hz, 2 H); 7.504 (d, $J = 5.12$ Hz, 2H); 9.000 (s, 2H); 9.061 (s, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 31.585, 120.213, 121.460, 121.511, 123.958, 130.015, 130.120, 155.100 ppm. MS (MALDI-TOF, no matrix) m/z 450 (100%, M$^+$).

Triethylgermyl acetylene (TEGA)

Triethylgermyl acetylene was prepared by adding 200 mL of 0.5 M (100 mmol) ethynyl Grignard in THF solution to a flame dried 500 mL round bottom flask under nitrogen. Triethylchlorogermane (4.87 g, 25 mmol) was added dropwise at room temperature and the solution was stirred overnight at room temperature. After TLC with potassium permanganate stain confirmed completion, the reaction mixture was quenched with water and 10% HCl solution. After extraction with pentane, the organic layer was dried, filtered, and the solvent removed by simple distillation. Silica chromatography with pentane was used to remove a slight brown color and after distillation of the pentane 3.54 g (77%) of the desired colorless liquid acetylene was isolated. $^1$H NMR (400 MHz, CDCl$_3$) δ: 1.141 (quart, $J = 7.3$ Hz, 6H), 2.054 (t, $J = 7.7$ Hz, 9H), 2.533 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 5.683, 8.923, 8.795, 93.385 ppm. MS (EI 70eV) m/z 182, 184, 185, 186, 188 (2.5:3.5:1:4.5:1, M$^+$), 153, 155, 156, 157, 159 (2.5:3.5:1:4.5:1, M$^+$-Et), 125, 127, 128, 129, 131 (2.5:3.5:1:4.5:1, M$^+$-Et$_2$H), 95, 97, 98, 99, 101(2.5:3.5:1:4.5:1, M$^+$-Et$_3$).

5,12-bis(triethylgermylene)anthra[2,3-b;6,7-b']dithiophene and 5,12-bis(triethylgermylene)anthra[2,3-b;7,6-b']dithiophene (TEG ADT, 21c)
63% dark purple crystals 21c. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$: 1.147 (quart, $J = 7.81$ Hz, 12H); 1.326 (t, $J = 7.655$ Hz, 18H); 7.430 (d, $J = 5.596$ Hz, 2 H); 7.520 (d, $J = 5.196$ Hz, 2H); 9.128 (s, 2H); 9.180 (s, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$: 6.421, 9.586, 103.358, 107.662, 120.324, 120.362, 131.600, 121.653, 123.976, 129.768, 129.821, 129.859, 129.904, 130.003, 130.094, 139.431, 139.583, 140.031, 140.129 ppm. MS (MALDI-TOF, no matrix) $m/z$ 650, 652, 654, 656, 658 (2.5:3.5:1:4.5:1, M$^+$).

2,8-difluoro-5,12-bis(trimethylsilyl)ethynyl]anthra[2,3-b;6,7-b']dithiophene and 2,8-difluoro-5,12-bis(trimethylsilyl)ethynyl]anthra[2,3-b;7,6-b']dithiophene (F TMS ADT, 45b)

50% red-purple fluffy crystals 45b. $^1$H NMR (200 MHz, CDCl$_3$): $\delta$: 0.455 (s, 18H); 6.820 (d, $J = 2.60$ Hz, 2 H); 8.781 (s, 2H); 8.865 (s, 2H) ppm. $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta$: 0.125, 102.810, 102.930, 112.525, 117.164, 120.495, 120.572, 120.784, 120.837, 120.927, 129.879, 130.053, 133.475, 136.340, 164.296 ppm. MS (MALDI-TOF, no matrix) $m/z$ 518 (100%, M$^+$).

2,8-difluoro-5,12-bis(tert-butyldimethylsilyl)ethynyl]anthra[2,3-b;6,7-b']dithiophene and 2,8-difluoro-5,12-bis(tert-butyldimethylsilyl)ethynyl]anthra[2,3-b;7,6-b']dithiophene (F TBDMS ADT, 45c)

68% red-purple crystals 45c. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$: 0.399 (s, 12H); 1.152 (s, 18H); 6.794 (d, $J = 2.598$ Hz, 2 H); 8.802 (s, 2H); 8.879 (s, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$: -4.266, 26.372, 102.810, 102.929, 112.520, 117.075, 120.469, 120.560, 120.734, 120.825, 120.916, 129.730, 120.823, 120.920, 129.885, 130.059, 133.475, 136.340, 164.285 ppm. MS (MALDI-TOF, no matrix) $m/z$ 602 (100%, M$^+$).

2,8-difluoro-5,12-bis(tert-butylethynyl]anthra[2,3-b;6,7-b']dithiophene and 2,8-difluoro-5,12-bis(tert-butylethynyl]anthra[2,3-b;7,6-b']dithiophene (F t-Bu ADT, 45d)

71% red-purple crystals 45d. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$: 1.581 (s, 18H); 6.792 (d, $J = 2.63$ Hz, 2 H); 8.719 (s, 2H); 8.802 (s, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$: 31.585, 102.812, 102.926, 112.521, 117.075, 120.469, 120.560, 120.734, 120.825, 120.916, 129.874, 130.056, 133.472, 136.334, 164.276 ppm. MS (MALDI-TOF, no matrix) $m/z$ 486 (100%).

2,8-difluoro-5,12-bis(triethylgermylethynyl]anthra[2,3-b;6,7-b']dithiophene and 2,8-difluoro-5,12-bis(triethylgermylethynyl]anthra[2,3-b;7,6-b']dithiophene (F TEG ADT, 45e)

0.9558 g (83%) dark purple solid was recrystallized from hot hexanes to yield 0.7716 g (67%) dark purple crystals 45e. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$: 1.146 (quart,
$J = 8.394 \text{ Hz, } 6\text{H)}, 1.321 \text{ (t, } J = 7.195 \text{ Hz, } 9\text{H)}, 6.796 \text{ (d, } J = 2.60 \text{ Hz, } 2\text{H)}, 8.859 \text{ (s, } 2\text{H)}, 8.939 \text{ (s, } 2\text{H)}$  $^{13}\text{C NMR (100 MHz, CDCl}_3\text{)} \delta$: $6.375, 9.571, 102.804, 102.910, 120.681, 120.772, 120.954, 121.038, 125.744, 128.462, 129.532, 129.745, 130.079, 130.276, 133.768, 135.962, 136.561, 151.736 \text{ ppm. MS (MALDI-TOF, no matrix) } m/z 686, 688, 690, 692, 694 \text{ (2.5:3.5:1:4.5:1, M}^+)$. 
Chapter 3: Heteroatom (Y) functionalization

The heteroatom (Y) from the generic model can be substituted with group 16 elements to form new heteroacenes that can be functionalized with group 14 containing solubilizing groups. The sulfur analogue ADT has been discussed in detail in Chapter 2 so a comparison can now be made with oxygen-containing anthradifuran (ADF).

\[
\text{Anthadifuran (ADF)}
\]

This heterocycle is not known in the literature possibly because of the lower stability of furans to conditions used in common synthetic methods. There is a reference to anthradifuran, but it refers to this quinone structure.\[107\]

3.1 ADF Synthesis

Synthesis of furan dialdehyde, 51 was much less straight forward than that of the thiophene analogue (Scheme 3.1).\[108\] Furans seem to be much less stable to acid than thiophenes, thus deprotection of the 3-acetal-2-furancarboxaldehyde was not reached before significant decomposition occurred. It was also not possible to remove the mono acetal via recrystallization, as is the case for thiophene dialdehyde.
The aldol condensation to form ADF quinone, 52 has a much lower yield than that found with the corresponding ADT, 34. This low yield is probably due to decreased purity of 51 discussed above. The final ADF acenes 53 are much more soluble in nonpolar solvents than ADTs which has also been reported for oligofurans compared to oligothiophenes synthesized by Bendikov\textsuperscript{[9,10]}

As a result of the low yields for 51 and 52, other synthetic pathways to the desired dialdehyde were explored (Scheme 3.2).

Zaluski and coworkers suggested another method for obtaining the desired dialdehyde from 2,3-dibromofuran\textsuperscript{[11]}. Nitrile functionalized furans that can be obtained from 2,3-dibromofuran were reduced to the corresponding aldehydes with diisobutylaluminum hydride. Bromination of furan and functionalized furan, even in the presence of base, seems to generate enough HBr to decompose the resulting aldehyde\textsuperscript{[11]} or acid\textsuperscript{[13]}. Condensation of the impure 51 did yield the desired quinone, 52, which could be reacted with lithiated alkynes using the same conditions as ADT derivatives discussed in chapter 2\textsuperscript{[40]}. 

\textit{synthesis of group 14 ethynyl ADF derivatives 53}
3.2 TES ADF/TES ADT comparison

There is a blueshift in absorption for TES ADF compared to both TES ADT and F TES ADT in the absorption spectrum implying that ADF has less delocalization than ADT (figure 3.1).

![Figure 3.1](image)

*absorption spectral comparison for acenes TIPS Pn 6a, TES ADT 21a, F TES ADT 35a, and TES ADF 53a*

3.2.1 Electronic characteristics

![Figure 3.2](image)

*absorption spectra for TES ADF 53a and TES ADT 21a dissolved in dichloromethane and thin film drop-cast from toluene onto glass.*

A specific comparison shows that TES ADF has a two-fold increase in redshift from solution compared to thin film over TES ADT (Figure 3.2). This redshift indicates that drop cast films for TES ADF are more crystalline than those of TES ADT. Electronically, TES ADF has a larger bandgap than TES ADT and a slightly lower
HOMO that does not fully explain the dramatically longer thin film halftime (Table 3.1).

<table>
<thead>
<tr>
<th>Acene</th>
<th>Solution $\lambda_{\text{max}}$ (nm)</th>
<th>Film $\lambda_{\text{max}}$ (nm)</th>
<th>Shift (nm)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>$E_g$ (eV)</th>
<th>Film $t_{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TES ADT</td>
<td>554</td>
<td>560</td>
<td>6</td>
<td>5.22</td>
<td>3.05</td>
<td>2.17</td>
<td>14.2 min.</td>
</tr>
<tr>
<td>TES ADF</td>
<td>512</td>
<td>525</td>
<td>13</td>
<td>5.27</td>
<td>2.29</td>
<td>2.35</td>
<td>8.0 days</td>
</tr>
</tbody>
</table>

Table 3.1 *electronic characteristic comparison for TES ADF 53a and TES ADT 21a*

### 3.2.2 Crystal structure

TES ADF stacks in a 2-D $\pi$-stack (Figure 3.3) with much more overlap than TES ADT (Figure 3.4).

*Figure 3.3*

*crystal structure for TES ADF 53a and crystals with solution under ambient and UV illumination*

The increased overlap is a result of the stacks being in plane with each other, as opposed to TES ADT, where the stacks are offset.
3.2.3 Thermal properties

TES ADF has only one transition due to melting at 181.15°C in the DSC (Figure 3.5).

3.2.4 TFT performance

TFTs of TES ADF are being fabricated by Jes Sherman (Professor Thuc-Quyen Nguyen group, University of California, Santa Barbara, UCSB). Preliminary results...
show that OFET characteristics can be observed, but the mobility value of $1 \times 10^{-4}$ cm$^2$/V·s is quite low since little fabrication optimization has been done.

Figure 3.6

AFM images of TES ADF cast from solution and exposed to solvent-vapor annealing from Jes Sherman (UCSB)

Work is still being done to obtain uniform films, but film quality improves with solvent-vapor annealing similar to TES ADT (Figure 3.6).
3.3 Group 14 functionalized ADF

absorption spectral comparison for ADF (53a-c) and ADT (21a-c) derivatives in thin film and chloroform solution

The doubling of red shift from solution to film absorption is again present for t-Bu and TEG ADFs. We also see a similar trend with thin film stability, where the silyl derivative has the longest half-life (Figure 3.7).

<table>
<thead>
<tr>
<th>Acene</th>
<th>Solution $\lambda_{\text{max}}$ (nm)</th>
<th>Film $\lambda_{\text{max}}$ (nm)</th>
<th>Shift (nm)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>$E_g$ (eV)</th>
<th>Film $t_{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-Bu ADT</td>
<td>543</td>
<td>547</td>
<td>4</td>
<td>5.21</td>
<td>3.01</td>
<td>2.21</td>
<td>7.8 min.</td>
</tr>
<tr>
<td>TES ADT</td>
<td>554</td>
<td>560</td>
<td>6</td>
<td>5.22</td>
<td>3.05</td>
<td>2.17</td>
<td>14.2 min.</td>
</tr>
<tr>
<td>TEG ADT</td>
<td>553</td>
<td>557</td>
<td>4</td>
<td>5.28</td>
<td>3.14</td>
<td>2.13</td>
<td>9.5 min.</td>
</tr>
<tr>
<td>t-Bu ADF</td>
<td>504</td>
<td>517</td>
<td>13</td>
<td>5.21</td>
<td>2.82</td>
<td>2.39</td>
<td>3.2 days</td>
</tr>
<tr>
<td>TES ADF</td>
<td>512</td>
<td>525</td>
<td>13</td>
<td>5.27</td>
<td>2.92</td>
<td>2.35</td>
<td>8.0 days</td>
</tr>
<tr>
<td>TEG ADF</td>
<td>511</td>
<td>520</td>
<td>9</td>
<td>5.31</td>
<td>3.00</td>
<td>2.13</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 3.2 electronic characteristics for ADF (53a-c) and ADT (21a-c) derivatives

Electronically, ADFs have a similar trend to ADTs with a decreased bandgap down the table and lower LUMO value (Table 3.2).
3.4 Functionalized TES ADFs

Synthesis of halogenated ADFs following Subramanian's method\(^\text{40}\) was not possible since deprotection of the diacetal was never reached before decomposition (Scheme 3.3). As a result, direct lithiation was explored as an alternative route to dihalogenated derivatives (Scheme 3.4).

Unlike ADTs, it was possible to halogenate by direct lithiation with electrophilic halide sources (Figure 3.8). The yields are correlated to the electrophile’s solubility in heptane, the best solvent for lithiation (Table 3.3).

![Scheme 3.3 attempted synthesis of 5-halofuran-2,3-dialdehyde following Subramanian\(^\text{40}\)]

**Table 3.3 halogenation yields from direct lithiation of TES ADF 53a**
Electronically, halogenated ADFs behave similarly to halogenated ADTs, with a blue shift associated with fluorination (Figure 3.9).

![Figure 3.9](image)

*absorption spectrum for halogenated TES ADF derivatives*

### 3.5 Summary

Several derivatives of the new ADF chromophore were synthesized and characterized for electronic and crystallographic purposes. ADF has a dramatically improved stability to light compared with ADTs and adopts a similar crystal packing, so it should be promising for device applications. Preliminary TFT results show transistor properties, but optimization must be done to get a better estimate of the mobility.

### 3.6 Experimental

Bulk solvents (methylene chloride (DCM), chloroform, pentane, hexane, heptane, ethyl acetate (EtOAc), toluene, isopropanol, absolute ethanol, 95% ethanol (EtOH), methanol (MeOH), diethyl ether, tetrahydrofuran (THF), glacial acetic acid (AcOH)) were purchased from Pharmco Aaper. Unless specified, organic phases were dried using anhydrous magnesium sulfate 99.5% purchased from Alfa Aesar. N-formylmorpholine 99+% was purchased from TCI America. 1,4-cyclohexanedione 98% and bromine 99.8% were purchased from Acros Organics. Furan-3-aldehyde 96%, anhydrous potassium carbonate 99%, sodium thiosulfate pentahydrate 99+%, and reagent grade stannous chloride (SnCl2) dihydrate were purchased from Alfa Aesar. Chloroform-D 99.8% was purchased from Cambridge isotope labs Inc. Benzene ACS grade, ACS grade concentrated hydrochloric acid (HCl), and ACS grade sodium hydroxide (NaOH) were purchased from VWR. (Triethyilsilyl)acetylene (TESA) 97% and 3,3-dimethyl-1-butyne (t-buA) 98% were purchased from GFS chemicals. Triethylgermylchloride and camphor sulfonic acid >98% were purchased from Fisher. \(N\)-fluorobenzenesulfonylimide (NFSI) 98% was purchased
from Matrix Scientific. Ethylene glycol 99+%, N-chlorosuccinimide (NCS) 98%, iodine >99.8%, carbon tetrachloride 99.9%, anhydrous THF ≥99.9% inhibitor free, 2.5 M n-butyllithium solution (n-BuLi) in hexanes, and 0.5 M ethynylmagnesium bromide solution in THF were purchased from Sigma Aldrich.

Flash chromatography was performed using 60 Å pore size, 230 x 400 mesh silica gel purchased from Sorbent technologies. Nuclear magnetic resonance (NMR) spectra were measured on Varian instruments (Gemini 200 MHz / Unity 400 MHz) spectrometer. Chemical shifts were reported in ppm relative to CDCl₃ or C₆D₆ as internal standard. Absorption spectra were measured on a UV-2501PC Shimadzu instrument or an Evolution 300 BB UV-Visible spectrometer from Thermo Scientific. Mass spectroscopy was analyzed in El mode at 70 eV on a JEOL (JMS-700T) Mass Spectrometer and Bruker Daltonics MALDI-TOFMS in the positive ion mode with no matrix or TCNQ matrix. Cyclic voltammetry was carried out on a BAS CV-50W and BASInc. EpsilonEC potentiostat, with ferrocene as the internal standard in a 1M Bu₄NPF₆ solution in DCM.

**Furan-3-aldehyde ethylene acetal (50)**

3-furaldehyde, 49 (25 g, 260 mmol) was dissolved in 150 mL benzene along with 17.9 mL (322 mmol) ethylene glycol and 10 mg camphor sulfonic acid. The mixture was distilled overnight using a Dean-Stark trap. After cooling to room temperature, the mixture was neutralized, extracted with ether, and concentrated to yield 35.00 (87%) brown oil 50. ¹H NMR (400 MHz, CDCl₃) δ: 3.902 (m, 4H); 5.724 (s, 1H); 6.350 (dd, J₁ = 1.76 Hz, J₂ = 0.88 Hz, 1H); 7.287 (t, J = 1.76 Hz,1H); 7.422 (dd, J₁ = 1.62 Hz, J₂ = 0.88 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ: 65.130, 98.652, 108.422, 123.953, 141.177, 143.638 ppm. MS (El 70eV) m/z 140 (M⁺).

**Furan-2,3-dialdehyde (51)**

In a 250 mL flame dried round bottom flask with 50 mL dry THF, 7.0 g (50 mmol) 50 was dissolved. After cooling to -78°C, 20 mL (2.5M, 50 mmol) n-BuLi was added. The mixture was stirred for 20 minutes at -78°C, then 10.1 mL (100 mmol) N-formylmorpholine was added. The mixture was allowed to warm to room temperature while stirring overnight. After quenching with water, the product was extracted with ether, dried and concentrated. Silica chromatography using a 2:1 mixture of hexane/ethyl acetate gave 7.39 g (88%) yellow oil, furan-2-aldehyde-3-acetal. The protecting group was removed by stirring in 100 mL 80% acetic acid overnight at 60°C. After cooling to room temperature, the acid was diluted with 300 mL water and the product extracted with ethyl acetate, dried, and concentrated. Silica chromatography using a 5:1 mixture hexane/ethyl acetate was undergone followed by another silica column with 1:1 hexane/DCM to DCM to yield 4.54 g yellow solid (76% crude). After recrystallization from hexane, 6.08 g (43%) fluffy yellow-white crystals 51 were obtained. ¹H NMR (400 MHz, CDCl₃) δ: 6.659 (d, J = 2.05 Hz, 1H), 7.387 (d, J = 2.05 Hz, 1H), 9.323 (s, 1H), 9.903 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ: 130.686, 145.542, 184.658, 194.375 ppm. MS (El 70eV) m/z
124 (M⁺); 95 (M⁺ - CHO).

2,3-furan dialdehyde ethylene diacetal (54)

To a 250 mL round bottom flask flame dried and cooled under nitrogen 14 g (100 mmol) 50 was dissolved in 100 mL dry THF. The mixture was cooled to -78°C then 40 mL of 2.5M n-BuLi in hexane (100 mmol) was added. The mixture was stirred for 20 minutes followed by addition of 22 mL (215 mmol) N-formylmorpholine. After stirring at room temperature for 5 hours the mixture was quenched with water and extracted with ether. The organic layer was dried with magnesium sulfate and concentrated. After silica chromatography using a mixture of 5:1 hexane and ethyl acetate 12.69 g (76%) furan-3-acetal-2-aldehyde was isolated.

Furan-3-acetal-2-aldehyde was directly dissolved in benzene with 6.3 mL (113 mmol) ethylene glycol and 10 mg camphor sulfonic acid and distilled overnight with a Dean-Stark trap. After cooling to room temperature, the mixture was poured into 100 mL sodium carbonate solution, extracted with ether, dried over magnesium sulfate and concentrated. No further purification was necessary resulting in 15.53 g (97%, 73% for 2 steps) viscous brown oil 54. 1H NMR (400 MHz, CDCl₃) δ: 3.920 (m, 2H), 3.956 (m, 2H), 4.032 (m, 2H), 4.105 (m, 2H), 5.943 (s, 1H), 6.056 (s, 1H), 6.407 (d, J = 2.00 Hz, 1H), 7.323 (d, J = 1.60 Hz, 1H) ppm. 13C NMR (100 MHz, CDCl₃) δ: 65.153, 65.388, 97.027, 97.900, 109.522, 122.488, 142.687, 148.297 ppm. MS (EI 70eV) m/z 212 (M⁺).

anthra[2,3;6,7']difuran-5,11-dione and anthra[2,3;7,6']difuran-5,11-dione (ADF quinone, 52)

A mass of 0.6200 g (5 mmol) 51 was dissolved in 5 mL ethanol with 0.2800 (2.5 mmol) cyclohexanedione in a 25 mL round bottom flask. While stirring at room temperature, 2 drops of 15% KOH solution was added and a precipitate formed. The sides of the flask were washed clean with 20 mL methanol and the mixture was stirred at room temperature for 2 hours. After filtering, the sandy tan solid was washed 3 times with methanol and once with ether to yield 0.7200g (35%) tan powder 52 after drying. MS (MALDI-TOF, no matrix) m/z 288 (100%, M⁺).

5,12-bis(triethylsilylethynyl)anthra[2,3;6,7']difuran and 5,12-bis(triethylsilylethynyl)anthra[2,3;7,6']difuran (TES ADF, 53a) (general procedure for making ADT derivatives) (general procedure for making ADF derivatives)

Into a 100 mL flame dried round bottom flask under nitrogen, 2 mL (11 mmol) triethylsilyl acetylene (TES acetylene) was dissolved in 10 mL. A volume of 3.75 mL (9 mmol) n-BuLi 2.5M solution in hexane was added slowly at room temperature. After stirring under nitrogen for 1 hour, the quinone (0.5289 g, 1.8 mmol) was added along with 80 mL heptane and 10 mL dry THF and stirred at room temperature overnight. After quenching with wet THF, tin chloride dihydrate (1.69
g, 7.5 mmol) was added along with 50 mL 10% HCl and stirred for 1 hour. The product was washed with water, dried, then poured directly through a silica plug with dichloromethane. After concentration, another silica plug was run with hexane to yield 0.8336 g (85%) orange solid. The product was recrystallized from hexane to give 0.6865 g (70%) orange crystals 53a. ¹H NMR (400 MHz, CDCl₃) δ: 0.896 (quart, J = 7.90 Hz, 12H); 1.231 (t, J = 7.90 Hz, 18H); 6.938 (s, 2H); 7.768 (s, 2H); 8.681 (d, J = 5.85 Hz, 2H); 8.861 (d, J = 6.29 Hz, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ: 4.948, 8.045, 103.971, 103.973, 104.133, 105.522, 105.704, 105.970, 106.144, 106.342, 117.675, 118.085, 118.389 118.647, 129.373, 129.783, 130.375, 130.405, 130.603, 130.845, 148.965, 149.056, 154.742, 154.932 ppm. MS (MALDI-TOF, no matrix) m/z 534 (100%, M⁺).

5,12-bis(tert-butylethynyl)anthra[2,3;6,7′]difuran and 5,12-bis(tert-butylethynyl)anthra[2,3;7,6′]difuran (t-Bu ADF, 53b)

70% crude yield, 62% recrystallized fluffy orange powder 53b. ¹H NMR (400 MHz, CDCl₃) δ: 1.592 (s, 18H); 6.935 (s, 2H); 7.744 (s, 2H); 8.589 (d, J = 6.44 Hz, 2H); 8.764 (d, J = 7.03 Hz, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ: 29.308, 31.638, 105.271, 105.461, 106.805, 111.769, 117.857, 118.222, 118.487, 129.062, 129.479, 129.881, 130.466, 148.654, 148.753, 154.507, 154.689 ppm. MS (MALDI-TOF, no matrix) m/z 418 (100%, M⁺).

5,12-bis(triethylgermylethynyl)anthra[2,3;6,7′]difuran and 5,12-bis(triethylgermylethynyl)anthra[2,3;7,6′]difuran (TEG ADF, 53c)

97% crude yield, 40% recrystallized fluffy orange crystals 53c. ¹H NMR (400 MHz, CDCl₃) δ: 0.860 (quad, J = 7.03 Hz, 12H); 1.303 (t, J = 7.76 Hz, 12H); 6.920 (s, 2H), 7.748 (s, 2H), 8.686 (d, J = 5.85 Hz, 2H), 8.871 (d, J = 6.14 Hz, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ: 29.308, 31.638, 105.271, 105.461, 106.805, 111.769, 117.857, 118.222, 118.487, 129.062, 129.479, 129.881, 130.466, 148.654, 148.753, 154.507, 154.689 ppm. MS (MALDI-TOF, no matrix) m/z 620, 622, 624, 626, 628 (2.5:3.5:1:4.5:1, M⁺).

General procedure for TES ADT lithiation

A mass of 0.267 g (0.5 mmol) 53a was dissolved in 100 mL heptane in a flame dried 250 mL round bottom flask and cooled to -78°C under nitrogen atmosphere. A volume of 0.22 mL (0.55 mmol) n-BuLi (2.5M solution in hexanes) was added dropwise and the reaction was allowed to stir for 10 minutes at-78°C. The halide source (1.25 mmol) was dissolved in heptane with enough dry THF to dissolve and added dropwise at -78°C. The reaction mixture was allowed to warm to room temperature overnight while stirring. The crude product was then quenched with water and diluted with pentane. The reaction mixture was extracted with pentane, washed with brine, dried and concentrated. Silica chromatography with pentane was used to isolate the dihalide, monohalide, and starting material.
2-fluoro-5,12-bis(triethylsilylethynyl)anthra[2,3;6,7']difuran and 2-fluoro-5,12-bis(triethylsilylethynyl)anthra[2,3;7,6']difuran (mono F TES ADF, 55a)

49% crude yield, 55a. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 0.876 (quart, $J = 8.05$ Hz, 12H); 1.207 (t, $J = 7.99$ Hz, 18H); 6.012 (d, $J = 0.88$ Hz, 1H); 6.935 (s, 1H); 7.77 (s, 2H); 8.554 (d, $J = 5.27$ Hz, 1H); 8.656 (d, $J = 6.005$ Hz, 1H); 8.837 (d, $J = 7.32$ Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 4.925, 8.015, 103.480, 103.654, 103.783, 103.958, 105.636, 105.749, 105.863, 106.129, 106.167, 106.288, 106.349, 106.820, 117.432, 117.516, 117.667, 117.751, 118.070, 118.464, 118.631, 129.426, 129.532, 129.699, 129.745, 130.117, 130.231, 130.291, 130.572, 149.231, 149.413, 154.894, 161.923, 161.923, 164.747 ppm. MS (MALDI-TOF, no matrix) $m/z$ 552 (10%, M$^+$).

2,8-difluoro-5,12-bis(triethylsilylethynyl)anthra[2,3;6,7']difuran and 2,8-difluoro-5,12-bis(triethylsilylethynyl)anthra[2,3;7,6']difuran (di F TES ADF, 55b)

7% crude yield 55b. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 0.872 (quart, $J = 7.728$ Hz, 12H); 1.200 (t, $J = 7.994$ Hz, 18H); 6.017 (dt, $J_1 = 6.45$ Hz, $J_2 = 0.88$Hz, 2H); 8.544 (d, $J = 6.44$, 2H); 8.644 (d, $J = 7.02$ Hz, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 8.007, 103.138, 103.438, 103.730, 105.939, 106.053, 106.311, 106.364, 117.485, 117.569, 117.629, 117.713, 117.834, 129.745, 129.951, 130.496, 130.627, 149.322, 161.878, 164.701 ppm. MS (MALDI-TOF, no matrix) $m/z$ 570 (100%, M$^+$).

2,8-dichloro-5,12-bis(triethylsilylethynyl)anthra[2,3;6,7']difuran and 2,8-dichloro-5,12-bis(triethylsilylethynyl)anthra[2,3;7,6']difuran (Cl TES ADF, 56)

54% crude yield 56. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 0.870 (quad, $J = 7.90$ Hz, 12H); 1.198 (t, $J = 7.90$ Hz, 18H); 6.756 (s, 2H); 8.572 (d, $J = 4.69$ Hz, 2H); 8.694 (d, $J = 5.27$ Hz, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 4.950, 8.043, 103.970, 103.973, 104.134, 105.525, 105.711, 105.965, 106.145, 106.337, 106.796, 106.831, 117.677, 118.085, 118.390, 118.645, 129.374, 129.780, 130.380, 130.401, 130.602, 148.965, 149.054, 154.741, 154.931 ppm. MS (MALDI-TOF, no matrix) $m/z$ 602, 604 (3:1, M$^+$).

2,8-diiodo-5,12-bis(triethylsilylethynyl)anthra[2,3;6,7']difuran and 2,8-diiodo-5,12-bis(triethylsilylethynyl)anthra[2,3;7,6']difuran (I TES ADF, 57)

51% crude yield, 57. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 0.868 (quart, $J = 7.90$ Hz, 12H); 1.198 (t, $J = 7.90$ Hz, 18H); 7.145 (s, 2H); 8.593 (d, $J = 4.10$ Hz, 2H); 8.722 (d, $J = 4.98$ Hz, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 4.950, 8.045, 103.970, 103.981, 104.134, 105.515, 105.710, 105.972, 106.147, 106.341, 106.797, 106.828, 117.680, 118.089, 118.390, 118.645, 129.373, 129.783, 130.377, 130.405, 130.610, 130.850, 148.965, 149.057, 154.741, 154.932 ppm. (MALDI-TOF, no matrix) $m/z$ 786 (60%, M$^+$).
I also explored changing the location of the heteroatom from the external rings to inside the acene core. This approach allowed us to synthesize an isomerically pure heteroacene similar to BTAs described by Takimiya and Shinmura in Chapter 1.

### 4.1 BBBT

This target acene benzo[1,2-b:4,5-b’]bis[b]benzothiophene (BBBT, 58a) is known in the literature to have modest mobilities for devices fabricated from vacuum and solution processed methods (Table 4.1).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Deposition</th>
<th>$\mu_{\text{FET}}$ (cm$^2$/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>58a$^{114}$</td>
<td>vacuum</td>
<td>2.4 x 10^{-3}</td>
</tr>
<tr>
<td>58a$^{115}$</td>
<td>drop cast</td>
<td>1 x 10^{-2}</td>
</tr>
<tr>
<td>58b$^{115}$</td>
<td>drop cast</td>
<td>1 x 10^{-3}</td>
</tr>
</tbody>
</table>

Table 4.1 TFT mobilities for 58a and 58b according to processing conditions

The 58a adopts a herringbone packing (Figure 4.1) while 58b adopts a 1-D π-stack (Figure 4.2).
The mobility for 58b is characteristic of a 1-D π-stack, but the low mobility for 58a is surprising since it adopts a 2-D herringbone interaction similar to pentacene (Figure 1.6). Gao et al. reported that due to its low solubility it is difficult to process uniform thin films of 58a from solution. They used the solvent 1,1,2,2-tetrachloroethane for drop casting films.

4.1.1 Synthesis of R functionalized BBBT

Our approach to the ethynyl functionalized derivatives, was to prepare the necessary quinone by condensing a corresponding benzo[b]thiophene amide
(Scheme 4.1). The quinone could then be reacted with various lithiated ethynyl derivatives for solubility as well as to control crystal packing.

Scheme 4.1

*synthetic approach to isomerically pure BBBT quinone*

Unlike ADT and ADF, which are a mixture of *cis* and *trans* isomers, BBBT synthesized using this method is isomerically pure (Scheme 4.2).

Scheme 4.2

*synthesis of BBBT quinone, 65*

The synthesis of 64 was relatively straight forward starting with the bromination of commercially available benzo[b]thiophene, 59\(^{16,17}\). After selective debromination at the 2-position\(^{118,119}\), 61 was converted to the nitrile 62\(^{20}\) with improved yields by quenching the reaction with FeCl\(_3\) in 8M HCl\(^{21}\). 62 was hydrolyzed in the presence of base to the carboxylic acid 63, which was reacted with oxalyl chloride to form an acid chloride and reacted with the desired amine to form 64. Cyclic amines pyrrolidin and piperidine were used, but higher yields and easier purification of the resulting amide were obtained from diethyl amine. The quinone 65 was formed in very low yields (9-30%) when using lithium diisopropyl amide (LDA) and reacting overnight, so alternative conditions were explored. The best results used n-BuLi for only 1 hour at 0°C, which led to consistently increased yields.
BBBT quinone 65 was reacted with various lithiated alkynes and deoxygenated with stannous chloride in acid to form the final yellow semiconductors 66 (Scheme 4.3) that are almost colorless in solution. Alkynes were chosen based on the road map for achieving 2-D π-stacking in linear acenes discussed in chapter 1. Since the acene backbone length is smaller than ADT, small symmetric alkyl and alkylsilyl groups were applied first.

### 4.1.2 Crystal packing

Various derivatives were synthesized, but currently no 2-D π-stacking was achieved. For smaller R groups, twinned crystals resulted suggesting less orientation preference driven by silylethynyl functionalization than ADT and ADF derivatives.
**Figure 4.4**

twinned t-Bu BBBT 66b crystal structure and crystals with solution under ambient and UV illumination

**Figure 4.5**

twinned TMS BBBT 66c crystal structure and crystals
As substituent group size was increased, herringbone packing was obtained with triisobutylsilylacetylene (TIBS) (66d). N-alkyl chains were also attempted, but n-butyl (66e) resulted in no π-stacking (Figure 4.7). With TIBS as an endpoint and nothing available smaller than t-Bu, we have turned our attention to asymmetric substituent groups.
4.1.3 Electronic characteristics

The functionalized BBBT (66) absorbance is dramatically blue-shifted compared with other acenes of the same number fused rings (Figure 4.8). The bandgap for 66 greatly increased with a decreased HOMO that resulted in improved photostability (Table 4.2). As discussed in chapter 1, other BTAs showed excellent photostability even up to seven linearly fused rings. The thin film half-life increased to several weeks rather than days for ADF and minutes for ADT. All BBBT derivatives were less soluble in non-polar solvents than other acenes.

<table>
<thead>
<tr>
<th>Acene</th>
<th>Solution $\lambda_{\text{max}}$ (nm)</th>
<th>Film $\lambda_{\text{max}}$ (nm)</th>
<th>Shift (nm)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>$E_g$ (eV)</th>
<th>Film $t_{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TES ADT</td>
<td>554</td>
<td>560</td>
<td>6</td>
<td>5.22</td>
<td>3.05</td>
<td>2.17</td>
<td>14 min.</td>
</tr>
<tr>
<td>TES ADF</td>
<td>512</td>
<td>525</td>
<td>13</td>
<td>5.27</td>
<td>2.29</td>
<td>2.35</td>
<td>8 days</td>
</tr>
<tr>
<td>TES BBBT</td>
<td>413</td>
<td>422</td>
<td>9</td>
<td>5.67</td>
<td>2.61</td>
<td>3.06</td>
<td>18 days</td>
</tr>
</tbody>
</table>

Table 4.2 comparison of electronic characteristics for various acenes

4.1.4 Group 14 functionalized BBBT

Electronically, the trend is not as clear for bandgap as with ADT and ADF. We see a decrease in bandgap from t-Bu (66b) to TEG (66f), but TES (66a) is the lowest. The redshift is also largest for the TEG derivative meaning it forms the most crystalline films from drop casting (Table 4.3).

<table>
<thead>
<tr>
<th>Acene</th>
<th>$\lambda_{\text{max}}$(CHCl$_3$) (nm)</th>
<th>$\lambda_{\text{max}}$(film) (nm)</th>
<th>redshift (nm)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>$E_g$ (eV)</th>
<th>$t_{1/2}$ (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-Bu BBBT</td>
<td>403</td>
<td>407</td>
<td>4</td>
<td>5.75</td>
<td>2.23</td>
<td>3.52</td>
<td>16.4</td>
</tr>
<tr>
<td>TES BBBT</td>
<td>413</td>
<td>422</td>
<td>9</td>
<td>5.67</td>
<td>2.61</td>
<td>3.06</td>
<td>18.0</td>
</tr>
<tr>
<td>TEG BBBT</td>
<td>412</td>
<td>423</td>
<td>11</td>
<td>5.79</td>
<td>2.49</td>
<td>3.30</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.3 electronic characteristics of 66 derivatives

350 400 450 500 550 600 650
Absorbance
Wavelength (nm)
absorption spectra for various acenes
Transistors are being tested on site by Rawad Hallani. Results for t-Bu BBBT were obtained by John Anthony (Figure 4.9).

Figure 4.9

Transistor curves for spin cast t-Bu BBBT 66b on prepatterned 5 μm x 5 μm channel bottom contact devices with PFBT treatment on gold electrodes and HMDS treatment on SiO₂ dielectric

<table>
<thead>
<tr>
<th>Compound</th>
<th>μFET (cm²/Vs)</th>
<th>V_T (V)</th>
<th>S (V/decade)</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-Bu BBBT</td>
<td>7.34 x 10⁻³</td>
<td>6</td>
<td>13</td>
</tr>
</tbody>
</table>

Table 4.34 t-Bu BBBT 66b TFT results

The mobility is on the order of other 1-D π-stacked materials, but devices showed low on/off current ratios suggesting non-uniform films (Table 4.3).

4.1.5 BBBT Uses

Since BBBT compounds are active in transistors and have an absorption that is completely offset from other acenes, they can be used as a matrix materials for guest-host single molecule fluorescence spectroscopy (SMFS) to study charge transfer.

Figure 4.10

representation of SMFS as interpreted from Moerner
SMFS was developed to simulate the improved fluorescence quantum yield of charge transport materials in solution within thin films necessary for transistor studies. This approach uses a dopant quantity of charger transport material within a thin film of a polymer host material such as poly(methyl methacrylate) (PMMA). The isolated fluorescence of a single molecule of the guest material can be observed because the host prevents aggregation of the guest.

Our collaborator Professor Oksana Ostroverkhova at Oregon State University has previously discussed the charge transfer dynamics of functionalized ADTs. She found that thin film fluorescence lifetimes were dramatically reduced from their solution values due to aggregation in the solid state. This lead to a 20-35% decrease in fluorescence quantum yields for functionalized ADTs making charge transfer dynamics harder to study. When ADTs were embedded in a polymer matrix of PMMA, spectra similar to solution results were found. She also found that by using a small guest dopant (10% CN TES ADT) within a host (F TES ADT) it was possible to increase the transient photocurrent by an order of magnitude.

Ostroverkhova began using t-Bu BBBT as the matrix material to study charge transport of F TES ADT, which has a much higher mobility. Their molecular structure and film formation are similar, but their absorbance is completely offset so only the F TES ADT fluoresced at 532 nm excitation (Figure 4.11). Devices from F TES ADT/t-Bu BBBT blends showed improved fluorescence lifetime compared to traditional polymer blends.

F TES ADT films showed the highest red-shift when dropcast (Table 4.5).

<table>
<thead>
<tr>
<th>Acene</th>
<th>Redshift (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TES ADT</td>
<td>6</td>
</tr>
<tr>
<td>F TES ADT</td>
<td>27</td>
</tr>
<tr>
<td>TES ADF</td>
<td>13</td>
</tr>
<tr>
<td>t-Bu BBBT</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 4.5 redshift from solution/thin film data for various acenes
When guest-host films with a small mol % of F TES ADT were prepared, the redshift was decreased to 10 nm meaning more dispersion of F TES ADT within the matrix.

Similar photoluminescence (PL) lifetimes were measured for blended t-Bu BBBT/F TES ADT thin films as F TES ADT in solution due to decreased aggregation. PL lifetimes for pristine F TES ADT and t-Bu BBBT films were lower by almost an order of magnitude.

Dark currents improved as the concentration of F TES ADT increased due to the improved hole injection from gold electrodes. The higher F TES ADT HOMO (Table 2.5) is better matched with the work function of gold (5.1 eV). Transient photocurrent was measured for t-Bu BBBT films excited at 355 nm, but no measureable photocurrent was found at 532 nm illumination. This result means only F TES ADT is responsible for the increased photocurrent at 532 nm illumination.

4.1.6 Purity

There was a noticeable amount of background noise from 532 nm illumination within BBBT matrixes resulting from an impurity that broadens the maximum absorption of t-Bu BBBT (Figure 4.12).

![Figure 4.12](image)

The more yellow the sample, the more background noise it produced. Purity could be improved by using multiple recrystallizations from isopropanol/toluene followed by hexanes, but other another chromophore could be used to prevent this impurity.

4.2 BBBF

To decrease the background noise from guest-host single molecule fluorescence spectroscopy, another type of heteroacene was developed. Substitution of the group...
16 heteroatom sulfur from the internal thiophene rings in BBBT with oxygen leads to the compound benzo[1,2-b:4,5-b']bisbenzofuran (BBBF, 67).

![Image of compound 67]

In chapter 3, I showed that the absorption spectrum for TES ADF was blue shifted compared to TES ADT (Table 3.2) by 42 nm (in solution), so if functionalized BBBF derivatives is also shifted the impurity that is excited with F TES ADT at 552 nm will no longer be excited at 532 nm. 67 has been made previously as a mixture in low yields by cyclodehydrogenation of 1,4-diphenoxylbenzene using palladium acetate in acetic acid (Scheme 4.4).

![Scheme 4.4: Initial synthesis of 67]

More recently, 67 was synthesized using an intramolecular O-arylation and characterized according to Kawaguchi and coworkers (Scheme 4.5).

![Scheme 4.5: Isomerically pure synthesis of 67]

Kawaguchi et al. also synthesized mono-alkyl and nitrile functionalized derivatives 67a and 67b (Scheme 4.6).
67 adopts herringbone packing in the solid state (Figure 4.13).

The absorption maximum for 67 was blue shifted compared to 58a (Table 4.6). This 12 nm shift is smaller than the 42 nm shift from TES ADF to TES ADT, though a direct comparison cannot be made since the acene ADF has not been synthesized.

Electronically, there is an increase in the oxidation potential with an increased bandgap and lower HOMO compared to BBBT (Table 4.6). Comparison can also be made with benzo[1,2-b:4,5-b’]bis[b]benzoselenophene (BBBS, 68) as synthesized by Ebata and coworkers. 68 adopts a 1-D sandwich herringbone packing in the solid state (Figure 4.14) and has mobility of 3.8 x 10^-3 cm^2/Vs on HMDS treated dielectric with an I_on/off of 5 x 10^7.

<table>
<thead>
<tr>
<th>acene</th>
<th>( \lambda_{\text{max}} ) (solution) (nm)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>( E_g ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BBBF 67</td>
<td>354</td>
<td>5.78</td>
<td>2.28</td>
<td>3.50</td>
</tr>
<tr>
<td>BBBT 58a</td>
<td>366</td>
<td>5.4</td>
<td>2.1</td>
<td>3.30</td>
</tr>
<tr>
<td>BBBS 68</td>
<td>374</td>
<td>5.6</td>
<td>2.4</td>
<td>3.2</td>
</tr>
<tr>
<td>67a</td>
<td>356</td>
<td>5.80</td>
<td>2.32</td>
<td>3.48</td>
</tr>
<tr>
<td>58b</td>
<td>369</td>
<td>5.4</td>
<td>2.2</td>
<td>3.24</td>
</tr>
<tr>
<td>67b</td>
<td>381</td>
<td>6.04</td>
<td>2.78</td>
<td>3.26</td>
</tr>
</tbody>
</table>

Table 4.6 comparison of electronic characteristics for various acenes.
4.3 Synthetic efforts towards functionalized BBBF

My attempted synthesis of BBBF quinone 75 was achieved following a similar method to BBBT quinone 65, though due to its lower stability and less reaction optimization, the yields on some steps were lower (Scheme 4.7).

The initial bromination of 69 is very dependent on conditions. If 2.2 equivalents of bromine are used, the major products isolated were the desired dibrominated 70 and a tribrominated benzofuran in a 1:1 ratio. When 2.0 equivalents were used on a 50 mmol scale the major products were 2-bromobenzofuran and 70. By decreasing to 25 mmol scale and carefully controlling the reaction time it was possible to prevent tribromination. Selective debromination was achieved using heptane solvent, but not with dry ether or THF to form 71. Conversion to 72 proceeded cleanly despite the use of strong acid with a less stable furan derivative. Hydrolysis in base to 73 and conversion to 74 via acid chloride proceeded under the same conditions as the benzothiophene
analogue (Scheme 4.2). Condensation to form BBBF quinone has not yet been successful due to the need for solvent, temperature, and time optimization.

Though 69 is commercially available, the use of inexpensive precursors or to obtain functionalized benzofurans have been reported\textsuperscript{134,135,136}. If we had found a less than selective debromination of 70 to 71, an alternative method (Scheme 4.8) may have been preferred since it generates an ester only at the 3-position starting from salicylaldehyde\textsuperscript{37}.

![Scheme 4.8](image)

\textit{alternative synthesis of 3-benzofuran carbonyl}

Dudley and coworkers also reported the synthesis of higher fused ring systems starting from 2-hydroxy-1-naphthaldehyde in quantitative yields (Scheme 4.9)\textsuperscript{136}.

![Scheme 4.9](image)

\textit{synthesis of naphthafuran carbonyl}

Lithiated ethynyl derivatives with group 14 elements will be used to functionalize the final acene once 75 have been successfully synthesized (Scheme 4.10).

![Scheme 4.10](image)

\textit{proposed synthesis of group 14 ethynyl BBBF derivatives}

4.4 Summary

By moving the heteroatom to the inside rings it is possible to dramatically affect the electronic properties of functionalized BBBTs compared to their ADT isomers.
While BBBTs compounds adopt a less desirable crystal packing for TFTs, they are useful as matrix materials for the study of charge transport with other acenes.

4.5 Experimental

Bulk solvents (methylene chloride (DCM), chloroform, pentane, hexane, heptane, ethyl acetate (EtOAc), toluene, isopropanol, absolute ethanol, 95% ethanol, methanol, diethyl ether, tetrahydrofuran (THF), glacial acetic acid (AcOH), and N,N-dimethylformamide (DMF)) ACS grade were purchased from Pharmco Aaper. Diethyl ether was dried using distillation over sodium metal. Unless specified, organic phases were dried using anhydrous magnesium sulfate 99.5% purchased from Alfa Aesar. Oxalyl chloride 98%, copper(I) cyanide 99%, diethylamine 99+%, and bromine 99.8% were purchased from Acros Organics. Anhydrous potassium carbonate 99%, sodium thiosulfate pentahydrate 99+%, 2,3-benzofuran 99.0%, and reagent grade stannous chloride (SnCl₂) dehydrate were purchased from Alfa Aesar. Chloroform-D 99.8% was purchased from Cambridge isotope labs Inc. Benzene ACS grade, ACS grade concentrated hydrochloric acid (HCl), ACS grade ammonium chloride, ACS grade potassium hydroxide (KOH), and ACS grade sodium hydroxide (NaOH) were purchased from VWR. (Trimethylsilyl)acetylene (TMSA) 98%, (Triethylsilyl)acetylene (TESA) 97%, (trisopropylsilyl)acetylene (TIPSA) 97%, and 3,3-dimethyl-1-butylene (t-buA) 98% were purchased from GFS chemicals. Triethylgermylchloride was purchased from Fisher. Anhydrous THF ≥99.9% inhibitor free, 2.5 M n-butyllithium solution (n-BuLi) in hexanes, 1-hexyne 97%, benzo[b]thiophene 98%, iron(III)chloride 97%, potassium acetate 99+, and 0.5 M ethynylmagnesium bromide solution in THF were purchased from Sigma Aldrich.

Flash chromatography was performed using 60 Å pore size, 230 x 400 mesh silica gel purchased from Sorbent technologies. Nuclear magnetic resonance (NMR) spectra were measured on Varian instruments (Gemini 200 MHz / Unity 400 MHz) spectrometer. Chemical shifts were reported in ppm relative to CDCl₃ or C₆D₆ as internal standard. Absorption spectra were measured on a UV-2501PC Shimadzu instrument or an Evolution 300 BB UV-Visible spectrometer from Thermo Scientific. Mass spectroscopy was analyzed in El mode at 70 eV on a JEOL (JMS-700T) Mass Spectrometer and Bruker Daltonics MALDI-TOFMS in the positive ion mode with no matrix or TCNQ matrix. Cyclic voltammetry was carried out on a BAS CV-50W and BASInc. EpsilonEC potentiostat, with ferrocene as the internal standard in a 1M Bu₄NPF₆ solution in DCM.

2,3-dibromobenzo[b]thiophene (60)

To a round bottom flask 30 g (224 mmol) benzo[b]thiophene, 59 was dissolved in 112 mL chloroform and cooled to 0°C. Bromine (24.1 mL, 470 mmol) was slowly added and stirred for 1 hour at 0°C, then overnight at room temperature. The reaction mixture was washed with potassium carbonate and sodium thiosulfate solutions, dried with magnesium sulfate, and concentrated. The crude solid was recrystallized from methanol and dried to give 50.34 g (77%) fluffy white crystals
60. $^1$H NMR (200 MHz, CDCl$_3$) $\delta$: 7.390 ($t$, $J = 4.4$ Hz, 1H); 7.441 ($t$, $J = 4.0$ Hz, 1H); 7.669 ($d$ $J = 7.3$ Hz, 1H); 7.742 ($d$, $J = 7.0$ Hz, 1H) ppm. $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta$: 111.710, 114.221, 121.824, 123.266, 125.527, 125.671, 137.440, 138.897 ppm. MS (El 70eV) m/z 290, 292, 294 (1:2:1, M$^+$); 211, 213 (1:1, M$^+$-Br); 132 (M$^+$-Br$_2$).

3-bromobenzo[b]thiophene (61)

Into a 500 mL flamed dried round bottom flask, 20 g (68 mmol) 60 was added along with 400 mL dry ether. After cooling to -78°C, 27.4 mL n-BuLi (2.5 M, 68 mmol) was slowly added. The mixture was stirred at -78°C for 30 minutes before warming to 0°C and quenching with 200 mL saturated NH$_4$Cl solution. After extraction with ether, the yellow to brown product was dried, concentrated and purified by silica chromatography with pentane yielding 14.01 g (96%) colorless liquid 61. $^1$H NMR (200 MHz, CDCl$_3$) $\delta$: 7.468 ($t$, $J = 7.8$ Hz, 1H); 7.5 (s, 1H); 7.553 ($t$, $J = 8.0$ Hz, 1H); 7.907 ($d$ $J = 8.0$ Hz, 1H); 7.985 ($d$, $J = 7.6$ Hz, 1H) ppm. $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta$: 107.749, 122.659, 122.993, 123.539, 124.988, 125.246, 137.455, 138.556 ppm. MS (El 70eV) m/z 212, 214 (1:1, M$^+$); 133 (M$^+$-Br).

3-cyanobenzo[b]thiophene (62)

A mass of 21.3 g (100 mmol) 61 was dissolved in 75 mL DMF. Nitrogen was bubbled thorough the solution at room temperature for 30 minutes before 23.43 g (110 mmol) CuCN was added and refluxed for 38 hours. After cooling to room temperature, a mixture of 34.02 g (210 mmol) FeCl$_3$ dissolved in 150 mL 8M HCl was slowly added over ice. The mixture was allowed to stir at room temperature for 30 minutes. After pouring into 200 mL ice water, the mixture was extracted with dichloromethane, dried, and concentrated. The crude product was purified by silica chromatography with a 1:1 mixture of hexane and dichloromethane to yield 13.20 g (83%) white solid 62. $^1$H NMR (200 MHz, CDCl$_3$) $\delta$: 7.467 ($t$, $J = 7.0$ Hz, 1H); 7.518 ($t$, $J = 6.2$ Hz, 1H); 7.895 ($d$ $J = 7.6$ Hz, 1H); 7.989 ($d$, $J = 7.7$ Hz, 1H); 8.088 (s, 1H) ppm. $^{13}$C NMR (50 MHz, CDCl$_3$) $\delta$: 110.749, 117.399, 127.593, 128.581, 129.213, 130.098, 136.357, 142.462, 144.238 ppm. MS (El 70 eV) m/z 121, 214 (1:1, M$^+$); 133 (M$^+$-Br).

3-benzo[b]thiophene carboxylic acid (63)

15.9 g (100 mmol) 62 was dissolved in 250 mL of 95% ethanol. The solution was brought to reflux and 36 g (643 mmol) potassium hydroxide (use 1 g base/7 mL ethanol) was added down a condenser. The mixture was allowed to reflux overnight. After cooling to room temperature, ether was added and the mixture was acidified with concentrated HCl. The product was extracted with ethyl acetate, dried, concentrated, and purified using silica chromatography with a mixture of 1:1 hexane and dichloromethane to remove starting material. Ethyl acetate was then used to isolate the product of 17.8 g (90%) fluffy white crystals 63. $^1$H NMR (200 MHz, C$_3$D$_6$O) $\delta$: 3.678 (s, 1H); 7.552 ($t$, $J = 7.3$ Hz, 1H); 7.627 ($t$, $J = 7.0$ Hz, 1H); 8.087 ($d$, $J = 7.3$ Hz, 1H); 8.602 (s, 1H); 8.667 ($d$, $J = 7.0$ Hz, 1H) ppm. $^{13}$C NMR (50 MHz,
hexanes and ethyl acetate to give 9.90 g (85%) viscous brown oil.

hexane to give 0.24338 g (43%) yellow needles.

hexane to give 0.3566 g (63%) yellow solid. The solid was recrystallized using dried, and concentrated. The product was purified using column chromatography in temperature for 1 hour after which it was extracted with DCM, washed with water, with 50 mL 10% HCl was added. The mixture was allowed to stir at room temperature at 0°C for 30 minutes and then 1 hour at room temperature. The product was dissolved in dichloromethane, washed with 10% HCl, dried, and concentrated under reduced pressure. Purification was done using silica column chromatography in a mixture of 1:1 hexanes and ethyl acetate to give 9.90 g (85%) viscous brown oil 64. ¹H NMR (400 MHz, CDCl₃) δ: 0.955 (s, broad, 3H); 1.020 (s, broad, 3H); 3.022 (s, broad, 2H); 3.200 (s, broad, 2H); 7.134 (quintet, J₁ = 7.685 Hz, J₂ = 1.025 Hz, 3H); 7.549 (dd, J₁ = 7.03 Hz, J₂ = 1.46 Hz, 2H); 7.605 (dd, J₁ = 8.20 Hz, J₂ = 2.34 Hz, 2H); ppm. ¹³C NMR (100 MHz, C₃D₆) δ: 122.435, 122.776, 124.446, 124.666, 124.849, 132.637, 137.131, 139.568, 166.083 ppm. MS (EI 70eV) m/z 233 (M⁺); 161 (M⁺-NEt₂); 133 (M⁺-CONEt₂).

3-benzo[b]thiophene diethylamide (64)

8.90 g (50 mmol) 63 was added to 50 mL of dichloromethane with 5 drops of DMF in a 250 mL round bottom flask. Oxalyl chloride (8.7 mL, 100 mmol) was added at room temperature and the mixture was refluxed until the acid dissolved or about 30 minutes. The solution was concentrated to dryness and cooled to 0°C under nitrogen with a condenser. 21 mL (200 mmol) of diethylamine was added down the condenser to the neat acid chloride. The solution was allowed to stir at 0°C for 30 minutes and then 1 hour at room temperature. The product was dissolved in dichloromethane, washed with 10% HCl, dried, and concentrated under reduced pressure. The crude diol was dissolved in THF and 0.90 g (4 mmol) tin chloride with 50 mL 10% HCl was added. The mixture was allowed to stir at room temperature for 1 hour after which it was extracted with DCM, washed with water, dried, and concentrated. The product was purified using column chromatography in hexane to give 0.3566 g (63%) yellow solid. The solid was recrystallized using hexane to give 0.24338 g (43%) yellow needles 66a. ¹H NMR (400 MHz, CDCl₃) δ:

benzo[1,2-b:4,5-b']bis[b]benzo thiophene-3,6-dione (BBBT quinone, 65)

Into a 100 mL flame dried round bottom flask, 4.66 g (20 mmol) 64 was added along with 20 mL dry THF. The solution was cooled to 0°C, then 8.32 mL (2.5M, 20.8 mmol) n-BuLi was added. The mixture was stirred for 1 hr at 0°C, then quenched with 20 mL water. The product was filtered, washed with ether, and dried overnight to yield 1.92 g (30%) red-brown solid 65. MS (MALDI-TOF, no matrix) m/z 320 (75%, M⁺).

3,6-Bis(triethylsilyl ethynyl)benzo[1,2-b:4,5-b']bis[b]benzo thiophene (TES BBBT, 66a) (general procedure for making BBBT derivatives)

Into a flame dried round bottom flask, 0.72 mL (4 mmol) triethylsilyl acetylene dissolved in 10 mL of heptane was added. The vessel was cooled to 0°C and 1.4 mL (3.5 mmol) 2.5 M n-BuLi was added. After stirring at room temperature for 1 hour the quinone, 65 (0.32 g, 1 mmol) along with 90 mL heptane and 10 mL dry THF was added and the mixture was stirred room temperature overnight. After quenching with water the crude diol was dissolved in THF and 0.90 g (4 mmol) tin chloride with 50 mL 10% HCl was added. The mixture was allowed to stir at room temperature for 1 hour after which it was extracted with DCM, washed with water, dried, and concentrated. The product was purified using column chromatography in hexane to give 0.3566 g (63%) yellow solid. The solid was recrystallized using hexane to give 0.24338 g (43%) yellow needles 66a. ¹H NMR (400 MHz, CDCl₃) δ:
0.905 (quart, J = 7.995 Hz, 12H); 1.233 (t, J = 7.861 Hz, 18H); 7.455 (m, 4H); 7.909 (dd, J₁ = 7.32 Hz, J₂ = 1.17 Hz, 2H); 9.284 (dd, J₁ = 7.61 Hz, J₂ = 0.88 Hz, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ: 4.948, 8.045, 111.850, 112.491, 122.702, 124.301, 124.661, 127.205, 132.273, 135.918, 140.479, 142.451 ppm MS (MALDI, TCNQ matrix) m/z 566 (75%, M⁺).

3,6-Bis(tert-butylenyl)benzo[1,2-b:4,5-b’]bis[b]benzothiophene (t-Bu BBBT, 66b)

60% yield yellow needles 66b. ¹H NMR (200 MHz, CDCl₃) δ: 1.594 (s, 18H); 7.488 (m, 4H); 7.883 (m, 2H); 9.155 (m, 2H) ppm. ¹³C NMR (50 MHz, CDCl₃) δ: 29.300, 31.190, 111.845, 112.490, 122.700, 124.294, 124.666, 127.202, 132.273, 135.916, 140.486, 142.452 ppm. (MALDI-TOF, no matrix) m/z 450 (100%, M⁺).

3,6-Bis(n-butylenyl)benzo[1,2-b:4,5-b’]bis[b]benzothiophene (n-butyl BBBT, 66e)

70% yield yellow needles 66e. ¹H NMR (400 MHz, CDCl₃) δ: 1.059 (t, J = 7.32 Hz, 6H); 1.676 (sextet, J = 7.32 Hz, 4H); 1.829 (quintet, J = 7.46 Hz, 4H); 2.762 (t, J = 7.17 Hz, 4H); 7.457 (m, 4H); 7.854 (dd, J₁ = 6.00 Hz, J₂ = 1.61 Hz, 2H); 9.155 (dd, J₁ = 7.32 Hz, J₂ = 1.75 Hz, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ: 13.938, 20.111, 22.434, 30.958, 111.845, 112.490, 123.700, 124.294, 124.666, 127.202, 132.273, 135.791, 140.382, 142.452 ppm. MS (MALDI-TOF, no matrix) m/z 450 (100%, M⁺).

3,6-Bis(trimethylsilylenyl)benzo[1,2-b:4,5-b’]bis[b]benzothiophene (TMS BBBT, 66c)

70% yield dark-yellow fluffy crystals 66c. ¹H NMR (400 MHz, CDCl₃) δ: 0.445 (s, 18H); 7.498 (m, 4H); 7.894 (dd, J₁ = 7.76 Hz, J₂ = 1.46 Hz, 2H); 9.181 (dd, J₁ = 7.62 Hz, J₂ = 1.75 Hz, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ: 0.124, 105.979, 106.624, 120.995, 124.454, 124.560, 127.533, 131.596, 135.427, 140.949, 141.520 ppm. MS (MALDI-TOF, no matrix) m/z 482 (100%, M⁺).

3,6-Bis(triethylgermlylenyl)benzo[1,2-b:4,5-b’]bis[b]benzothiophene (TEG BBBT, 66f)

38% yield pale yellow powder 66f. ¹H NMR (400 MHz, CDCl₃) δ: 1.147 (quart, J = 7.81 Hz, 12H); 1.326 (t, J = 7.655 Hz, 18H); 1.233 (t, J = 7.861 Hz, 18H); 7.455 (m, 4H); 7.909 (dd, J₁ = 7.32 Hz, J₂ = 1.17 Hz, 2H); 9.284 (dd, J₁ = 7.61 Hz, J₂ = 0.88 Hz, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ: 6.421, 9.586, 111.850, 112.490, 122.701, 124.301, 124.660, 127.205, 132.275, 135.918, 140.484, 142.453 ppm. MS (MALDI-TOF, no matrix) m/z 655 (2.5:3.5:1:4.5:1, M⁺).

3,6-Bis(triisobutylsilylenyl)benzo[1,2-b:4,5-b’]bis[b]benzothiophene (TIBS BBBT, 66d)
11% yield yellow needles 66d. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta: 0.908 (d, J = 6.74\) Hz, 12H); 1.096 (d, \(J = 6.44\) Hz, 36H); 2.093 (sept, \(J = 6.73\) Hz, 6H); 7.493 (m, 4H); 7.911 (dd, \(J_1 = 7.61\) Hz, \(J_2 = 0.58\) Hz, 2H); 9.287 (dd, \(J_1 = 7.62\) Hz, \(J_2 = 0.59\) Hz, 2H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta: 25.387, 25.485, 26.759, 108.918, 112.557, 122.774, 124.286, 125.140, 127.491, 132.740, 133.958, 135.497, 140.522, 142.075, 143.237 ppm. MS (MALDI-TOF, no matrix) \(m/z\) 734 (100%, M\(^+\)).

2,3-dibromobenzofuran (70)

To a 250 mL round bottom flask, 2.95 g (25 mmol) benzofuran, 69 and 4.9 g (50 mmol) potassium acetate was dissolved in 100 mL chloroform with enough water to dissolve the acetate. Bromine (2.6 mL, 50 mmol) was slowly added and stirred for 8 hours at room temperature. The reaction mixture was washed with potassium carbonate and sodium thiosulfate solutions, dried with magnesium sulfate, and concentrated. Purification using silica gel and pentane resulted in 7.45g (54 %) colorless oil 70. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta: 7.354 (dt, J_1 = 8.2\) Hz, \(J_2 = 0.732\) Hz, 1H); 7.440 (td, \(J_1 = 7.47\) Hz, \(J_2 = 0.983\) Hz, 1H); 7.652 (td, \(J_1 = 7.83\) Hz, \(J_2 = 1.18\) Hz, 1H); 7.806 (ddd, \(J_1 = 7.62\) Hz, \(J_2 = 1.32\) Hz, \(J_3 = 0.59\) Hz, 1H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta: 100.142, 111.367, 119.415, 124.132, 125.560, 128.261, 128.667, 154.854 \) ppm. MS (EI 70eV) \(m/z\) 274, 276, 278 (1:2:1, M\(^+\)); 195, 197 (1:1, M\(^+\)-Br).

3-bromobenzofuran (71)

Into a 250 mL flamed dried round bottom flask, 6.9 g (25 mmol) 70 was added along with 100 mL heptane. After cooling to -78°C, 10 mL n-BuLi (2.5 M, 25 mmol) was slowly added. The mixture was stirred at -78°C for 1 hour before removal of the cold bath and quenching with 200 mL saturated NH\(_4\)Cl solution. After extraction with pentane, the yellow/brown product was dried, concentrated and purified by silica chromatography with pentane yielding 4.43 g (90%) colorless liquid 71. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta: 7.302 (s, 1H); 7.793 (td, J_1 = 6.98\) Hz, \(J_2 = 1.02\) Hz, 1H); 7.850 (td, \(J_1 = 8.05\) Hz, \(J_2 = 1.76\) Hz, 1H); 8.081 (dd, \(J_1 = 8.35\) Hz, \(J_2 = 0.88\) Hz, 1H); 8.157 (dd, \(J_1 = 6.88\) Hz, \(J_2 = 1.46\) Hz, 1H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta: 127.559, 128.356, 144.266, 144.578, 144.616, 145.466, 145.504, 155.129 \) ppm. MS (EI 70eV) \(m/z\) 196, 198 (1:1, M\(^+\)); 117 (M\(^+\)-Br).

3-cyanobenzofuran (72)

A mass of 4.93 g (25 mmol) 71 was dissolved in 50 mL DMF. Nitrogen was bubbled thorough the solution at room temperature for 30 minutes before 2.46 g (27.5 mmol) CuCN was added and refluxed for 38 hours. After cooling to room temperature, a solution of 8.51 g (52.5 mmol) FeCl\(_3\) dissolved in 32 mL 8M HCl was slowly added over ice. The mixture was allowed to stir at room temperature for 30 minutes. After pouring into 100 mL ice water, the mixture was extracted with dichloromethane, dried, and concentrated. The crude product was purified by silica chromatography with a 5:1 mixture of hexane and dichloromethane to yield 2.40 g (67%) off-white solid 72. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta: 7.408 (m, 2H); 7.567 (dd, J_1 =
8.05 Hz, $J_2 = 0.87$ Hz, 1H); 7.722 (dd, $J_1 = 7.18$ Hz, $J_2 = 0.87$ Hz, 1H); 8.124 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 105.909, 112.403, 120.423, 124.944, 126.791, 152.139, 154.602 ppm. MS (EI 70eV) m/z 143 (M$^+$).

**3-benzofuran carboxylic acid (73)**

3.58 g (25 mmol) 72 was dissolved in 100 mL 95% ethanol. The solution was brought to reflux and 14.3 g (255 mmol) potassium hydroxide (use 1 g base/7 mL ethanol) was added down a condenser. The mixture was allowed to reflux overnight. After cooling to room temperature, ether was added and the mixture was acidified with concentrated HCl. The product was extracted with ethyl acetate, dried and concentrated to give 3.65 g (90%) fluffy white crystals 73. $^1$H NMR (400 MHz, C$_3$D$_6$O) $\delta$: 6.794 (td, $J_1 = 7.32$ Hz, $J_2 = 1.17$ Hz, 1H); 6.854 (dd, $J_1 = 7.90$ Hz, $J_2 = 1.17$ Hz, 1H); 7.091 (td, $J_1 = 7.76$ Hz, $J_2 = 1.76$ Hz, 1H); 7.180 (dd, $J_1 = 7.61$ Hz, $J_2 = 1.76$ Hz, 1H); 8.431 (s, 1H) ppm. $^{13}$C NMR (100 MHz, C$_3$D$_6$O) $\delta$: 116.235, 120.616, 122.968, 129.224, 132.289, 144.452, 156.531, 173.593, 197.078 ppm. MS (EI 70eV) m/z 162 (M$^+$), 145 (M$^+$-OH), 117 (M$^+$-COOH).

**3-benzofuran diethylamide (74)**

4.05 g (25 mmol) 73 was added to 50 mL of dichloromethane with 5 drops of DMF in a 250 mL round bottom flask. Oxalyl chloride (4.4 mL, 50 mmol) was added at room temperature and the mixture was refluxed until the acid dissolved or about 30 minutes. The solution was concentrated to dryness and cooled to 0°C under nitrogen with a condenser. 6 mL (100 mmol) of diethylamine was added down the condenser to the neat acid chloride. The solution was allowed to stir at 0°C for 30 minutes and then enough dry THF was added to bring everything into solution and the mixture was stirred at room temperature overnight. The product was dissolved in DCM, washed with 10% HCl, dried, and concentrated under reduced pressure. Purification was done using silica gel chromatography in a mixture of 1:1 hexanes and ethyl acetate to give 9.90 g (59%) thick brown oil 74. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 1.121 (t, $J = 7.18$ Hz, 3H); 1.283 (t, $J = 7.18$ Hz, 3H); 3.387 (quart, $J = 7.03$ Hz, 2H); 3.500 (quart, $J = 7.32$ Hz, 2H); 6.809 (td, $J_1 = 7.39$ Hz, $J_2 = 1.37$ Hz, 1H); 6.973 (dd, $J_1 = 8.19$ Hz, $J_2 = 1.17$ Hz, 1H); 7.016 (dd, $J_1 = 7.32$ Hz, $J_2 = 1.47$ Hz, 1H); 7.169 (td, $J_1 = 7.69$ Hz, $J_2 = 1.76$ Hz, 1H); 7.253 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: ppm. MS (EI 70eV) m/z 217 (M$^+$), 202 (M$^+$-Me), 188 (M$^+$-Et), 145 (M$^+$-C$_4$H$_{10}$N), 117 (M$^+$-C$_5$H$_{10}$NO).
Chapter 5: Conclusion

Various new heteroacenes have been synthesized and characterized for light stability, electronics, and device results. By functionalizing heteroacenes with group 14 element containing ethynyl groups, it was possible to determine the periodic affect of the solubilizing group on the overall device performance and light stability.

Periodic functionalization on ethynyl derivatives did not have a dramatic affect on HOMO level for ADT derivatives, but processability and light stability changed. For ADT derivatives, the silyl derivative showed the highest stability to light, though all were on the order of minutes.

Stability was dramatically improved by fluorination to the heteroacene backbone. I improved the yields for halogenated ADT derivatives as well as introduced bromine and iodine directly to thiophene dialdehyde without protection. Halogenated ADT/TES ADT blends were made to control crystal growth. Halogenated ADT derivatives nucleated TES ADT crystal growth, but the optimal ratio for solution cast films used a slight excess of halogenated ADT to obtain good dispersion within TES ADT films.

New fluorinated derivatives were synthesized and discussed in terms of VGSC formation and high mobility blends with PTAA. F TEG ADT devices showed improved device-to-device uniformity as well as higher mobility from pristine films. For blends with PTAA, F TEG ADT mobilities were decreased compared to F TES ADT due to decreased stability to light, but no additional drying was necessary prior to annealing. Both materials achieved higher mobilities than TIPS Pentacene/PTAA blends under similar device fabrication showing the improved processability for heteroacenes.

Moving the heteroatom location decreased the HOMO noticeably for BBBT improving light stability to weeks, but also affected device performance and crystal packing. No high mobility 2-D π-stacking was achieved following the published roadmap so more research needs to be done with asymmetric silyl derivatives for this S-shaped chromophore. The measured mobility was on the order of a 1-D π-stack, but this material can still be used as an electronically active material for SMFS to study the charge transport of other heteroacenes.

Periodic functionalization on the heteroacene itself also did not significantly decrease the HOMO, but light stability was greatly increased from minutes for TES ADT to days for TES ADF in thin film. I have demonstrated the first synthesis of the previously unknown ADF heteroacene as a series of group 14 functionalized ethynyl derivatives. TES ADF adopts a 2-D π-stack with closer packing than TES ADT, but high mobility devices have not been fabricated. With more optimization for uniform thin film formation it is hoped that TES ADF will show higher mobilities than TES ADT due to decreased short axis slip.
I have also shown that ADF derivatives can be directly lithiated unlike their ADT analogue. This approach was used for halogenation, though yields were extremely low. After optimization, this method will present a fast approach to obtaining ADF derivatives functionalized on the heteroacene core at the last step. These derivatives should exhibit a similar improved light stability as halogenated ADT derivatives meaning halogenated ADF derivatives would be stable for years.

Synthesis of other heteroacenes such as group 15 elements nitrogen and phosphorous could be explored to determine a HOMO change between different groups as well as down the group. Light stability for these derivatives could also be compared to group 16 heteroacenes ADF and ADT.
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Vita

Marsha Loth was born on October 7, 1983 in Altoona, Pennsylvania, USA. She received her B.S. in chemistry from Juniata College in Huntingdon, Pennsylvania in 2006 working for Dr. I. David Reingold on 1,5-methylene semibullvalene synthesis. She joined Dr. Anthony's group at the University of Kentucky in Lexington, Kentucky in June 2006 to work on organic electronic materials for thin film transistors. In May 2009 she married fellow Ph. D. student Robert Grimminger whom she met as an undergraduate.

After finishing her Ph. D. she will begin working as a postdoctoral fellow for Dr. Steve Lipka at the Center for Applied Energy Research in Lexington, Kentucky with fluorinated carbon nanospheres for lithium ion batteries. She hopes to continue to work with energy related research particularly solar cells after her postdoctoral fellowship.

Marsha was awarded the Max Steckler Fellowship from August 2006 until December 2011 and the Gill Fellowship from February 2008-2010. She also received the Fast-Start award from the University of Kentucky Chemistry Department in May 2007 and first place in the graduate level chemistry division at the 2009 Kentucky Academy of Science Annual Meeting at Northern Kentucky University. She has been active in many outreach activities including organizing the annual demonstration show for National Chemistry Week in 2010 and visiting local elementary schools for laboratory instruction. Within the chemistry department, she has served as treasurer and vice president in the graduate student association and organized the spring prospective weekend.

Publications


**Conference Abstracts**

Poster: “Synthesis and characterization of functionalized nonlinear acenes for solution processable organic thin film transistors” at 8th International Conference on Functional Pi Electrons (F-Pi 8) at the Technical University Graz (TUG) in Graz, Austria, July 2008


Presentation: “Organic electronics for flexible applications” at Kentucky Academy of Science (KAS) 2009 Annual Meeting at Northern Kentucky University (NKU) in Highland Heights, Kentucky, USA, November, 2009

Presentation: “The new shape of organic electronics” presented at the University of Kentucky Graduate Student Interdisciplinary Conference in Lexington, Kentucky, USA April 2011

Poster: “Acene crystal engineering using heteroatoms for organic electronics” presented at the Materials Research Society (MRS) 2011 Spring Meeting in San Francisco, California, USA, April 2011

Poster: “Periodic trends in structure function relationship of organic heteroacene semiconductors” presented at the 42nd Central Regional Meeting of the American
Chemical Society (CERM ACS) in Indianapolis, Indiana, USA, June 2011

Presentation: “Crystal engineering of heteroacenes for thin film transistor applications” presented at SPIE Optics + Photonics, Photonic Devices + Applications Conference San Diego, California, USA August, 2011