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NEW PHOTOVOLTAIC ACCEPTORS: SYNTHESIS AND CHARACTERIZATION OF FUNCTIONALIZED C-FUSED ANTHRADITHIOPHENE QUINONES

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ABSTRACT OF MASTER’S THESIS

NEW PHOTOVOLTAIC ACCEPTORS: SYNTHESIS AND CHARACTERIZATION OF FUNCTIONALIZED C-FUSED ANTHRADIOPHENE QUINONES

Stable organic semiconductors are critical to produce inexpensive, efficient and flexible thin film organic solar cells. A current chemical focus is the synthesis of stable, electron-accepting materials to be utilized as an acceptor layer in photovoltaics.¹ The Anthony group has shown that the functionalization of pentacene with suitable electron withdrawing groups provides a catalog of suitable acceptors for this purpose.² These pentacenes can be further modified to pack in a unique 1-dimensional "sandwich herringbone" crystal packing, leading to improved device current.³ To improve the stability of acene acceptors, we have taken two hetero-atom themed approaches. First, we have studied the acenequinone as an electron-accepting chromophore.⁴ Further, we replaced the terminal aromatic rings with heterocycles, such as furan or thiophene. In order to enhance the crystal engineering versatility of the chromophore, we utilize c-fused heterocycles (rather than the more commonly used b-fused cycles seen in e.g. anthradithiophenes). The c-fused acenequinones can be tetra-functionalized with silylethynyl groups to influence crystal packing and increase solubility.⁵ The silylethynyl groups are known to increase the photostability and lower the energy gap (E_g) of pentacenes.⁵ The functionalization of the silylethynyl groups also aids in lowering the lowest unoccupied orbital (LUMO) of acene structures.⁵

KEY WORDS: organic solar cells, thin film morphology, crystal packing, anthradithiophene quinones, n-type

Kerri Shelton
04/18/2011
NEW PHOTOVOLTAIC ACCEPTORS: SYNTHESIS AND CHARACTERIZATION OF FUNCTIONALIZED C-FUSED ANTHRADITHIOPHENE QUINONES

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NEW PHOTOVOLTAIC ACCEPTORS: SYNTHESIS AND CHARACTERIZATION OF FUNCTIONALIZED C-FUSED ANTHRADIITHIOPHENE QUINONES

MASTER’S THESIS

A thesis submitted in fulfillment of the requirements for the degree of Master’s of Science in the College of Arts and Sciences at the University of Kentucky

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

Lexington, Kentucky
2011
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Chapter 1: Introduction

1.1 Solar Power

Global energy consumption continues to increase as the number of available resources decrease. Resources, such as oil and coal, are beginning to become scarce, placing more emphasis on renewable sources of energy, like wind and solar power.

Solar energy could be harnessed by photovoltaic devices. Photovoltaic cells are devices that convert solar energy into electricity, by way of the photovoltaic effect.\(^6\) Commercially, solar cells consist of a large scale of silicon with efficiencies as high as 23\%.\(^7\) Yet, the expensive energy source, more specifically the initial payment, can portray the devices as financially unforgiving. For example, a polycrystalline silicon DMSolar #DM280M2-36 280Watt Solar Module Panel sells for $518.00. The 51 lb panel has an area of 279.5 m\(^2\) (3007.2 ft\(^2\)) with \(\sim\)16% efficiency, yielding a maximum output of 160 Watts, as specified by the manufacturer.\(^8\) As noted by the Department of Energy, a household in Florida uses 38 trillion Btu per year and this \(1.12 \times 10^{10}\) kWh would require a family to use \(1.68 \times 10^{12}\) panels to run per day in order to compensate for the energy demand.\(^9\)

1.2 Organic Photovoltaic Fabrication and Operation

Organic photovoltaics (OPV) have been the focus of innovative research and have the potential to be an everyday energy source.\(^10\) These thin film devices would be inexpensive, lightweight and flexible, with the intention of increasing the power conversion efficiency (PCE) and develop solar cells on a large scale. The PCE calculates the solar cell’s performance. The efficiency (PCE) is the percentage of input power from a light source that is converted to an output current and produces the maximum power.
Other important parameters, like short-circuit current density ($J_{sc}$) and open-circuit voltage ($V_{oc}$), influence the parameters of the OPV device. The $J_{sc}$ and $V_{oc}$ are found at the boundaries in the current-voltage (J-V) graph, with the units of mA/cm$^2$ and V, respectively (Fig. 2).

The open-circuit voltage ($V_{oc}$) is the maximum voltage across the cell when there is no current flow present in the device ($J=0$) or when the circuit is open.\textsuperscript{11} In an OPV,
the $V_{oc}$ can be calculated through the difference of the ionization potential (HOMO DONOR) from the electron affinity (LUMO ACCEPTOR) (Fig. 1). Thus, to optimize the $V_{oc}$, the molecular energies of the acceptor can be changed, in terms of the structure’s synthetic design.

Short circuit current-density ($J_{sc}$) is the maximum current density that can be generated when the device has no load present ($V=0$) or when the device is shorted. $J_{sc}$ is dependent on the efficiency of charge separation at the donor/acceptor interface within the active layer of the solar cell, with regards to conversion of excitons into electrons and holes, and the device’s capability of transporting and collecting charges. More specifically, the short circuit current-density is identified as the photocurrent output of a solar cell when the output terminals are short-circuited.

$J_{sc}$ and $V_{oc}$ are the defining factors identifying the maximum current density and voltage that can be produced by exciting the device. Efficiency ($\eta$) can be rewritten using the 2 previous parameters as:

$$\eta = \frac{P_{max}}{P_{in}} \times 100\% = \frac{|J_{max}|V_{max}}{IL} \times 100 = FF \frac{|J_{sc}|V_{oc}}{IL} \times 100$$

where $P_{MAX}$ is correspondent to the maximum power produced by the OPV, the $P_{IN}$ is the input power, $J_{MAX}$ and $V_{MAX}$ are the current density and voltage, respectively, at the point where $P_{MAX}$ is produced, and $I_{L}$ is the illumination of the desired light source.

Fill Factor (FF) is termed as the percentage of the actual maximum power ($P_{MAX}$) obtained when compared to the theoretical maximum. The maximum electric power available from the cell is the open circuit voltage ($V_{oc}$) multiplied by the short circuit density ($J_{sc}$). In a normal J-V curve, the FF represents the intersecting point of the maximum voltage ($V_{max}$) and the current-density maximum ($J_{max}$) (Fig. 2).

$$FF = \frac{|J_{max}|V_{max}}{|J_{sc}|V_{oc}}$$

This parameter is contingent on degree of charge recombination strength, buildup of space charge and amount of series resistance. The square-ness of the FF is directly influenced by the slope of the $V_{oc}$ and $J_{sc}$.

The slope of the J-V curve is affected by the series and shunt resistances, which in turn influence the device’s FF. Series resistance ($R_s$) evolves from the resistance built up as a result of current flow within the device. The series resistance is a problem particularly at high current densities, such as instances of concentrated light. Shunt resistance ($R_{sh}$) develops from the leakage of current through the cell, specifically around the device’s edges and at contacts of different polarities. For an efficient cell, we want $R_s$ to be as small and the $R_{sh}$ to be as large as possible.
Key factors, such as $J_{sc}$, FF, and $V_{oc}$, are essential in the operation and optimization of a functioning OPV device. An ideal PV device must consist of high $V_{oc}$, $J_{sc}$, and a square FF almost equivalent to 1.\textsuperscript{11,12} In such an environment, all photons hitting the OPV’s surface should produce an exciton: an electron-hole pair. Yet, light can interact with the device at an alternate angle or with a minimal amount of light energy.\textsuperscript{15} The lack of excitation or reflection of light off of the device, results in a loss of energy captured by the OPV. Similarly, charge recombination could also be a factor in energy loss, as a result of the active layer thickness being larger than the exciton diffusion length (Fig. 3).\textsuperscript{15} Charge traps, resulting from defects in the active layer also aid in energy loss for the OPV device.

The overall efficiency of the diffused photo-induced charge within the organic solar cell can be termed by the incident photon to converted electron efficiency (IPCE). The IPCE is calculated by the number of electrons leaving the device under short circuit conditions per time and area divided by the number of incident photons per time and area.\textsuperscript{15}

$$IPCE = \frac{\text{# of extracted electrons}}{\text{# of incident photons}}.$$  

The IPCE is a term used to define the external quantum efficiency (EQE), which quantifies the amount of energy loss with respect to the light reflected off of the surface as well as the light transmitted through the device.\textsuperscript{15,16} The purpose of an organic photovoltaic is to harness solar energy; as such the affinity to light absorption of the active layer can play a part in current output.
In an OPV (Fig. 3, Fig. 4), light from a given light source is absorbed through the transparent electrode, and the organic donor material is photoexcited and excites the donor’s HOMO (Step 1). The multi-layered solar cell experiences charge photogeneration at the donor-acceptor interface and produces an exciton. The exciton, composed of a hole and an electron, moves from the donor-acceptor interface, and, the exciton splits transporting the electron to the acceptor material and the hole to the donor material (Step 2). An increased surface area of the donor-acceptor interface can aid in losing fewer excitons to recombination prior to the decomposition of the exciton. The exciton diffuses from the donor-acceptor interface leading to the electrons transport to the LUMO of the acceptor and the hole to the anode (Step 3). Finally, the electron moves from the acceptor’s LUMO to the cathode, providing the direct photocurrent through the device (Step 4). Holes are collected by the anode (the higher work function electrode), while the electrons are collected by the cathode (the lower work function electrode).

Figure 4. Basic schematic of an OPV.

The OPV device is composed of the desired substrate, anode, cathode and heterojunction. The heterojunction is composed of both donor and acceptor material. Presently, the thin film device can be fabricated in terms of two architectures, a planar heterojunction or bulk heterojunction. The active layer within the planar heterojunction consists of a thin layer of both the acceptor and donor. However, in the bulk heterojunction, the donor and acceptor material are blended together between the two electrodes, creating donor-acceptor interface throughout the active layer. The donor is responsible for transporting holes, while the acceptor is accountable for conducting the electrons.

The LUMO of the donor must be higher than the LUMO of the acceptor, in order to successfully transfer the electron from the donor’s LUMO to the acceptor’s LUMO. The HOMO level of the donor should be slightly higher when compared to
the HOMO level of the acceptor with the intent of favoring charge separation rather than charge recombination. However, a solar cell can function with the HOMO level of the acceptor at a higher energy level than the HOMO of the donor. Unfortunately, the latter situation, with the donor material at a lower HOMO energy level, charge recombination can be favored more than the desired charge separation, and limiting the OPV’s efficiency.\textsuperscript{15}

The optical band gap, Figure 1, corresponds to the difference between the HOMO/LUMO energies, and accounts for the minimum amount of energy needed to excite the donor material. Following excitation, it is essential for the photo-generated exciton to travel to the donor/acceptor interface. In order to achieve exciton dissociation, the distance traveled to the donor/acceptor interface must equate to the exciton diffusion length.\textsuperscript{18} The exciton diffusion length is roughly the same order of magnitude as the length of the donor acceptor phase separation.\textsuperscript{19} Organic semiconductors tend to have an exciton diffusion length ranging from 10-20nm.\textsuperscript{19} Furthermore, the transfer of the photo-induced charge from the donor LUMO to the acceptor LUMO needs to be roughly equivalent to the exciton binding energy ($E_B$). Exciton binding energies for organic semiconductors range from 0.2 eV to 1.5 eV, in comparison to silicon (0.32 eV)\textsuperscript{20,21} The intermolecular interactions of conjugated organic materials tend to decrease the $E_B$, while increasing the band width.\textsuperscript{20} Unlike the inorganic photovoltaic cells, the organic solar cell generates a mobile and electrically neutral electron-hole pair in the active layer, following excitation.\textsuperscript{22} The built-in electric fields within the organic semiconductors are not adequate enough to easily separate the hole and electron pair.\textsuperscript{23} Consequently, the exciton stays bound until reaching the donor-acceptor interface, where the device experiences a sharp drop in potential between the LUMOs.\textsuperscript{22,23} In order for dissociation to occur, the band offset between the donor and acceptor materials must be greater than the exciton binding energy.\textsuperscript{22}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure5.png}
\caption{Schematic diagram depicting energy level requirements for efficient charge transfer.}
\end{figure}
Figure 5 demonstrates the requirements for an efficient charge transfer within an OPV. The donor material has a lower ionization potential (IP_D), i.e. the donor’s HOMO, and the acceptor material tends to have a high electron affinity (EA_A), otherwise known as the LUMO.  

1.3. Architecture of Organic Photovoltaics

The architecture of organic solar cells has evolved throughout the past twenty years. Dye sensitized solar cells (DSSC) were originally fabricated by M. Gratzel in 1991, and incorporated an organic dye within the solar cell set-up. The architecture of the DSC consisted of the anode, cathode, and an active layer comprised of (1.) a mesoporous titanium dioxide covalently bound with an organic dye and (2.) a thin layer of an electrolyte. Excitation occurs with the conduction of an electron through the oxide layer. Sunlight hits the device and passes through the transparent electrode. The light then excites the dye (donor molecule) and allows for an electron to be transferred to the titanium dioxide. At that point, the dye molecule could decompose, due to the loss of the electron to the oxide layer. The electrolyte provides an electron to the oxidized dye. In the case of the first DSSC by Gratzel, an iodide/triiodide couple was used as the available redox system. The iodide would have an electron stripped by the organic dye and becomes oxidized to the triiodide ion. The missing electron of the triiodide is regenerated as the ion diffuses to the counter electrode and reintroduces the electron to make iodide. However, the organic liquid suspending the electrolyte can cause issues within the device, such as low long-term stability and leakage of the electrolyte. The liquid electrolyte in DSSCs is temperature sensitive. At high temperatures, the liquid expands creating issues for sealing the device. Alternative, the liquid electrolyte at low temperatures can freeze, making the device unusable.

Single layer organic solar cells (Fig. 6) are based on having the two metal electrodes of differing work functions with a sandwiched organic layer. This innovative class of solar cells functioned by the offset of the two electrodes. The difference in work functions between the anode (higher work function) and cathode (lower work function) creates the electric field through the device. Electron transfer occurred through the formation of a Schottky barrier as well as the asymmetry of the electron and hole pair into the π* and π molecular orbitals. By definition, the Schottky barrier is the potential barrier between a metal-semiconductor junction, with rectifying behavior. The PCE, of single layer solar cells, was poor, ranging from 10^-3 to 10^-2%. Following excitation of the organic material, the difference in the two electrodes aid in separating the electron and hole pair, transferring the electron to the cathode and the holes to the anode. Braun and Heeger noted through their experimentation and study of solar devices with Poly(2-methoxy-5-(2’-ethyl-hexyloxy)-p’-phenylenevinylene) (MEH-PPV) (Fig. 8.3) that the single layer set-up experienced competitive energetics with
radiative and non-radiative processes, which in turn dramatically decreased the efficiency of the device.\textsuperscript{29}

![Cathode
Donor
Anode]

Figure 6. Depiction of a single layer solar cell.

Bilayer organic solar cells (Fig. 7) incorporate a layer of a donor and acceptor material between the two electrodes.\textsuperscript{30} Tang demonstrated the alternative architecture using copper phthalocyanine (CuPc) (Fig. 8.7) as the donor and a perylene tetracarboxylate derivative (Fig. 8.8) as the acceptor and earned an efficiency of \(~0.95\%\).\textsuperscript{30} In 1995, the efficiency for Tang’s device was at that time one of the highest reported efficiencies for an organic cell.\textsuperscript{30} The dramatic increase in PCE is a result of the second layer that aids in electron transport within the solar device.\textsuperscript{23,30} The integration of a second component into the active layer places emphasis on the maximum width necessary to maintain efficient electron transport. The thickness of the semiconducting layer is restricted by the exciton diffusion length and requires organic cells to have a width of 10-20 nm between the two functioning electrodes.\textsuperscript{15,19,23}

![Cathode
Acceptor
Donor
Anode]

Figure 7. Depiction of a bilayer solar cell.

1.4. Bulk Heterojunction Solar Cells

A bulk heterojunction (BHJ) is similar to the architecture of a bilayer solar cell; however, the donor and acceptor materials are blended together in solution prior to their integration into the device.\textsuperscript{15,23} The intimate blend of these two organic materials increases the surface area of the donor-acceptor (DA) interface.\textsuperscript{19} As a result, the improved contact at the DA interface aids in a more efficient device, by shortened distance for charge diffusion.\textsuperscript{19,31}

The first reported BHJ solar cell was in 1995 by Heeger in Santa Barbara. The solar cell consisted of MEH-PPV (Fig. 8.2), as the donor, and phenyl C61-butyric acid...
methyl ester (PC$_{61}$BM), as the acceptor.$^{32}$ The two organic materials were blended together and spin-casted to a film thickness of 1000-2000 Å, while the metal electrode (Ca or Al) was vacuum evaporated to a thickness of 1000-5000 Å.$^{32}$ The cell’s efficiency was quite low; however, Heeger’s device demonstrated an architecture that experienced photo-induced electron and hole mobility between a polymer donor and fullerene acceptor.$^{32}$

The PCE has been greatly improved since the first fabricated device by Heeger. In 2005, the reported PCE was increased to 5% for devices using P3HT (Fig. 8.1) and PCBM in BHJ solar cells.$^{33}$ The high PCE was achieved by using chlorobenzene rather than chloroform as the solvent choice for dissolving the donor acceptor blend within the BHJ. The chlorobenzene provided better solubility of the PCBM, as well as producing smooth and uniform thin films.$^{33}$ The best device was composed of a P3HT:PCBM ratio of 1.0:0.8. Atomic force microscopy (AFM) studies demonstrated that alternate ratios of P3HT:PCBM provided clusters of PCBM crystals that disrupt the morphology and device performance.$^{33}$

Following the success of the P3HT:PCBM solar devices, researchers developed a polymer which alternates an ester substituted thieno[3,4-b]thiophene and benzodithiophene units.$^{34}$ The novel (PTB) polymer (Fig. 8.6) contains the quinoidal structure from the thieno[3,4-b]thiophene providing a low band gap.$^{34}$ The PTB7 polymer exhibited a PCE of 7.4%.$^{34}$ The BHJ contained PTB7:PC$_{71}$BM blend ranging in ratios of 1:1 to 1:2, with an optimum blend of 1:1.5 (PTB7:PC$_{71}$BM).$^{34}$ The polymer blend was further optimized by determining the solvent for film preparation. The solvents studied were chlorobenzene (CB), dichlorobenzene (DCB) as well as two 1:1 mixtures of the two previous solvents with 1,8-diiodooctane (DIO). The optimum conditions required the organic blend be dissolved in a 1:1 mixture of chlorobenzene and 1,8-diiodooctane, yielding an efficiency of 7.4%.$^{34}$ Transmission electron microscopy (TEM) images demonstrated that the mixture of CB and DIO solubilized the polymer:PC$_{71}$BM and provided a more homogeneous film as compared to the film incorporating CB as the solvent.$^{34}$

The morphology of the BHJ can influence the device’s efficiency, along with the other device parameters.$^{35}$ Likewise, many parameters can direct the morphology of the active layer and are as follows$^{35}$:

- spin cast solvent
- donor acceptor composition
- solution concentration
- controlled phase separation and induced crystallization
- chemical structure.
The solubility of the acceptor and donor in the same organic solvent is essential to intimately blend the two materials together. For instance, fullerenes can be insoluble in organic solvents, creating issues in device fabrication and cell efficiency. To remedy the issue, researchers attempt to incorporate functionalization into the molecule's structure. Compatibility between the donor and acceptor materials is important for efficient phase separation. Researchers have found that blending the solvents can increase the device’s efficiency. The donor and acceptor must be chemically inert from one another and the polymeric component must pack in an ordered arrangement, in order to create a crystalline lattice for diffraction and device purposes.

![Chemical structures](image)

Figure 8. Organic materials used in BHJ solar cells.

Overall, the BHJ in a solar cell is key for optimizing the device’s efficiency. However, to optimize the solar cell as a whole, researchers must tune the components within the BHJ.

1.5. Acceptor Research

A number of aspects need to be considered when conducting small molecule acceptor research. An organic acceptor material needs to be stable in the presence of air, moisture and light. Additionally, the organic material should exhibit photoconducting behavior, specifically high electron affinity and reasonable electron transport properties. The geometry and framework of the organic acceptor needs to be planar and rigid, to aid
in producing high short-circuit current densities.\textsuperscript{37} The acceptor needs to be able to phase separate from the donor to create the acceptor-donor interface.

Organic semiconducting materials tend to consist of alternating pi and sigma bonds that form a conjugated pi-framework. Interest in solar cell acceptor research initiated with perylene diimide molecules (PDI) (Fig. 8.4). These molecules are known to be strong, stable fluorescent chromophores, particularly used in dye chemistry.\textsuperscript{38} The photostability of the PDI aids in adjusting the HOMO and LUMO levels for use in solar cells as a possible acceptor molecule.\textsuperscript{18} Unfortunately, the PDI structure yields poor efficiencies unless paired with an inorganic component, such as a ZnO layer.\textsuperscript{39} Focus transitioned to C\textsubscript{60} fullerene molecules due to the high electron affinity, low optical gap and quick photo-induced charge transfer.\textsuperscript{32,40} C\textsubscript{60} fullerene materials, like PCBM, are great electron acceptors, present disadvantages incurred from high energy costs and low absorption in the visible range.\textsuperscript{40,41} Fullerenes are known to generate high amounts of singlet oxygen, leading to a decrease in device’s efficiency and stability.\textsuperscript{41}

Research for alternate n-type materials transitioned chemists’ focus to small molecules. The Vinazene analogs are considered promising materials due to their chemical flexibility, good film forming properties and high optical densities.\textsuperscript{42} Furthermore, these small n-type molecules are known to have high quantum efficiencies, and large open circuit voltage, yet issues arise from the molecules’ low mobilities.\textsuperscript{43,44} Shin et al. note that the low LUMO of the Vinazene provides efficient charge transfer; however, under white light illumination with a solar simulator.\textsuperscript{43} Success had been recently noted with 4,7-bis(2-(1-(2-ethylhexyl)-4,5-dicyanoimidazol-2-yl)vinyl)benzo[c][1,2,5]thiadiazole [EV-BT] (Fig. 8.5) with a PCE as high as 0.75%.\textsuperscript{45} The solubility of the Vinazene derivative increased with the substitution of the 2-ethylhexyl substituent. The device contained a 70 weight% of EV-BT and was annealed at 80\textdegree C, yielding a $V_{oc}$ of 1.36 V, FF of 0.49% and $J_{sc}$ of 1.14 mA/cm\textsuperscript{2}.\textsuperscript{45} These results demonstrated the potential for small molecule research of non-fullerene n-type acceptor molecules.

\textbf{Figure 9. Vinazene Core.}

The efficiency of the BHJ within the device can be influenced by parameter, such as the polydispersity, molecular weight (MW) and batch to batch variability. Polydispersity (PD) index measures the degree of polymerization in the sample and noted by the ratio of the weight-average molecular weight with respect to the number-average
molecular weight. The PD, when calculated, can have a value equal or greater to 1. However, a device with a perfectly monodisperse polymer will have a value of 1. Bronstein and Luscombe demonstrated, with the use of P3HT, that the semiconducting polymer needed to have a narrow polydispersity index and a high regioregularity (RR). Increasing the RR of a polymer acceptor can aid in increasing the mobility of charge carriers. In addition to the regioregularity of the polymer, the molecular weight of the polymer has a proportional relationship to the device’s performance. Researchers have found that the higher molecular weight of a polymer aids in better crystalline material, which increases the mobility and efficiency. Zen et al. observed four P3HT samples varying in MW and found that the increased MW provided more effective chain packing and an increased hole mobility in the annealed films. Batch-to-batch variability can negatively influence device optimization. Consequently, variability among batches of devices is very unsatisfactory. PD, MW and RR will influence the device’s morphology and ultimately the efficiency. Overall, researchers strive to fabricate BHJ solar devices that, in general, are characteristic of high MW and low PD. Controlling, and minimizing, the batch-to-batch variability of these material properties can aid in developing reproducible material processing and device fabrication.

1.6. Quinone Core

Acene quinones are promising n-type organic semiconductor materials for use in organic photovoltaics. Previous work has been conducted on benzoquinone and antraquinone derivatives. The best device reported incorporated 2,5-dibromobenzoquinone (DBBQ) (Fig. 8.3) as the acceptor material and exhibited an efficiency of 0.025%. Furthermore, as the acceptor, the DBBQ yielded a V_{oc} of 1.25 V, FF of 22.6% and J_{sc} of 0.0234 mA/cm². This class of n-type materials displayed a high electron affinity, similar to the fullerene molecules.

The quinone framework can accept electrons and reversibly undergo redox reactions (Fig. 10). Quinones, like benzoquinone and naphthaquinone, can be found in nature and operate as a strong oxidant. The charge transfer directs that one molecule donates electron pairs and undergoes oxidation while a second molecule acts as the electron acceptor and becomes reduced. In the case of solar cells, n-type materials are known to act as electron acceptors as seen in the π-deficient framework. Quinones have been exploited in nature through the actions of photosynthesis and are well known oxidizing agents.

The fused framework is introduced to free and excited electrons that are transferred from the donor source to the quinone via an electron transport mechanism. The trapping process is in competition with excited electron relaxation to its original state. The quinone unit, as the central component of the acceptor with the fused ring system, consists of an extended pi-conjugated system. The delocalized nature of the pi
electrons, along the fused framework, result in creating high electronic polarizability of the molecular structure.\textsuperscript{23}

![Quinone Core Redox Reaction](image)

**Figure 10.** Example redox reaction for the quinone core.

In addition to the electronics of the quinone backbone, quinones are known to be quite stable chemically and thermally. When comparing anthraquinone to benzoquinone and naphthoquinone, the anthraquinone has a higher chemical and thermal stability due to a lack of reactive olefinic subunits that are present in the benzoquinone and naphthoquinone. The arrangement or substitution of the carbonyl within the ring system tends to also influence the reactivity of the structure.

The pi-system can aid increased overlap of the pi-orbitals of adjacent molecules. The fused ring system can also influence and modify the HOMO-LUMO gap. The inclusion of aromatic rings in a linear arrangement can simultaneously raise the HOMO energy level and lower the LUMO energy level of the acceptor molecule. Additionally, the substitution of pi-acceptors, like carbonyls, can lower the LUMO energy and increase the structure’s conjugation.

The aromatic quinone core creates a planar molecule, which aids in eliminating the issue of flexibility along the backbone and provides a clear-cut definition in the molecular shape.\textsuperscript{60} Consequently, the attachment of the solubilizing groups to the anthradithiophene (ADT) quinone core can dictate the crystal packing arrangement. The herringbone structure, the simplest arrangement, positions the molecules in an edge-to-face contact at fixed, alternating angles.\textsuperscript{61,62} The second and most desired packing, sandwich herringbone, consists of a similar packing orientation of the herringbone, but is identified by pairs of arranged molecules.\textsuperscript{61,62} The third packing arrangement, γ-structure, flattens the contact angles and orients them at an edge-to-edge basis.\textsuperscript{61,62} The edge-to-edge contact provides more pi overlap within the sets of molecules rather than through the entire lattice. The last type, β-structure or brickwork, compactly layers the molecular structures upon one another.\textsuperscript{61,62} The molecules contact on an edge-to-edge bases at ~180° angle.

The two main interactions that drive the assigned crystal packing are C-C and C-H interactions. C-C interactions promote the parallel pi stacking, while the C-H
interactions prefer the herringbone motif. Increased C-C interactions are seen more in the γ and β-structure packing, and the herringbone and sandwich herringbone tend to have more C-H interaction throughout the crystal lattice. The C-H interactions are designated by the interaction of the carbon p_z orbital with the hydrogen of a neighboring molecule.

Of these four packing motifs, sandwich herringbone is the most desired arrangement, due to the creation of a one-dimensional (1D) π stack of dimerized subunits. The sandwich herringbone motif angles sets of two molecules at an edge-to-face interaction and incorporating π-stacking between the pairs of molecules.

Crystallization can affect the efficiency of the device, specifically the charge transport. As such, researchers can influence the rate of formation and crystal growth by regulating the rate of evaporation and cooling. In a similar manner, the rate of crystallization can be influenced by the solvent choice and solution concentration. Uncontrolled crystallization can cause issues within the device, as a result of the lack of homogeneous crystalline material can form defects and provide sites for possible charge traps, which reduces the current produced from the device. By controlling the assembly of crystal packing, the charge mobility of the OPV can be enhanced.

1.7. Five membered rings vs. Six membered rings

Previous work conducted by the Anthony group has focused on the synthesis and characterization of pentacene-based solar cells. In this present work, the chemical structure of the acene core has been modified to tune the crystal packing and energy levels of the organic acceptor material. In the anthradithiophene quinone core, the terminal benzene ring was replaced with a c-substituted thiophene ring at each end, creating a symmetric heteroacenequinone. The anthradithiophene quinone was functionalized with silylethynyl groups at the 1, 3, 7 and 9 positions rather than substituting the carbonyl positions at the 5 and 11 positions.

We chose to utilize a five membered ring, in our case the thiophene ring, with the goal of observing the degree of modification to the structures’ crystal packing and electronics. When fused into a linear backbone like the pentacene, the five membered ring systems help to eliminate steric issues that typically arise in the pentacene backbone. On a pentacene quinone, the solubilizing groups would be attached at the 2,3,9,10 positions at a 60 degree angle. These bulky groups would inhibit close packing due to the close proximity of the solubilizing groups. Rather than having the silylethynyl groups substituted alpha to one another, the anthradithiophene quinone arranges the solubilizing groups at opposing ends, at positions 1,3,7,9. On an anthradithiophene core, the silylethynyl groups are alpha to the sulfur atoms, which aid in eliminating the steric issue
of the two groups and increasing the 1-D packing. The two solubilizing groups, adjacent to the sulfur atom, are roughly 158.79° from one another.

In this work, we report on the synthesis, characterization and crystal packing of novel n-type acceptor molecules for use in bulk heterojunction organic photovoltaics.

Chapter 2: Electrochemistry

Following the synthesis and purification, the organic material is characterized by 1HNMR, 13CNMR, x-ray diffraction, melting point and combustion analysis for the intent of publication in scientific journals and introducing innovative science into everyday use. Further characterization is completed to distinguish the electronic properties with the use of solution-based electrochemistry and UV-vis in order to obtain the HOMO and LUMO energy levels as well as the energy gap (E_g).

2.1. Electrochemistry

Electrochemistry is a technique to characterize the redox properties of organic materials. Solution-based electrochemistry can estimate the HOMO and LUMO energy level of the small molecules intended for use in OPVs. The ease of gathering large amounts of electrochemical data provides the researcher with the opportunity to compare the HOMO and LUMO energy levels across a group of organic structures.

Cyclic Voltammetry (CV) and Differential Pulse Voltammetry (DPV) are examples of electrochemical experiments used to measure the current changes (mA) with respect to the scanning potential (V) of electronic conduction of the dissolved organic materials and supporting electrolyte. Typically, the organic material is dissolved in an anhydrous solution of a particular electrolyte. The solution of electrolyte is degassed with nitrogen (N_2) gas. Once the solution has both the electrolyte and organic material completely dissolved and degassed, the working, reference and counter electrodes are placed securely in the electrochemical cell, making sure no contact is made among the three electrodes within the solution. The solution is electrolyzed by either oxidizing or reducing the organic material dissolved in the cell.

The electrolytic process demonstrates the reversibility of the oxidation and reduction processes. Electrolysis provides the interchanging of ions by removal and addition of electrons to an organic compound from an external circuit. The working electrode can be programmed from a negative to positive potential, oxidizing the dissolved organic material and showing the anodic current.

The organic material in the solution will, both, accept an electron from the electrodes or donate an electron to the electrodes. As a result, the phenomenon of electron transfers can be measured by the current flow within the cell. In the molecular
perspective, the organic molecule can undergo either situation, depending on the structure’s electronic properties:

$$\text{Donor} - e^- \rightarrow \text{Donor}^+$$

$$\text{Acceptor} + e^- \rightarrow \text{Acceptor}^-$$

Figure 11. Electron transfer reaction.

The above figure represents the same molecule and its conversion to the corresponding HOMO and LUMO. The radical cation (LUMO) and the radical anion (HOMO) can be accessed electrochemically and are represented as the following:

Figure 12. Example image of reduction and oxidation of ADT quinone, respectively.

The electrochemical experiment provides the oxidation and reduction potentials, as well as the HOMO and LUMO energies. Electrochemical analysis is concentration dependent. In this work, the tested organic material is at a concentration of 1 mM in a 0.1 M solution of tetrabutyl ammonium hexafluorophosphate in dichloromethane. The reduction potential ($E_{\text{red}}$) can be gathered from the cathodic reduction current and is a direct measurement of the molecule’s electron affinity. The LUMO of the organic material could be estimated by using the $E_{\text{red}}$. Similarly, the oxidation potential ($E_{\text{ox}}$) can be gathered using the anodic oxidation current and is a direct measurement of the molecule’s ionization potential. The HOMO of the material can be estimated with the $E_{\text{ox}}$.

Electrochemical data were recorded against an internal standard, typically ferrocene/ferrocenium (Fc/Fc$^+$). The standard has an estimated potential, under vacuum,
of ~4.8 eV. The first oxidation and first reduction potentials of the organic material are determined in relation to the ferrocene/ferrocenium standard.

2.2. Cyclic Voltammetry (CV) and Differential Pulse Voltammetry (DPV)

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) are electroanalytical techniques used to determine the oxidation/reduction potentials of a desired organic molecule and these values can be converted to estimates of the HOMO and LUMO energy levels. These parameters, as well as the optical gap, can be calculated from the onset of the initial energy transition or at the peak values in the current-voltage graph. The Anthony group chooses to use the peak current values to calculate the HOMO and LUMO values. The energy gap ($E_g$) can be calculated by the difference in energies of the HOMO and LUMO or from the solution-based UV-vis, by way of the equation below:

$$E_g = \frac{1240}{\lambda}$$

However, the calculation of the $E_g$ from the maximum absorbance wavelength from the UV-vis tends to give an approximation of the energy difference between the HOMO LUMO energy levels the optical energy gap. The number calculated from the above equation only notes the difference in the energy levels, providing no description of the actual HOMO and LUMO levels. The optical band gap is considered an approximation because the maximum wavelength ($\lambda$) can be influenced by a number of factors surrounding the UV-vis operation and measurement. The UV-vis can be affected by the solvent, temperature and concentration of the observed sample. Consequently, all three can vary, causing the optical energy gap to be noted as an approximation.

CV consists of cycling a controlled potential across two electrodes and measures the resulting current. The potential applied at the working electrode and controlled against the reference electrode. Furthermore, the controlling potential acts as an excitation signal, as it is applied across the two other electrodes. The initial excitation signal causes the device to scan negatively, allowing researchers to note the cathodic peak and the scan continues in the reverse direction (positively) in order to observe the anodic peak. During the cathodic scan, the electrode acts as a strong reductant. Upon accumulation of the reduced organic material at the working electrode, the anodic current occurs initiating the oxidation of the organic material in solution.

DPV is more sensitive than CV, providing a more accurate reading of the $E_{\text{red}}$ and $E_{\text{ox}}$. In DPV, the current is sampled twice, both prior to and after the pulse. The current difference is plotted versus the applied potential of the instrument. These two types of electrochemical instrumentation provide the researcher with comparable values. In the Anthony group, both DPV and CV were used when gathering electrochemical data.
2.3. Estimation of HOMO and LUMO energies from the electrochemical data

To estimate the HOMO and LUMO from the electrochemical data:

\[
\text{HOMO} = -4.8 - \text{[anodic oxidation (Eox)-average of cathodic and anodic ferrocene oxidation]}
\]

\[
\text{LUMO} = -4.8 - \text{[cathodic reduction (Ered)-average of cathodic and anodic ferrocene oxidation]}
\]

In the case of 1,3,7,9-tetrakis(triisopropylsilyl)ethynyl-anthra[2,3-c;6,7-c’]dithiophene-5,11-dione quinone (TIPS ADT), the \(E_{\text{red}} = 960 \text{ mV}, \text{Fc/Fc}^+ = 446 \text{ mV} \) and \(E_g = 2.58 \text{ eV}\)

\[
\text{LUMO} = -4.8 - [-960 - 0.446] = -3.39 \text{ eV}
\]

\[
\text{HOMO} = \text{LUMO} - E_g = -3.39 - 2.58 = -5.97 \text{ eV}
\]

Electrochemical data was easily collected for the cathodic current providing an estimate for the reduction potential. Unfortunately, once the quinone accepted the electron, the electron was not able to be stripped from the reduced molecule, inhibiting the detection of the oxidation potential by the electrochemical experiments. The oxidation potential was calculated using the LUMO and optical energy gap \(E_g\), which was calculated using the UV vis.

Chapter 3: Methods

General. Bulk solvents (hexanes, dichloromethane, diethyl ether, pentane, and acetone) were purchased from Pharmco-Aaper. Dry THF was purchased from Aldrich. Commercial acetylene trisopropylsilylacetylene, trimethylsilylacetylene and tertbutyldimethylsilylacetylene were purchased from GFS chemicals. Silica gel 230-400 mesh was bought from Sorbent Technologies. NMR spectra were measured on Varian (Gemini 200 & 400) spectrometer, chemical shifts were reported in ppm relative to CDCl\(_3\) as an internal standard. Mass spectroscopy was performed by laser-desorption ionization (LDI) on a JEOL JMS-700T Mass Spectrometer.

3.1. Thiophene Chemistry

Procedure for the preparation of 2,5-dibromo-3,4-thiophene-dicarbaldehyde.

The synthesis of 2, 5-dibromo- 3, 4-thiophene-dicarbaldehyde (8) (Fig. 13) began with commercially available thiophene (1). Compound 1 is brominated with Br\(_2\) to create 2, 3, 4, 5-tetramethoxothiophene (2)\(^{72}\). The brominated thiophene (2) was debrominated with activated Zn in a HOAc/H\(_2\)O solution and converted to 3, 4-dibromothiophene (3)\(^{72}\). The dibromoproduct (3) is further reacted in Kumada reaction to yield compound 4, 3, 4-dimethylthiophene\(^73\). The methylated thiophene (4) is exhaustively brominated with Br\(_2\).
and azobisisobutyronitrile (AIBN) to give the 2,5-Dibromo-3,4-bis-bromomethyl-thiophene (5). The brominated starting material was reacted with potassium acetate in DMF to generate diacetate (6). Compound 6 is then hydrolyzed with anhydrous potassium carbonate in ethanol to produce 7, which was oxidized with pyridinium chlorochromate to generate the 2, 5-dibromo-3, 4-thiophene-dicarbaldehyde (8).

\[
\text{Figure 13. Synthesis of 2,5-dibromo-3,4-thiophene-dialdehyde}
\]

**General procedure for the preparation of the tetrasubstituted anthradithiophene quinones.** The synthesis of the tetrasubstituted anthradithiophene quinones (Fig. 14) began by condensing 2,5-dibromo-3,4-thiophene-dicarbaldehyde (8) with 1,4-cyclohexadiene using 15% NaOH to yield the brominated anthradithiophene quinone (9). The tetrabromo-anthradithiophene (9) was further reacted through a Sonogashira coupling to provide a number functionalized c-substituted anthradithiophene quinones (10-26).
Figure 14. Synthesis of tetrasubstituted anthradithiophene quinones.

**General procedure for synthesis of the tri-substituted silylacetylenes.** The synthesis of the trialkylsilylacetylenes (Fig. 15) occurred by reaction between ethynylmagnesium bromide and the desired chlorosilane. The synthesized acetylene can distilled to obtain the purified acetylene.

Figure 15. Synthesis of silyl acetylenes
3.2 Furan Chemistry

**Procedure for the preparation of 2,5-dibromo-3,4-furan-dicarbaldehyde.**

The synthesis of 2,5-dibromo-3,4-furan-dialdehyde (Fig. 17), was initiated with commercially available, diethyl 3,4-furan-dicarboxylate (38). Compound 38 is brominated with Br$_2$ in the presence of acetonitrile to create diethyl-2, 5-dibromofuran-3, 4-dicarboxylate (39)$^{78}$, which was reduced with diisobutylaluminum hydride (DIBAIH) in dichloromethane to (2,5-dibromo-4-hydroxymethyl-furan-3-yl)-methanol (40)$^{79}$, then oxidized with pyridinium chlorochromate to generate the 2, 5-dibromo-3, 4-furan-dicarbaldehyde (41).$^{74}$
Figure 17. Synthesis of 2,5-dibromo-3,4-furan-dicarbaldehyde.

3.3. Selenophene Chemistry

**Procedure for the preparation of 2,5-dibromo-3,4-selenophene-dicarbaldehyde.** The synthesis of 2,5-dibromo-3,4-selenophene-dicarbaldehyde (50) (Fig. 18) began with commercially available selenophene (42), which was exhaustively brominated\(^80\) then selectively reduced with activated Zn in HOAc/H\(_2\)O to 3, 4-dibromothiophene 44\(^81\). The dibromide 44 is converted to the dinitrile (45) with copper (I) cyanide\(^82\), which is then hydrolyzed under basic conditions to 3,4-selenophene-dicarboxylic acid 46\(^83\). Esterification (47)\(^84\) followed by bromination (NBS / 50:50 (v/v) CHCl\(_3\)-HOAc) produced 48\(^85\), which was reduced with DIBAIH to diol 49\(^79\). PCC oxidation of this diol yielded the desired 2, 5-dibromo-3, 4-selenophene-dicarbaldehyde (50).\(^74\)
3.4. Experimental

2, 3, 4, 5-tetrabromo-thiophene (2)

33.0 mL of Bromine (0.642 mmol) was slowly added directly to the stirred thiophene (12.0 g, 0.143 mol) at 0 °C. Following the precipitation of solid, chloroform (10mL) was added to the reaction mixture. The reaction mixture was left under constant stirring overnight and allowed to warm to room temperature. The next day, sodium thiosulfate (Na$_2$S$_2$O$_3$) was added to quench any unreacted bromine and stirred at room temperature for 30 minutes. Crude product was isolated by vacuum filtration, washed with cold acetone, and recrystallized with chloroform to give 45.44 g (79%) of 2 as a crème colored solid. $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 117.17, 110.51 ppm. MS (EI 70 eV) m/z 399 (M$^+$), 320 (M$^+$-Br), 240 (M$^+$-2Br), 161 (M$^+$-3Br), 80 (M$^+$-4Br).

3, 4-dibromo thiophene (3)

The entirety of 2 (41.0g, 0.103 mol) was dissolved in 82 mL of acetic acid/water (HOAc:H$_2$O) solution (11.09 mol:8.82 mol) in a round bottom flask equipped with a stir bar. The reaction mixture was cooled to 0 °C in an ice bath and stirred for 30 minutes. Activated zinc (26.8g, 0.410 mol) was slowly added to the tetrabromo thiophene mixture,
stirred for 6 hours and warmed to room temperature. The product was extracted with hexanes (3x), and the organic layer was then washed (extracted) with saturated sodium hydroxide (NaOH) to remove any remaining HOAc. The final organic layer was dried with magnesium sulfate (MgSO₄), and concentrated to give the colorless viscous oil.

Vacuum distillation gave the pure dibromo-product as a clear oil (17.81 g, 70 %). ¹H NMR (400 MHz, CDCl₃) δ: 7.28 (s, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ: 114.16, 123.98 ppm. MS (EI 70 eV) m/z 242 (M⁺), 163 (M⁺-Br), 82 (M⁺-2Br).

3, 4-dimethylthiophene (4)

3,4-Dibromo thiophene 3 (16.0g, 0.0661 mol) and NiCl₂ (dppp) (0.359 g, 0.661 mmol) was dissolved in 108 mL of anhydrous tetrahydrofuran (THF) in a flame dried round bottom flask equipped with a stir bar, under N₂ atmosphere. Methylmagnesiumbromide (CH₃MgBr) (88.2 mL, 0.265 mol) was added to 108 mL THF in a second flame dried round bottom flask under N₂ atmosphere, equipped with a stir bar, and cooled to 0 °C by an ice bath. The dibromothiophene and catalyst mixture was poured into the methylmagnesiumbromide solution and let stir for 30 minutes at 0 °C under an N₂ atmosphere. Following the 30 minutes, the reaction mixture was refluxed 20-24 hours and treated dropwise with 80 mL of HCl (2M) in an ice bath to remove the excess MgMeBr. The organic layer was washed with H₂O, extracted with ether (2-3x) and, later, extracted with sat. NaCl. Following the extractions, the organic layer was dried and concentrated. The crude product gave a dark brown liquid (7.10 g, 95%). Vacuum distillation can be used to remove THF from the 3,4-dimethylthiophene to give a clear, colorless oil 4. ¹H NMR (400 MHz, CDCl₃) δ: 2.13 (s, 6H), 6.84 (s, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ: 14.65, 120.82, 137.52 ppm. MS (EI 70 eV) m/z 112 (M⁺), 97 (M⁺-CH₃), 82 (M⁺-2CH₃).

2,5-Dibromo-3,4-bis-bromomethyl-thiophene (5)

96.8 mL 1, 2-Dichloroethane was added and followed by the addition of 6.82 g (0.0608 mol) 3, 4-dimethylthiophene (4) into a one-necked round bottom flask, equipped with a stir bar, was flame dried and introduced to a N₂ environment. Bromine (15.6 mL, 0.304 mol) was slowly added directly to the dissolved dimethylthiophene and refluxed for 7 hours. After the 7 hour refluxing, 0.200g (1.20 mmol) 2, 2’-Azobis (2-methylpropionitrile) (AIBN) in 1,2-dichloroethane was added to the reaction mixture and the solution continued stirring and refluxing overnight (14-16 hours). The next day, Na₂S₂O₃ was added to quench any unreacted bromine and stirred at room temperature for 30 minutes. The reaction mixture was extracted with ether (3x), dried with MgSO₄, and concentrated. The crude product was recrystalized with ethanol. The product was isolated by vacuum filtration and washed with cold methanol to give 9.06 g (34 %) of 5 as a fluffy, brown solid. ¹H NMR (400 MHz, CDCl₃) δ: 4.52 (s, 4H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ: 14.65, 120.82, 137.52 ppm. MS (EI 70 eV) m/z 112 (M⁺), 97 (M⁺-CH₃), 82 (M⁺-2CH₃).
MHz, CDCl$_3$ δ: 23.85, 114.13, 136.22 ppm. MS (EI 70 eV) m/z 428 (M$^+$), 349 (M$^+$-Br), 268 (M$^+$-2Br), 189 (M$^+$-3Br), 108 (M$^+$-4Br).

Acetic acid 4-acetoxymethyl-2,5-dibromo-thiophen-3-ylmethyl ester (6)

In 250 mL flame, dried round bottom flask, 3, 4-bisbromomethyl-2,5-dibromo-thiophene (5) (7.0 g, 0.0164 mol) was added and dissolved along with 4.82 g (0.049 mol) potassium acetate into 16.5 mL of N,N-dimethylformamide (DMF) (1M). The reaction mixture was allowed to stir overnight at 80 °C. The reaction mixture was cooled to room temperature and extracted with ethyl acetate (2-3x). The combined organic layers were washed with 5% aqueous sodium chloride (NaCl) (3-4x), dried with MgSO$_4$, and concentrated. The crude product was dried and concentrated to form a dark, purplish, black mixture. The product was purified by recrystallization with heptanes to yield 3.98 g of light, brown crystals (62%) 6. $^1$H NMR (400 MHz, CDCl$_3$) δ: 2.03 (s, 6H), 5.05 (s, 4H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 20.88, 59.02, 114.46, 135.57, 170.66 ppm. MS (EI 70 eV) m/z 386 (M$^+$), 326 (M$^+$-CO$_2$CH$_3$), 266 (M$^+$-2CO$_2$CH$_3$), 205 (M$^+$-2CO$_2$CH$_3$(Br)).

(2,5-Dibromo-4-hydroxymethyl-thiophen-3-yl)-methanol (7)

Anhydrous potassium bicarbonate (K$_2$CO$_3$) (5.21 g, 0.038 mol) was added to a solution of 6 (3.64 g, 9.43 mmol) in ethanol (90 mL) and the mixture was refluxed for 18 hours. The residue was treated with water (75 mL) to dissolve the remaining K$_2$CO$_3$. The crude product was extracted with diethyl ether (Et$_2$O) (2-3x), the combined organic layers were dried with MgSO$_4$, and concentrated. The product was purified by elution through a silica gel-filled plug (ether) to give 2.81 g (98 %) of the fluffy white solid 7. $^1$H NMR (400 MHz, CDCl$_3$) δ: 2.89 (t, J = 12.4, 2H), 4.65 (d, J = 12, 4H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 58.64, 111.64, 140.02 ppm. MS (EI 70 eV) m/z 302 (M$^+$), 285 (M$^+$-OH).

2,5-Dibromo-thiophene-3,4-dicarbaldehyde (8)

To 130 mL dichloromethane (DCM), 5.25 g (24.3 mmol) pyridinium chlorochromate (PCC), 5.25g celite, and 5.25 g molecular sieves were added to a round bottom flask and stirred for 1 minute. Compound 7 (2.45 g, 8.11 mmol) dissolved in 65 mL dichloromethane was added at room temperature to the PCC solution. After stirring at room temperature for 10 hours, the product was poured directly through silica gel and concentrated to yield 1.92 g (79 %) 8. $^1$H NMR (400 MHz, CDCl$_3$) δ: 10.15 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 123.84, 136.70, 184.99 ppm. MS (EI 70 eV) m/z 298 (M$^+$), 269 (M$^+$-CHO), 81 (M$^+$-2BrCHO)).

1, 3, 7,9-tetrabromo-anthra[2,3-c; 6,7-c’]dithiophene-5,11-dione (9)
8 (3.0 g, 10.1 mmol) was dissolved in 20 mL of THF, and diluted with 20 mL absolute ethanol (EtOH) with 1.07 g (9.56 mmol) of 1, 4-cyclohexanedione. 0.5 mL of 15% NaOH was added slowly and a precipitate formed. The sides of the reaction flask and precipitate were washed down with methanol. The solution was allowed to stir at room temperature for 2 hours before filtration. Crude product was washed with THF and followed by ether. The remaining solid in the Buchner funnel was triturated with 60 mL hot DMF. The reaction yielded 1.93 g (60%) dark, green solid 9. MS (EI 70 eV) m/z 636 (M+), 557 (M+ - Br).

1,3,7,9-tetrakis(triisopropylsilyl)ethynyl)-anthra[2,3-c;6,7-c']dithiophene-5,11-dione (10)

Into a flame dried round bottom flask under nitrogen atmosphere, 0.97 mL (4.30 mmol) (triisopropyl)silylethynylacetylene, 0.01 g (0.054 mmol) copper (I) iodide, 0.6 mL (4.30 mmol) triethylamine, 0.06 g (0.09 mmol) Pd(PPh3)2Cl2, 0.57 g (0.90 mmol) 9 was dissolved in 8 mL dry benzene. The reaction mixture was refluxed and stirred overnight. Once cooled, the crude quinone was extracted with dichloromethane, dried, and concentrated. The product was purified using chromatography with hexane to yield 0.25 g (27%) product, which was recrystallized from toluene to give 0.13 g (14%) dark red crystals 10. 1H NMR (400 MHz, CDCl3) δ: 1.19 (m, 84H), 8.837 (s, 4H) ppm. 13C NMR (50 MHz, CDCl3) δ: 11.56, 18.96, 97.34, 105.73, 123.60, 124.71, 130.22, 140.04, 181.94 ppm. MS (EI 70 eV) m/z 1042 (M+), 1029 (M+ - CH3), 859 (M+ - CSSi(CH(CH3)2)3).

1,3,7,9-tetrakis(triethylsilyl)ethynyl)-anthra[2,3-c;6,7-c']dithiophene-5,11-dione (11)

Into a flame dried round bottom flask under nitrogen atmosphere, 0.68 mL (3.77 mmol) triethylsilylacetylene, 0.01 g (0.05 mmol) copper (I) iodide, 0.53 mL (3.77 mmol) triethylamine, 0.06 g (0.08 mmol) Pd(PPh3)2Cl2, 0.5 g (0.79 mmol) 9 was dissolved in 8 mL dry benzene. The reaction mixture was refluxed and stirred overnight. Once cooled, the crude quinone was extracted with dichloromethane, dried, and concentrated. The product was purified using chromatography with hexane to yield 0.24 g (35%) of 11 as an orange powder. 1H NMR (400 MHz, CDCl3) δ: 0.77 (q, J = 8 Hz, 24H), 1.10 (t, J = 8Hz, 36H), 8.82 (s, 4H) ppm. 13C NMR (100 MHz, CDCl3) δ: 4.54, 7.80, 96.56, 106.65, 121.11, 124.78, 130.08, 140.16, 182.88 ppm. MS (EI 70 eV) m/z 873 (M+), 848 (M+ - C2H5), 733 (M+ - CSSi(CH2H5)2).

1,3,7,9-tetrakis(diisopropyl-octylsilyl)ethynyl)-anthra[2,3-c;6,7-c']dithiophene-5,11-dione (12)

Into a flame dried round bottom flask under nitrogen atmosphere, 0.95 mL (3.78 mmol) (diisopropyl-octyl)isilyl acetylene, 0.01 g (0.047 mmol) copper iodide, 0.53 mL (3.78 mmol) triethylamine, 0.06 g (0.08 mmol) Pd(PPh3)2Cl2, 0.5 g (0.79 mmol) 9 was dissolved in 8 mL dry benzene. The reaction mixture was refluxed and stirred overnight.
Once cooled, the crude quinone was extracted with dichloromethane, dried, and concentrated. The product was eluted using chromatography with hexane to yield 0.6 g (58%) of a dark, red oil 12. $^1$H NMR (400 MHz, CDCl$_3$) δ: 0.83 (m, 24H), 0.99 (t, $J = 5.6$ Hz, 12H), 1.16 (d, $J = 9.6$ Hz, 24H), 1.24 (d, $J = 6.4$ Hz, 24H), 1.190 (d, $J = 4.10$ Hz, 18H), 1.32 (m, $J = 7.2$ Hz, 8H), 1.39 (m, $J = 8.4$ Hz, 8H), 1.49 (m, $J = 7.6$ Hz, 8H), 1.51 (m, $J = 8.4$ Hz, 8H) 1.523 (m, 3H), 8.84 (s, 4H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 10.23, 12.02, 14.34, 22.92, 24.67, 29.50, 29.91, 32.17, 30.02, 96.56, 106.65, 121.11, 124.77, 130.08, 140.16, 182.88 ppm. MS (EI 70 eV) m/z 1323 (M$^+$), 1280 (M$^+$-C(CH$_3$)$_2$), 1241 (M$^+$-2(C(CH$_3$)$_2$)), 1210 (M$^+$-2(C(CH$_3$)$_2$)(C$_8$H$_{17}$)), 1070 (M$^+$-CCSi(2(C(CH$_3$)$_2$)(C$_8$H$_{17}$))).  

1,3,7,9-tetraakis(tertbutyldimethylsilylethynyl)-anthra[2,3-c;6,7-c']dithiophene-5,11-dione (13)  

Into a flame dried round bottom flask under nitrogen atmosphere, 0.71 mL (3.78 mmol) tertbutyldimethylsilyl acetylene, 0.08 g (0.05 mmol) copper (I) iodide, 0.53 mL (3.78 mmol) triethylamine, 0.04 g (0.08 mmol) Pd(PPh$_3$)$_2$Cl$_2$, 0.5 g (0.79 mmol) 9 was dissolved in 8 mL dry benzene. The reaction mixture was refluxed and stirred overnight. Once cooled, the crude quinone was extracted with dichloromethane, dried, and concentrated. The product was purified using chromatography with hexane to yield 0.34 g (49%) red solid powder 13. $^1$H NMR (400 MHz, CDCl$_3$) δ: 0.27 (s, 24H), 1.05(s, 36H), 8.81 (s, 4H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 10.23, 12.02, 14.34, 22.92, 24.67, 29.50, 29.91, 32.17, 30.02, 96.56, 106.65, 121.11, 124.77, 130.08, 140.16, 182.88 ppm. MS (EI 70 eV) m/z 1323 (M$^+$), 1280 (M$^+$-C(CH$_3$)$_2$), 1241 (M$^+$-2(C(CH$_3$)$_2$)), 1210 (M$^+$-2(C(CH$_3$)$_2$)(C$_8$H$_{17}$)), 1070 (M$^+$-CCSi(2(C(CH$_3$)$_2$)(C$_8$H$_{17}$))).  

1,3,7,9-tetrakis(trimethylsilylethynyl)-anthra[2,3-c;6,7-c']dithiophene-5,11-dione (14)  

Into a flame dried sealed tube under nitrogen atmosphere, 0.89 mL (6.29 mmol) (trimethyl)silyl acetylene, 0.01 g (0.04 mmol) copper (I) iodide, 0.50 mL (3.78 mmol) triethylamine, 0.06 g (0.08 mmol) Pd(PPh$_3$)$_2$Cl$_2$, 0.50 g (0.79 mmol) 9 was dissolved in 8 mL dry benzene. The reaction mixture was refluxed in a sealed tube and stirred overnight. Once cooled, the crude quinone was extracted with dichloromethane, dried, and concentrated. The product was purified using chromatography with hexane to yield 0.02 g (4%) product of a dark red powder material 14. $^1$H NMR (400 MHz, CDCl$_3$) δ: 0.34 (s, 36H), 8.80(s, 4H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 0.064, 95.4, 105.0, 108.8, 124.8, 130.1, 140.2, 182.6 ppm. MS (EI 70 eV) m/z 704 (M$^+$), 607 (M$^+$-CCSi(CH$_3$)$_3$).  

1,3,7,9-tetrakis(tri-n-propylsilylethynyl)-anthra[2,3-c;6,7-c']dithiophene-5,11-dione (15)
Into a flame dried round bottom flask under nitrogen atmosphere, 0.87 mL (3.78 mmol) (tri-n-propyl)silyl acetylene, 0.01 g (0.0472 mmol) copper iodide, 0.53 mL (3.78 mmol) triethylamine, 0.06 g (0.08 mmol) Pd(PPh₃)₂Cl₂, 0.5 g (0.79 mmol) 9 was dissolved in 8 mL dry benzene. The reaction mixture was refluxed and stirred overnight. Once cooled, the crude quinone was extracted with dichloromethane, dried, and concentrated. The product was eluted using chromatography with hexane to yield 0.20 g (24%) product in an oil form 15. ¹H NMR (400 MHz, CDCl₃) δ: 0.76 (h, J = 4.8 Hz, 18H), 1.05 (t, J = 7.2 Hz, 36H), 1.52 (m, J = 2.8 Hz, 24H), 8.81 (s, 4H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ: 16.12, 17.89, 18.45, 96.65, 107.43, 121.09, 124.76, 130.12, 140.16, 182.84 ppm. MS (EI 70 eV) m/z 1004 (M⁺), 998 (M⁺-C₃H₇), 956 (M⁺-2(C₃H₇)), 915 (M⁺-3(C₃H₇)), 858 (M⁺-CCSi(C₃H₇)₃).

1,3,7,9-tetrakis(dimethylctysilylethynyl)-anthra[2,3-c;6,7-c’]dithiophene-5,11-dione (16)

Into a flame dried round bottom flask under nitrogen atmosphere, 0.74 g (3.78 mmol) (dimethylctysilyl)silyl acetylene, 0.01 g (0.05 mmol) copper (I) iodide, 0.53 mL (3.78 mmol) triethylamine, 0.06 g (0.08 mmol) Pd(PPh₃)₂Cl₂, 0.50 g (0.79 mmol) 9 was dissolved in 8 mL dry benzene. The reaction mixture was refluxed and stirred overnight. Once cooled, the crude quinone was extracted with dichloromethane, dried, and concentrated. The product was purified using chromatography with hexane to yield 0.46 g (53%) product, which was recrystallized from acetone to give 0.233 g (27%) dark red crystals 16. ¹H NMR (400 MHz, CDCl₃) δ: 0.31 (s, 24H), 0.77 (dd, J = 9.6, 8.4 Hz, 8H), 0.83 (t, J = 7.2 Hz, 12H), 1.26 (m, 32H), 1.38 (t, J = 6.8 Hz, 8H), 1.47 (dd, J = 5.2, 10.8 Hz, 8H), 8.81 (s, 4H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ: -1.59, 14.34, 16.16, 22.91, 24.08, 29.50, 32.16, 33.49, 95.73, 108.39, 121.08, 124.75, 130.10, 140.15, 182.81 ppm. MS (EI 70 eV) m/z 1096 (M⁺), 998 (M⁺-C₃H₇), 956 (M⁺-2(C₃H₇)), 915 (M⁺-3(C₃H₇)), 858 (M⁺-CCSi(C₃H₇)₃).

1,3,7,9-tetrakis(n-butyldimethylsilylethynyl)-anthra[2,3-c;6,7-c’]dithiophene-5,11-dione (17)

Into a flame dried round bottom flask under nitrogen atmosphere, 0.53 g (3.78 mmol) (butyldimethyl)silyl acetylene, 0.01 g (0.05 mmol) copper iodide, 0.53 mL (3.78mmol) triethylamine, 0.06 g (0.08 mmol) Pd(PPh₃)₂Cl₂, 0.50 g (0.79 mmol) 9 was dissolved in 8 mL dry benzene. The reaction mixture was refluxed and stirred overnight. Once cooled, the crude quinone was extracted with dichloromethane, dried, and concentrated. The product was purified using chromatography with hexane to yield 0.46 g (53%) product, which was recrystallized from 1, 2-dichloroethane to give 0.223 g (32 %) dark red crystals 17. ¹H NMR (400 MHz, CDCl₃) δ: 0.32 (s, 24H), 0.78 (m, 12 H), 0.94 (t, J = 7.2 Hz, 8H), 1.44 (m, 8H), 1.52 (s, 8H), 8.81 (s, 4H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ: -1.59, 1.24, 14.03, 26.28, 26.46, 96.73, 108.37, 121.08, 124.76, 130.10, 140.18, 182.89 ppm. MS (EI 70 eV) m/z 873 (M⁺), 816 (M⁺-C₄H₉), 733 (M⁺-CCSi(CH₃)₂C₄H₉).
1,3,7,9-tetrakis(dimethylthexylysilylthynyl)-anthra[2,3-c;6,7-c']dithiophene-5,11-dione (18)

Into a flame dried round bottom flask under nitrogen atmosphere, 0.64 g (3.78 mmol) (dimethylthexyl)silyl acetylene, 0.01 g (0.05 mmol) copper (I) iodide, 0.53 mL (3.78 mmol) triethylamine, 0.06 g (0.08 mmol) Pd(PPh₃)₂Cl₂, 0.57 g (0.79 mmol) 9 was dissolved in 8 mL dry benzene. The reaction mixture was refluxed and stirred overnight. Once cooled, the crude quinone was extracted with dichloromethane, dried, and concentrated. The product was purified using chromatography with hexane to yield 0.02 g (1%) of the reddish powdery product 18, following seven different recrystallizations. ¹H NMR (400 MHz, CDCl₃) δ: 0.31, (s, 24H), 0.98 (s, 24H), 1.00 (d, J = 3.2 Hz, 24H), 2.14 (s, 4H), 8.80 (s, 4H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ: -2.37, 2, 18.93, 21.07, 24.00, 34.96, 96.35, 108.88, 121.17, 124.76, 130.10, 140.11, 181.21 ppm. MS (EI 70 eV) m/z 985 (M⁺), 900 (M⁺-C(CH₃)₂CH(CH₃)₂), 842 (M⁺-Si(CH₃)₂(C(CH₃)₂CH(CH₃)₂)).

1,3,7,9-tetrakis(4-chlorobutyl-dimethyl-silylthynyl)-anthra[2,3-c;6,7-c']dithiophene-5,11-dione (19)

Into a flame dried round bottom flask under nitrogen atmosphere, 0.66 g (3.78 mmol) (4-chlorobutyl-dimethyl)silylacetylene, 0.01 g (0.05 mmol) copper iodide, 0.53 mL (3.78 mmol) triethylamine, 0.06 g (0.08 mmol) Pd(PPh₃)₂Cl₂, and 0.50 g (0.79 mmol) 9 was dissolved in 8 mL dry benzene. The reaction mixture was refluxed and stirred overnight. Once cooled, the crude quinone was extracted with dichloromethane, dried, and concentrated. The product was purified using chromatography with hexane and recrystallized from ethyl acetate to give 0.23 g (28 %) orange-red crystals 19. ¹H NMR (400 MHz, CDCl₃) δ: 0.34 (s, 24H), 0.83 (dp, J = 7.2, 8.4, 8H), 1.66 (dp, J = 8.4, 6.8 Hz, 8H), 1.91 (p, J = 7.2 Hz, 8H), 3.61 (t, J = 6.8 Hz, 8H), 8.80 (s, 4H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ: -1.66, 15.41, 121.48, 36.01, 44.81, 96.04, 107.84, 120.99, 124.72, 130.13, 140.26, 182.78 ppm. MS (EI 70 eV) m/z 1011 (M⁺), 975 (M⁺-Cl), 919 (M⁺-C₄H₈Cl), 863 (M⁺-SiC₄H₈Cl).

1,3,7,9-tetrakis(dimethyl-3,3,3-trifluoropropylsilylthynyl)-anthra[2,3-c;6,7-c']dithiophene-5,11-dione (20)

Into a flame dried round bottom flask under nitrogen atmosphere, 0.78 g (4.33 mmol) (dimethyl-3,3,3-trifluoropropyl)silyl acetylene, 0.01 g (0.05 mmol) copper iodide, 0.53 mL (3.78 mmol) triethylamine, 0.06 g (0.08 mmol) Pd(PPh₃)₂Cl₂, 0.50 g (0.79 mmol) 9 was dissolved in 8 mL dry benzene. The reaction mixture was refluxed and stirred overnight. Once cooled, the crude quinone was extracted with dichloromethane, dried, and concentrated. The product was purified using chromatography with hexane to yield 0.12 g (14%) product, which was recrystallized from 1, 2-dichloroethane to give 20 mg (2 %) dark red crystals 20. ¹H NMR (400 MHz, CDCl₃) δ: 0.39 (s, 24H), 1.02 (t, J = 4.0
Hz, 8 H), 2.23 (m, $J = 4.4$ Hz, 8H), 8.80 (s, 4H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) δ: -1.89, 8.19, 29.88, 96.70, 106.07, 120.84, 124.66, 129.55, 130.25, 140.25, 140.36, 182.67 ppm. MS (EI 70 eV) $m/z$ 869 (M$^+$), 840 (M$^+ - 3$F), 720 (M$^+ - $CCSi(CH$_3$)$_2$(C$_2$H$_4$(CF$_3$))).

**1,3,7,9-tetrakis(dimethyl-n-propylsilylethynyl)-anthra[2,3-c;6,7-c']dithiophene-5,11-dione (21)**

Into a flame dried round bottom flask under nitrogen atmosphere, 0.48 g (3.78 mmol) (dimethyl-n-propyl)silyl acetylene, 0.01 g (0.05 mmol) copper iodide, 0.53 mL (3.78 mmol) triethylamine, 0.06 g (0.08 mmol) Pd(PPh$_3$)$_2$Cl$_2$, 0.50 g (0.79 mmol) 9 was dissolved in 8 mL dry benzene. The reaction mixture was refluxed and stirred overnight. Once cooled, the crude quinone was extracted with dichloromethane, dried, and concentrated. The product was purified using chromatography with hexane to yield 53 mg (8%) product, which was recrystallized from 1-chlorobutane to give 10 mg (1 %) red crystals 21.

$^1$H NMR (400 MHz, CDCl$_3$) δ: 0.32 (s, 24H), 0.78 (m, $J = 8$ Hz, 8 H), 1.06 (t, $J = 7.2$ Hz, 12H), 1.54 (h, $J = 4.8$ Hz, 8H), 8.81 (s, 4H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) δ: -1.53, 1.24, 18.72, 29.92, 95.75, 108.37, 121.10, 124.78, 130.08, 140.16, 182.91 ppm. MS (EI 70 eV) $m/z$ 817 (M$^+$), 774 (M$^+ - $C$_3$H$_7$), 691 (M$^+ - $CCSi(CH$_3$)$_2$(C$_3$H$_7$)).

**1,3,7,9-tetrakis(isobutyl-dimethylsilylethynyl)-anthra[2,3-c;6,7-c']dithiophene-5,11-dione (22)**

Into a flame dried round bottom flask under nitrogen atmosphere, 0.53 g (3.78 mmol) (isobutyl(dimethyl)silyl acetylene, 0.01 g (0.05 mmol) copper iodide, 0.53 mL (3.78 mmol) triethylamine, 0.06 g (0.08 mmol) Pd(PPh$_3$)$_2$Cl$_2$, 0.50 g (0.79 mmol) 9 was dissolved in 8 mL dry benzene. The reaction mixture was refluxed and stirred overnight. Once cooled, the crude quinone was extracted with dichloromethane, dried, and concentrated. The product was purified using chromatography with hexane to yield 0.44 g (65%) product, which was recrystallized from 1, 2-dichloroethane to give 0.28 g (40 %) dark red crystals 22. $^1$H NMR (400 MHz, CDCl$_3$) δ: 0.32 (s, 24H), 0.81 (d, $J = 7.2$ Hz, 24H), 1.07 (d, $J = 6.8$ Hz, 8H), 1.97 (m, $J = 6.8$ Hz, 4H), 8.81 (s, 4H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) δ: -0.68, 25.41, 26.35, 29.92, 96.92, 108.78, 121.13, 124.78, 130.13, 140.16, 182.88 ppm. MS (EI 70 eV) $m/z$ 873 (M$^+$), 816 (M$^+ - $C$_4$H$_9$).

**1,3,7,9-tetrakis(dimethyl-phenylsilylethynyl)-anthra[2,3-c;6,7-c']dithiophene-5,11-dione (23)**

Into a flame dried round bottom flask under nitrogen atmosphere, 0.61 g (3.78 mmol) (dimethyl-phenyl)silyl acetylene, 0.01 g (0.05 mmol) copper iodide, 0.53 mL (3.78 mmol) triethylamine, 0.06 g (0.08 mmol) Pd(PPh$_3$)$_2$Cl$_2$, 0.50 g (0.79 mmol) 9 was dissolved in 8 mL dry benzene. The reaction mixture was refluxed and stirred overnight. Once cooled, the crude quinone was extracted with dichloromethane, dried, and concentrated. The
product was purified using chromatography with hexane and recrystallized from 1,2-dichloroethane to give 0.13 g (17%) dark, purple, red crystals. $^1$H NMR (400 MHz, CDCl$_3$) δ: 0.62 (s, 24H), 7.46 (dd, $J = 2.8$, 1.6 Hz, 8H), 7.75 (dd, $J = 2.0$, 3.2 Hz, 4H), 7.84 (d, $J = 1.2$ Hz, 8H), 8.85 (s, 4H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) δ: -0.79, 96.81, 104.94, 106.93, 121.07, 124.75, 128.38, 130.06, 134.04, 136.10, 140.37, 182.74 ppm. MS (EI 70 eV) m/z 952 (M$^+$), 937 (M$^+$-CH$_3$), 922 (M$^+$-2(CH$_3$)).

$^{1,3,7,9}$-tetrakis(dimethyl-isopropylsilylethynyl)-anthra[2,3-c;6,7-c']dithiophene-5,11-dione (24)

Into a flame dried round bottom flask under nitrogen atmosphere, 0.48 g (3.78 mmol) (dimethyl-isopropyl)silyl acetylene, 0.01 g (0.05 mmol) copper iodide, 0.53 mL (3.78 mmol) triethylamine, 0.06 g (0.08 mmol) Pd(PPh$_3$)$_2$Cl$_2$, 0.50 g (0.79 mmol) 9 was dissolved in 8 mL dry benzene. The reaction mixture was refluxed and stirred overnight. Once cooled, the crude quinone was extracted with dichloromethane, dried, and concentrated. The product was purified using chromatography with hexane and yielded 32% of an orange powder. $^1$H NMR (400 MHz, CDCl$_3$) δ: 0.29 (s, 24H), 1.12 (d, $J = 7.2$ Hz, 24H), 1.01 (dq, $J = 6.8$, 4.4 Hz, 4H), 8.82 (s, 4H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) δ: -3.66, 14.16, 17.66, 95.96, 107.53, 121.06, 124.71, 130.06, 140.16, 182.77 ppm. MS (EI 70 eV) m/z 817 (M$^+$), 773 (M$^+$-C(CH$_3$)$_2$).

$^{1,3,7,9}$-tetrakis(cyclohexyl-dimethyl-silylethynyl)-anthra[2,3-c;6,7-c']dithiophene-5,11-dione (25)

Into a flame dried round bottom flask under nitrogen atmosphere, 0.63 g (3.78 mmol) (cyclohexyl-dimethyl)silyl acetylene, 0.01 g (0.05 mmol) copper iodide, 0.53 mL (3.78 mmol) triethylamine, 0.06 g (0.08 mmol) Pd(PPh$_3$)$_2$Cl$_2$, 0.50 g (0.79 mmol) 9 was dissolved in 8 mL dry benzene. The reaction mixture was refluxed and stirred overnight. Once cooled, the crude quinone was extracted with dichloromethane, dried, and concentrated. The product was purified using chromatography with hexane to yield 0.55 g (71%) product, which was recrystallized from isopropanol to give 0.12 g (15%) red crystals. $^1$H NMR (400 MHz, CDCl$_3$) δ: 0.27 (s, 24H), 0.78 (m, 12 H), 0.94 (t, $J = 7.2$ Hz, 8H), 1.44 (m, 8H), 1.52 (s, 8H), 8.82 (s, 4H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) δ: -3.54, 25.85, 27.03, 27.57, 28.03, 96.08, 107.80, 121.05, 124.76, 130.10, 140.18, 182.86 ppm. MS (EI 70 eV) m/z 977 (M$^+$), 893 (M$^+$-C$_6$H$_{11}$), 836 (M$^+$-Si(CH$_3$)$_2$(C$_6$H$_{11}$)).

$^{1,3,7,9}$-tetrakis(3,3-dimethylbutyl-dimethyl-silylethynyl)-anthra[2,3-c;6,7-c']dithiophene-5,11-dione (26)

Into a flame dried round bottom flask under nitrogen atmosphere, 0.64 g (3.78 mmol) (3,3-dimethylbutyl-dimethyl)silylacetylene, 0.01 g (0.05 mmol) copper iodide, 0.53 mL (3.78 mmol) triethylamine, 0.06 g (0.08 mmol) Pd(PPh$_3$)$_2$Cl$_2$, 0.50 g (0.79 mmol) 9 was dissolved in 8 mL dry benzene. The reaction mixture was refluxed and stirred overnight.
Once cooled, the crude quinone was extracted with dichloromethane, dried, and concentrated. The product was purified using chromatography with hexane and recrystallized from 1,2-dichloroethane to give 80 mg (7%) orange, red crystals. 

\[1^1H\text{NMR (400 MHz, CDCl}_3\text{)} \delta: 0.32 (s, 24H), 0.90 (s, 36H), 1.24 (m, \text{J} = 9.6 \text{ Hz}, 8H), 2.14 (s, 8H), 8.81 (s, 4H) \text{ ppm.} \]

\[1^{13}C\text{NMR (100 MHz, CDCl}_3\text{)} \delta: -1.83, 10.53, 39.09, 31.36, 37.93, 95.77, 108.28, 121.07, 124.75, 130.14, 140.20, 182.85 \text{ ppm.} \]

**MS (EI 70 eV) m/z 985 (M^+), 900 (M^+-C}_2H_4C(CH}_3)_2\text{).} \]

(n-Butyl-dimethyl)silyl-acetylene (27)

Into a flame dried flask 27.7 mL of 0.5 M (13.82 mmol) ethynyl Grignard in THF was added. Butylchlorodimethylsilane (2 mL, 11.52 mmol) was added neat at room temperature and stirred 4 days. The product was extracted with hexane, dried, and concentrated. No purification was necessary. The silyl-acetylene was a colorless oil and yielded 1.70 g (98%) 27. 

\[1^1H\text{NMR (400 MHz, CDCl}_3\text{)} \delta: 0.14 (s, 6H), 0.61 (t, \text{J} = 4.4 \text{ Hz}, 3H), 1.24 (t, \text{J} = 2.4, 2H), 1.33 (t, \text{J} = 2.8, 2H), 1.34 (t, \text{J} = 3.6, 2H), 2.33 (s, 1H) \text{ ppm.} \]

\[1^{13}C\text{NMR (100 MHz, CDCl}_3\text{)} \delta: -1.76, 13.95, 15.83, 26.10, 26.46, 89.70, 93.50 \text{ ppm.} \]

**MS (EI 70 eV) m/z 140 (M^+), 115 (M^+-CCH), 57 (M^+-Si(CH}_3)_2CCH). \]

(Dimethyl-octyl)silyl-acetylene (28)

Into a flame dried flask 20.3 mL of 0.5 M (10.13 mmol) ethynyl Grignard in THF was added. Butylchlorodimethylsilane (2 mL, 8.44 mmol) was added neat at room temperature and stirred 5 days. The product was extracted with hexane, dried, and concentrated. No purification was necessary. The silyl-acetylene was a colorless oil and yielded 1.58 g (95%) 28. 

\[1^1H\text{NMR (400 MHz, CDCl}_3\text{)} \delta: 0.15 (s, 6H), 0.87 (t, \text{J} = 2.8 \text{ Hz}, 3H), 1.25 (m, 6H), 8.81 (s, 1H) \text{ ppm.} \]

\[1^{13}C\text{NMR (100 MHz, CDCl}_3\text{)} \delta: -1.76, 13.95, 15.83, 26.10, 26.46, 89.70, 93.50 \text{ ppm.} \]

**MS (EI 70 eV) m/z 196 (M^+), 170 (M^+-CCH), 111 (M^+-Si(CH}_3)_2CCH). \]

((4-Chloro-butyl)-dimethyl)silyl-acetylene (29)

Into a flame dried flask 38.88 mL of 0.5 M (19.44 mmol) ethynyl Grignard in THF was added. (4-chloro-butyl)dimethylchlorosilane (2.5 mL, 16.32 mmol) was added neat at room temperature and stirred 5 days. The product was extracted with hexane, dried, and concentrated. No purification was necessary. The silyl-acetylene was a colorless oil and yielded 2.84 g (99%) 29. 

\[1^1H\text{NMR (400 MHz, CDCl}_3\text{)} \delta: 0.16 (s, 6H), 1.25m, J = 7.6 \text{ Hz}, 2H), 1.52 (dp, \text{J} =8.4, 6.8 \text{ Hz}, 6H), 1.81 (p, \text{J} = 7.6Hz, 2H), 2.35 (s, 1H) 3.52 (t, \text{J} = 6.8, 2H) \text{ ppm.} \]

\[1^{13}C\text{NMR (100 MHz, CDCl}_3\text{)} \delta: -1.84, 15.43, 21.27, 35.99, 44.72, 89.13 , 93.97 \text{ ppm.} \]

**MS (EI 70 eV) m/z 174 (M^+), 139 (M^+-Cl), 125 (M^+-CH}_2Cl), 111 (M^+-C}_2H_4Cl), 97 (M^+-C}_3H_6Cl). \]

(Dimethyl-thexyl)silyl-acetylene (30)
Into a flame dried flask 24.5 mL of 0.5 M (12.20 mmol) ethynyl Grignard in THF was added. Dimethylthexylchlorosilane (2 mL, 10.17 mmol) was added neat at room temperature and stirred 5 days. The product was extracted with hexane, dried, and concentrated. No purification was necessary. The silyl-acetylene was a colorless oil and yielded 1.7 g (99%) 30. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 0.12 (s, 6H), 0.92 (s, 6H), 1.25 (m, \(J = 8.4\) Hz, 6H), 1.72 (p, \(J = 6.8\) Hz, 1H), 2.35 (s, 1H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): -1.27, 11.64, 18.81, 20.19, 25.53, 90.02, 94.03 ppm. MS (EI 70 eV) \(m/z\) 168 (M\(^+\)), 153 (M\(^+\) - CH\(_3\)), 125 (M\(^+\) - CH(CH\(_3\))\(_2\)), 83 (M\(^+\) - C(CH\(_3\))CH(CH\(_3\))).

(Dimethyl-3,3,3-trifluoropropyl)silylacetylene (31)

Into a flame dried flask 24.5 mL of 0.5 M (12.20 mmol) ethynyl Grignard in THF was added. (Dimethyl-3,3,3-trifluoropropyl)chlorosilane (2 mL, 10.17 mmol) was added neat at room temperature and stirred 5 days. The product was extracted with hexane, dried, and concentrated. No purification was necessary. The silyl-acetylene was a colorless oil and yielded 1.7 g (99%) 31. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 0.17 (s, 6H), 1.22 (t, \(J = 4.8\) Hz, 2H), 1.80 (t, \(J = 3.6, 2\)H), 2.35 (s, 1H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): -2.25, 7.97, 28.45, 68.09, 95.01, 129.51 ppm. MS (EI 70 eV) \(m/z\) 171 (M\(^+\)), 151 (M\(^+\) - F), 133 (M\(^+\) - 2F), 105 (M\(^+\) - CF\(_3\)).

(Dimethyl-n-propyl)silylacetylene (32)

Into a flame dried flask 24.5 mL of 0.5 M (12.20 mmol) ethynyl Grignard in THF was added. (Dimethyl-n-propyl)chlorosilane (2 mL, 10.17 mmol) was added neat at room temperature and stirred 5 days. The product was extracted with hexane, dried, and concentrated. No purification was necessary. The silyl-acetylene was a colorless oil and yielded 1.7 g (99%) 32. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 0.15 (s, 6H), 0.96 (t, \(J = 4.8\) Hz, 2H), 1.80 (t, \(J = 3.6, 2\)H), 2.35 (s, 1H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): -1.70, 17.45, 18.34, 18.65, 89.67, 93.54 ppm. MS (EI 70 eV) \(m/z\) 127 (M\(^+\)), 83 (M\(^+\) - C\(_3\)H\(_7\)), 203 (M\(^+\) - C\(_3\)H\(_5\)O\(_2\)).

(Isobutyl-dimethyl)silylacetylene (33)

Into a flame dried flask 24.5 mL of 0.5 M (12.20 mmol) ethynyl Grignard in THF was added. (Isobutyl-dimethyl)chlorosilane (2 mL, 10.17 mmol) was added neat at room temperature and stirred 5 days. The product was extracted with hexane, dried, and concentrated. No purification was necessary. The silyl-acetylene was a colorless oil and yielded 1.7 g (99%) 33. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 0.17 (s, 6H), 0.64 (d, \(J = 7.2\) Hz, 6H), 1.43 (d, \(J = 1.2\) Hz, 2H), 1.85 (m, \(J = 6.6\) Hz, 1H), 2.36 (s, 1H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): -0.76, 25.20, 26.25, 26.6390.16, 93.66 ppm. MS (EI 70 eV) \(m/z\) 133 (M\(^+\)), 119 (M\(^+\) - CH\(_3\)), 73 (M\(^+\) - CH\(_2\)CH(CH\(_3\))\(_2\)), 203 (M\(^+\) - C\(_3\)H\(_5\)O\(_2\)).

(Dimethyl-phenyl)silylacetylene (34)
Into a flame dried flask 24.5 mL of 0.5 M (12.20 mmol) ethynyl Grignard in THF was added. (Dimethyl-phenyl)chlorosilane (2 mL, 10.17 mmol) was added neat at room temperature and stirred 5 days. The product was extracted with hexane, dried, and concentrated. No purification was necessary. The silyl-acetylene was a colorless oil and yielded 1.7 g (99%) 34. ¹H NMR (400 MHz, CDCl₃) δ: 0.49 (s, 6H), 2.53 (s, 1H), 7.42 (dd, J = 2.4, 3.2 Hz, 2H), 7.67 (dd, J = 1.2, 3.2 Hz, 2H), 7.69 (d, J = 2.4 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ: -0.92, 88.32, 95.01, 128.18, 129.82, 133.88, 136.44 ppm. MS (EI 70 eV) m/z 160 (M⁺), 145 (M⁺-CH₃), 129 (M⁺-2CH₃).

(Dimethyl-isopropyl)silylacetylene (35)

Into a flame dried flask 24.5 mL of 0.5 M (12.20 mmol) ethynyl Grignard in THF was added. (Dimethyl-isopropyl)chlorosilane (2 mL, 10.17 mmol) was added neat at room temperature and stirred 5 days. The product was extracted with hexane, dried, and concentrated. No purification was necessary. The silyl-acetylene was a colorless oil and yielded 1.7 g (99%) 35. ¹H NMR (400 MHz, CDCl₃) δ: 0.12 (s, 6H), 1.00 (d, 6H), 1.25 (m, 1H), 2.33 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ: -3.80, 13.88, 17.07, 88.76, 93.78 ppm. MS (EI 70 eV) m/z 133 (M⁺), 117 (M⁺-CH₃), 103 (M⁺-2(CH₃)), 87 (M⁺-C₃H₇).

(Cyclohexyl-dimethyl)silylacetylene (36)

Into a flame dried flask 24.5 mL of 0.5 M (12.20 mmol) ethynyl Grignard in THF was added. (Cyclohexyl-dimethyl)chlorosilane (2 mL, 10.17 mmol) was added neat at room temperature and stirred 5 days. The product was extracted with hexane, dried, and concentrated. No purification was necessary. The silyl-acetylene was a colorless oil and yielded 1.7 g (99%) 36. ¹H NMR (400 MHz, CDCl₃) δ: 0.10 (s, 6H), 1.22 (m, 2H), 1.25 (m, 2H), 1.72 (m, 2H), 2.53 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ: -3.80, 25.60, 27.12, 27.27, 28.06, 89.00, 93.78 ppm. MS (EI 70 eV) m/z 133 (M⁺), 117 (M⁺-CH₃), 103 (M⁺-2(CH₃)), 87 (M⁺-C₃H₇).

(3,3-Dimethylbutyl-dimethyl)silylacetylene (37)

Into a flame dried flask 24.5 mL of 0.5 M (12.20 mmol) ethynyl Grignard in THF was added. (3,3-Dimethylbutyl-dimethyl)chlorosilane (2 mL, 10.17 mmol) was added neat at room temperature and stirred 5 days. The product was extracted with hexane, dried, and concentrated. No purification was necessary. The silyl-acetylene was a colorless oil and yielded 1.7 g (99%) 37. ¹H NMR (400 MHz, CDCl₃) δ: 0.15 (s, 6H), 0.85 (s, 6H), 0.87 (t, J = 5.2 Hz, 6H), 1.25 (m, 2H), 2.35 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ: -1.95, 10.39, 29.01, 31.85, 37.73, 89.63, 93.55 ppm. MS (EI 70 eV) m/z 166 (M⁺), 151 (M⁺-CH₃), 138 (M⁺-2(CH₃)), 83 (M⁺-Si(CH₃)₂CCH).

(2,5-Dibromo-4-hydroxymethyl-furan-3-yl)-methanol (40)
5.0 g (26.9 mmol) 3,4-furan-diethyl-carboxylate was dissolved into 50 mL acetonitrile (CH₃CN) to a one-necked round bottom flask with a stir bar. Bromine (4.5 mL, 87.6 mmol) was slowly added directly to the dissolved furan. After 1 day, 6% Fe catalyst (0.09 g, 1.61 mmol) was added to the reaction mixture. The reaction mixture was monitored with TLC and left under constant stirring overnight. After stirring for two days, the reaction mixture was quenched with Na₂S₂O₃ and extracted with diethyl ether. Crude product was purified by flash chromatography with dichloromethane/hexane (1:1), and followed by flash chromatography with ether to give 39 as a brownish colored liquid.

A one-necked round bottom flask was flame dried with a stir bar and introduced to a N₂ environment. 9.0g (24.3 mmol) of 39 was dissolved into 49 mL dichloromethane and cooled to 0°C. At 0°C, diisobutylaluminum hydride (103 mL, 103.0 mmol) was slowly added directly to the stirred chilled furan. The reaction mixture was left under constant stirring overnight and monitored with TLC. At 0°C, H₂O (4 mL) was slowly added, followed by slow addition of 15% NaOH (4 mL) and a final addition of H₂O (10 mL). The mixture stirred for a minimum of 15 minutes. Crude product was isolated as filtrant by vacuum filtration. Salts remaining in Buchner funnel were boiled (5x) for 15 minutes in ethyl acetate. Boiled salts were filtered by vacuum filtration and filtrant organic layers were combined, dried and concentrated to give 3.25 g (50%) of 40 as a dark brown liquid. ¹H NMR (400 MHz, CDCl₃) δ: 3.22 (s, 2H), 4.48 (s, 4H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ: 55.97, 121.70, 125.74 ppm. MS (EI 70 eV) m/z 286 (M⁺), 268 (M⁺-OH), 187 (M⁺-Br(OH)).

2, 5-dibromo- 3, 4-furan-dicarbaldehyde (41)

To 100 mL of dichloromethane, 6.03 g (28.0 mmol) pyridinium chlorochromate (PCC), 6.03 g celite, and 6.03 g molecular sieves were added to a round bottom flask and stirred for 1 minute. Compound 40 (2.5 g, 8.75 mmol) dissolved in 50 mL dichloromethane was added at room temperature to the PCC solution. After stirring at room temperature for 2 days, the product was poured directly through silica gel and concentrated to give 0.79 g (31 %) 41. ¹H NMR (400 MHz, CDCl₃) δ: 10.15 (s, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ: 124.16, 133.25, 183.96 ppm. MS (EI 70 eV) m/z 282 (M⁺), 253 (M⁺-CHO), 224 (M⁺-2(CHO)), 145 (M⁺-Br(2(CHO))), 66 (M⁺-2Br(2CHO)).

2, 3, 4, 5-tetrabromoselenophene (43)

10.0 g (0.0763 mol) selenophene was dissolved in 100 mL of chloroform and cooled to 0°C. After cooling the thiophene to 0 °C in an ice bath, bromine (33.0 mL, 0.642 mmol) was slowly added directly to the dissolved thiophene and stirred at 0°C for 1 hour. Following that initial hour, the reaction mixture was warmed to 35°C and stirred overnight. The next day, Na₂S₂O₃ was added to quench any unreacted bromine and stirred at room temperature for 30 minutes. Crude product was isolated by vacuum
filtration, extracted with chloroform and dichloromethane respectively. The organic layer
was dried, concentrated, and recrystallized with hexane to give 27.71 g (80%) of 43 as a
light yellow solid. $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 117.17, 110.51 ppm. MS (EI 70 eV)
m/z 477 (M$^+$), 367 (M$^+$-Br), 288 (M$^+$-2Br), 208 (M$^+$-3Br), 129(M$^+$-4Br).

3, 4-dibromoselenophene (44)
The entirety of 43 (10.0 g, 0.0223 mol) was dissolved in 30 mL of HOAc:H$_2$O solution
(0.472 mol:0.197 mol) in a round bottom flask equipped with a stir bar. The reaction
mixture was cooled to 0 °C in an ice bath and the mixture was let stir for 30 minutes.
After 30 minutes of stirring, activated zinc (17.0 g, 0.260 mol) was slowly added to the
tetrabromoselenophene mixture, and the mixture was allowed to stir at room temperature
for 2 days, followed by 3 hours at 60 °C. The solution was allowed to cool to room
temperature and the product was extracted with hexanes (3x), and the organic layer was
then washed (extracted) with saturated NaOH to remove any remaining HOAc. The final
organic layer was dried with MgSO$_4$, and concentrated to give the colorless viscous oil.
Vacuum distillation gave the pure dibromo-product as a slight yellow oil (5.19 g, 80 %) 44
$^1$H NMR (400 MHz, CDCl$_3$) δ: 7.28 (s, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) δ:
114.16, 127.65 ppm. MS (EI 70 eV) m/z 290 (M$^+$), 209 (M$^+$-Br), 130 (M$^+$-2Br).

Selenophene-3,4-dicarbonitrile (45)
3,4-Dibromoselenophene 44 (5.0 g, 0.0661 mol) dissolved in 51 mL of DMF in a flame
dried round bottom flask equipped with a stir bar and introduced to N$_2$ gas environment.
Following 20 minutes of degassing, copper (I) cyanide was added at room temperature,
equipped with a reflux condenser and refluxed at 153 °C for 3 days. The reaction mixture
was monitored by TLC in (1:1) Hexane: DCM and cooled to room temperature. While in
an ice bath, a solution of FeCl$_3$ in HCl (8 M) was slowly added to the reaction mixture
with the reflux condenser still connected. The mixture was allowed to stir for 30 minutes
at room temperature, followed by pouring the contents of the round bottom into water.
The organic layer was extracted with DCM (2-3x) and then, later, extracted with 5% 
NaCl. Following the extractions, the organic layer was dried and concentrated. The
 crude product was filtered by vacuum filtration and the filtrate was further purified by
elution through a silica gel-filled plug with DCM to give a white fluffy crystals (0.83 g,
25%) 45. $^1$H NMR (400 MHz, CDCl$_3$) δ: 8.80 (s, 2H) ppm. $^{13}$C NMR (100 MHz,
CDCl$_3$) δ: 113.32, 115.06, 114.25 ppm. MS (EI 70 eV) m/z 182 (M$^+$), 157 (M$^+$-CN), 130
(M$^+$-2(CN)).

3,4-selenophene-diethyl-carboxylate (47)
0.80 g (4.39 mmol) of selenophene-3,4-dicarbonitrile (45) was dissolved in EtOH in 250
mL round bottom flask and set to reflux at 80 °C. Potassium hydroxide (KOH) (1.43 g)
was added down the condenser and allowed to reflux overnight. The reaction was
monitored by TLC in 1:1 hexanes:dichloromethane. The next day, the reaction mixture was cooled to room temperature and was slowly acidified by the addition of conc. HCl. Following acidification, the reaction mixture was washed with water and extracted with ethyl acetate (2-3x). The organic layers were combined, dried with MgSO4 and concentrated to give 0.7 g of a brown solid 46.

The entirety of 46 (0.70 g, 3.18 mmol) was dissolved in 56 mL of EtOH in a round bottom flask equipped with a stir bar and followed with the slow addition of H2SO4 (3.00 mL). The reaction mixture was refluxed at 95°C overnight and monitored by TLC (dichloromethane). After stirring overnight, the mixture was allowed to cool to room temperature and the product was washed with 25 mL of water. The organic layer was extracted with large amounts of DCM (2-3x). The organic layers were combined, dried with MgSO4, and concentrated to give the light, yellow, viscous oil (0.83 g, 94 %) 47.

1HNMR (400 MHz, CDCl3) δ: 1.26 (t, J = 7.2 Hz, 6 H), 4.24 (q, J = 7.2 Hz, 4H), 8.46 (s, 2H) ppm. 13CNMR (100 MHz, CDCl3) δ: 14.13, 61.29, 135.99, 137.41, 164.03 ppm.

Diethyl-2, 5-dibromoseolenophene-3, 4-dicarboxylate (48)

0.83 g (3.005 mmol) 3,4-seleophene-diethyl-carboxylate (47) was dissolved into 12 mL of a 50:50 (v/v) mixture of chloroform-acetic acid in a one-necked round bottom flask with a stir bar. N-bromosuccinimide (NBS) (1.61 g, 9.02 mmol) was slowly added directly to the dissolved seleophene and refluxed overnight (24 hrs). The reaction mixture was monitored with TLC and left under constant stirring overnight. The reaction mixture was quenched with Na2S2O3 and extracted with chloroform, dried with MgSO4 and concentrated. Crude product was purified by flash chromatography with dichloromethane to give 0.96 g (73%) as a brownish colored liquid 48. 1HNMR (400 MHz, CDCl3) δ: 1.30 (t, J = 6.8 Hz, 6H), 4.29 (q, J = 7.2 Hz, 4H) ppm. 13CNMR (100 MHz, CDCl3) δ: 14.16, 62.10, 120.10, 136.40, 162.39 ppm. MS (EI 70 eV) m/z 434 (M⁺), 389 (M⁺-C2H5O), 361 (M⁺- C3H5O2).

(2,5-Dibromo-4-hydroxymethyl-selelophene-3-yl)-methanol (49)

A one-necked round bottom flask was flame dried with a stir bar and introduced to a N2 environment. 1.65g (3.80 mmol) of 48 was dissolved into 7 mL dichloromethane and cooled to 0°C. At, 0°C, diisobutylaluminum hydride (16 mL, 15.97 mmol) was slowly added directly to the stirred chilled selendephene. The reaction mixture was left under constant stirring overnight and monitored with TLC. At 0°C, H2O (X mL) was slowly added, followed by slow addition of 15% NaOH (X mL) and a final addition of H2O (X mL). The mixture stirred for a minimum of 15 minutes. Crude product was isolated as filtrant by vacuum filtration. Salts remaining in Buchner funnel were boiled (5x) for 15 minutes in ethyl acetate. Boiled salts were filtered by vacuum filtration and filtrant
organic layers were combined, dried and concentrated to give 0.4 g (49%) of 49 as a dark brown liquid. $^1$H NMR (400 MHz, CDCl$_3$) δ: 2.97 (s, 2H), 4.63 (s, 4H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 59.67, 115.46, 141.99 ppm. MS (EI 70 eV) m/z 276 (M$^+$), 231 (M$^+$-C$_2$H$_5$O), 203 (M$^+$- C$_3$H$_5$O$_2$).

2, 5-dibromo-3, 4-selenophene-dicarbaldehyde (50)

To 20 mL of dichloromethane, 0.83 g (3.85 mmol) pyridinium chlorochromate (PCC), 0.83 g celite, and 0.83 g molecular sieves were added to a round bottom flask and stirred for 1 minute. Compound 49 (0.4 g, 1.15 mmol) dissolved in 20 mL dichloromethane was added at room temperature to the PCC solution. After stirring at room temperature for 2 days, the product was poured directly through silica gel and concentrated to yield 0.3 g (75 %) 50. $^1$H NMR (400 MHz, CDCl$_3$) δ: 10.06 (s, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 128.97, 139.65, 185.58 ppm. MS (EI 70 eV) m/z 344 (M$^+$), 317 (M$^+$-CHO), 289 (M$^+$- (2CHO)), 209 (M$^+$-2(CHO)Br), 130 (M$^+$- (2(CHO))(2Br)).

Crystal Data for compound 10. C$_{66}$H$_{88}$O$_2$S$_2$Si$_4$, M = 1041.80, triclinic, a = 8.420(2), b = 11.3710(3), c = 16.9050(5) Å, α = 107.56º, β = 96.76º, γ = 93.82º, V = 1523.46 Å$^3$, T = 90.0(2) K, space group P-1, Z =1, 30999 reflections measured, 6939 unique (Rint = 0.0550), R1[I > 2σ(I)] = 0.0483.

Crystal Data for compound 16. C$_{66}$H$_{96}$O$_2$S$_2$Si$_4$, M = 1097.91, monoclinic, a = 14.2146(2), b = 10.2389(2), c = 23.0871(4) Å, α = 90.00º, β = 101.48º, γ = 90.00º, V = 3292.89 Å$^3$, T = 150.0(2) K, space group P-1, Z =2, 67969 reflections measured, 5778 unique (Rint = 0.0690), R1[I > 2σ(I)] = 0.0684.

Crystal Data for compound 17. C$_{50}$H$_{64}$O$_2$S$_2$Si$_4$, M = 873.49, triclinic, a = 6.1201(2), b = 11.81195(4), c = 17.1089(6) Å, α = 88.39º, β = 81.55º, γ = 87.54º, V = 1294.99 Å$^3$, T = 90.0(2) K, space group P-1, Z =1, 17197 reflections measured, 4404 unique (Rint = 0.0421), R1[I > 2σ(I)] = 0.0324.

Crystal Data for compound 19. C$_{50}$H$_{60}$Cl$_4$O$_2$S$_2$Si$_4$, M = 1011.26, triclinic, a = 6.0213(2), b = 12.1842(4), c = 17.8658(6) Å, α = 84.87º, β = 80.65º, γ = 77.16º, V = 1171.15 Å$^3$, T = 90.0(2) K, space group P-1, Z =1, 15610 reflections measured, 4447 unique (Rint = 0.0441), R1[I > 2σ(I)] = 0.0567.

Crystal Data for compound 20. C$_{46}$H$_{44}$F$_{12}$O$_2$S$_2$Si$_4$, M = 1033.29, triclinic, a = 8.6674(5), b = 9.5783(6), c = 15.7457(10) Å, α = 104.07º, β = 96.81º, γ = 99.27º, V = 1234.24 Å$^3$, T = 90.0(2) K, space group P-1, Z =1, 15557 reflections measured, 4273 unique (Rint = 0.0813), R1[I > 2σ(I)] = 0.071.

Crystal Data for compound 21. C$_{46}$H$_{56}$O$_2$S$_2$Si$_4$, M = 817.39, triclinic, a = 7.5416 (3), b = 12.0038(6), c = 13.4681(6) Å, α = 84.87º, β = 80.64º, γ = 77.16º, V = 1171.15 Å$^3$, T =
90.0(2) K, space group P-1, Z =1, 13424 reflections measured, 3974 unique (Rint = 0.0428), R1[I > 2σ(I)] = 0.0620.

Crystal Data for compound 22. C_{50}H_{64}O_{2}S_{2}Si_{4}, M = 873.49, triclinic, a = 9.7582 (2), b = 16.6561(4), c = 16.6586(4) Å, α = 105.79º, β = 96.77º, γ = 102.66º, V = 2496.14 Å³, T = 90.0(2) K, space group P-1, Z =2, 35187 reflections measured, 8945 unique (Rint = 0.0419), R1[I > 2σ(I)] = 0.0424.

Crystal Data for compound 23. C_{58}H_{48}O_{2}S_{2}Si_{4}, M = 953.44, monoclinic, a = 21.6023 (6), b = 7.7833(2), c = 31.0510(8) Å, α = 90.00º, β = 100.98º, γ = 90.00º, V = 5125.1 Å³, T = 90.0(2) K, space group C 2/c, Z =4, 29864 reflections measured, 4612 unique (Rint = 0.0479), R1[I > 2σ(I)] = 0.0498.

Crystal Data for compound 25. C_{58}H_{72}O_{2}S_{2}Si_{4}, M = 977.64, triclinic, a = 8.1222(2), b = 12.3914(2), c = 14.2653(3) Å, α = 76.71º, β = 81.20º, γ = 76.88º, V = 1353.14 Å³, T = 90.0(2) K, space group P-1, Z =1, 19429 reflections measured, 4864 unique (Rint = 0.0455), R1[I > 2σ(I)] = 0.0339.

Crystal Data for compound 26. C_{58}H_{80}O_{2}S_{2}Si_{4}, M = 985.70, triclinic, a = 5.6824(5), b = 13.5668(11), c = 18.8181(15) Å, α = 89.19º, β = 89.13º, γ = 81.33º, V = 1433.9 Å³, T = 90.0(2) K, space group P-1, Z =1, 13628 reflections measured, 4964 unique (Rint = 0.0757), R1[I > 2σ(I)] = 0.0801.

Chapter 4: Results and Discussion

4.1. Heterocyclic Dicarbaldehyde

The synthesis of thiophene dicarbaldehyde proved far easier than the corresponding selenophene and furan analogs. As seen in Figure 16, the commercial starting material for the furan dicarbaldehyde was already substituted at the 3 and 4 positions, because bromination of furan proved quite difficult – the furan ring was exposed to bromine in both NEAT and protic environments and did not result in the tetrabromofuran. The choice of the diethyl 3, 4-furan dicarboxylate aided in direct electrophilic aromatic substitution at the 2 and 5 positions (Fig. 17). The ester substituents could then be converted into the dialdehyde functional groups. Unlike the other heterocyclic systems, the furan ring prefers to form the β-isomer (Fig. 19), rather than addition onto the aromatic framework (α-isomer).\(^{86}\)

Furan rings are known to undergo electrophilic aromatic substitution, like the thiophene and selenophene. However, furans tend to have lower aromatic stabilization energy, which leads the heterocycle to both the α-isomer and β-isomer.\(^{86}\) The β-isomer occurs because the furan system incurs less energy to regain with the loss of the H and lacks the arrangement of the aromatic furan (Fig. 17).
The oxygen heteroatom within the ring system also influences the reactivity of the furan. When comparing thiophene to furan, the specific heteroatom (i.e. oxygen and sulfur) induces a slight difference in the bond with the alpha carbon of the chalcogen (Fig. 20). Due to the bonding radius of the sulfur to the neighboring carbon and the similar electronegativities of the two atoms, the thiophene has the ability to evenly distribute electron density with the ring system. On the other hand, the oxygen and carbon differ in electronegativities, which aids in the oxygen’s partial donation of the electrons and localization of the electrons in the double bonds of the ring system furan. Consequently, the furan tends to have larger ring strain than thiophene.

Selenophene appeared to be similar in reactivity to the thiophene heterocycle. The selenophene ring was exhaustively brominated and selectively converted to 3,4-dibromoselenophene. However, the time necessary for the adequate debromination was much longer in comparison to the thiophene synthesis. The Kumada coupling was attempted with the 3,4-dibromoselenophene but the reaction was unsuccessful and yielded multiple products at a generally small percentage. The 3,4-dibromoselenophene was converted to a 3,4-dicyanoselenophene. The cyanide substitution at the 3 and 4 positions on the selenophene was the lowest yielding reaction. Following the cyanation reaction, the synthetic route to the selenophene dicarbaldehyde provided high yields (Fig. 18).
Selenophene is most effective at releasing the electron pair into the ring, making the electrophilic aromatic substitution quite simple. The energetics of the selenophene and its free d-orbitals stabilized the onium state of the heterocycle, allowing the chemistry to be similar to the thiophene (Fig. 13). Furthermore, the heavy atom effect aids in the stability of the selenophene.

4.2. Substituent Choice/Sterics/Atom Restrictions

The functionalized c-fused ADT quinones were prepared with yields ranging from 3%-50%. The sterics of the solubilizing groups installed by the Sonogashira coupling, along with the number of carbons in the alkyl chains, influenced the packing orientation and interplanar distance of each ADT quinone derivative.

Figure 21. Example ADT quinone crystal image: 1,3,7,9-tetrakis(triisopropylsilyl)ethynyl]-anthra[2,3-c:6,7-c’]dithiophene-5,11-dione (TIPS).

Figure 20 displays the crystal packing of TIPS derivative 10, our first synthesized ADT quinone. The TIPS ADT quinone appeared to have a close-atom-contact of 3.527 Å (Fig. 20). These results were satisfactory, being I aimed to create acceptors with crystal packing similar to the van der Waals distance between 2 carbons atoms (~3.4 Å).

Hydrocarbon anthradithiophene quinones such as decynyl derivative and tert-butylphenylethynyl derivative were synthesized, but I could not isolate or purify the materials. The silylphenylethynyl solubilizing groups appeared to allow easier separation from the remaining acetylene reactant as compared to the hydrocarbon quinones.

While maintaining the trialkylsilyl motif, the TES derivative 11 produced an orange powder at a yield of 35%. Unfortunately, the sterics of the three ethyl groups seem to inhibit efficient intermolecular packing and prevented the formation of crystalline material. I thus next prepared the diisopropyl-n-octysilyl(Oct) derivative (12), which appeared to be an oil. The oil of 12 was due to the inability to separate the excess acetylene from the quinone, and, consequently, prohibited the examination of potential sterics resulting from the three bulky groups connected to the quinone core.
In order to tune the packing distance, the research focus transitioned from using trisubstituted silylacetylenes with the same bulky groups to incorporating silylacetylenes with two methyl attachments and a third, varied substituent. The third group ranged from 3 to 9 carbons and consisted of alkyl and cyclic substituents. The alkyl substituents were also varied by slight branching and halogen substitution.

Tertbutyldimethylsilylacetylene (TBDMS) was the first terminal acetylene chosen with the DMA geometry to produce a orange-reddish powder (13) in 50% yield. The trimethylsilyl (TMS) derivative 14 was then prepared in 4% yield. The low yield of 14 could have been due to the volatility of the acetylene. Unlike the other synthesized quinone derivatives, the Sonogashira coupling for the TMS derivative required a sealed tube. Consequently, the TMS may have slightly vaporized during the initial set up. Furthermore, the low yield of 14 could be a result of issues with work up and transfer from the sealed tube apparatus. 14 was a reddish-orange powder and the lowest yielding structure of the synthesized heteroacene derivatives.

Dimethyloctylsilylethynyl (DMOct) derivative 16 finally yielded a second crystalline material, showing a 1-dimensional packing between molecules (Fig. 36, Fig. 38). The DMOct quinone appeared to have an increased close atom-to-atom distance of 7.56 Å, at least twice the distance of the TIPS quinone. The linear eight carbon, alkyl, chain seemed to limit the pi-pi stacking interactions between the anthradithiophene quinone molecules.

The alkyl chain was further varied to create 8 additional crystalline ADT quinones. Table 1 displays the ADT quinone derivatives and corresponding packing distances. For example, 1,3,7,9-tetrakis(n-butyldimethylsilylethynyl)-anthra[2,3-c:6,7-c’]dithiophene-5,11-dione (17) yielded 58% of a reddish crystalline material with a close atom packing distance of 3.33 Å. The short 4 carbon chain led to a closer intermolecular atom-to-atom distance.

Due to the success with the butyl alkyl chain, the latter derivatives differed by the number of carbons as well as the connectivity within the third substituent attached to the silyl atom. The dimethylthexylsilyl (DMTh) derivative 18 was a reddish, orange powdery material, from which suitable crystals could not be grown.
<table>
<thead>
<tr>
<th>ADT Quinone</th>
<th>Packing Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TIPS</td>
<td>3.53</td>
</tr>
<tr>
<td>DMOct</td>
<td>7.56</td>
</tr>
<tr>
<td>DMBu</td>
<td>3.33</td>
</tr>
<tr>
<td>DMBuCl</td>
<td>3.27</td>
</tr>
<tr>
<td>DMP</td>
<td>3.55</td>
</tr>
<tr>
<td>DMPh</td>
<td>3.46</td>
</tr>
<tr>
<td>DMisoBu</td>
<td>3.50</td>
</tr>
<tr>
<td>DMCyc</td>
<td>3.47</td>
</tr>
<tr>
<td>DMP3F</td>
<td>3.52</td>
</tr>
<tr>
<td>DMBuDM</td>
<td>3.32</td>
</tr>
</tbody>
</table>

Table 1. Packing Distance of the ADT quinones.

As seen with the TBDMS, TES, and DMTh derivatives, bulky, branched alkyl chains inhibit packing and tend to create materials that are powders. Due to the success with the DMBu and DMOct derivatives, the alkyl chain was restricted to having minimal branching and a small carbon count. The four carbon alkyl chain was revisited; however, varied slightly from the DMBu ADT quinone with the addition of a halogen on the terminal carbon of the butyl chain. 4-chlorobutyl-dimethylsilyl (DMBuCl) derivative 19 yielded an orange-reddish crystalline material in 28% yield. Even with the addition of the chlorine atom to the butyl chain, the packing distance of the DMBuCl was slightly smaller in comparison to the other ADT quinones (Table 1).

The latter derivatives explored the possibility of the third substituent with slight branching, varied ring substituents or multiple halogen attachments. isobutyl-dimethylsilyl (DMisoBu) derivative 22 provided satisfactory results with a recrystallized yield of 40% in the form of dark red crystals. The DMisoBu ADT quinone demonstrated strong 1-D packing with a close-atom distance of 3.49 Å. The slight branching did not disrupt the packing, but rather aided in enhancing the pi-pi stacking as seen in Figure 31. The concept of branching was further examined with 3,3-dimethylbutyl-dimethylsilyl (DMBuDM) derivative 26, which showed small packing distance (Table 1), although the molecules were significantly offset from one another, by 2.3-2.4 Å (Fig. 35).

I prepared cyclohexyl-dimethylsilyl (DMCyclohex) 25 and phenyl dimethylsilyl (DMPh) 23 to observe the influence of cyclic substituents on the crystal packing and HOMO/LUMO energy levels. Both derivatives generated positive results and formed red crystalline materials. The DMPh ADT quinone had a packing distance of 3.46 Å with a yield of 17% and the DMCyclohex ADT quinone yielded 15% with an intermolecular distance of 3.47 Å. In comparison, the hybridization of the ring system made some difference with regards to the packing. The DMPh appeared to have more overlap than the DMCyclohex derivative. The cyclohexyl rings may have prohibited the efficient pi-
stacking within the heteroacene core, due to the steric of the rings’ sp$^3$ atoms and lack of pi-overlap in the adjacent phenyl substituents.

Similar to the DMBuCl, the dimethyl-3,3,3-trifluoropropylsilyl (DMP3F) quinone 20 offered insight about halogen substitution and how the presence of halogens could alter the crystal packing. The DMP3F ADT quinone also produced dark, red crystals, but in a small yield, 14% prior to recrystallization and 2% post recrystallization from 1, 2-dichloroethane. DMP3F ADT had a packing distance of 3.52 Å with direct pi-pi overlap of the heteroacene core; however, the overlap was observed only among the outer quinoid rings attached to the dione core (Fig. 42).

As the catalog of functionalized quinones is reviewed, the heteroacene quinones promote more 1-D packing with the incorporation of dimethyl-alkyl-silyl groups. This conclusion has led our research focus to utilize the dimethylalkyl arrangement for future acetylenes. Additionally, the number of carbons in the varied alkyl chain has a likelihood of influencing the functionalized molecule’s crystal packing. A shortened chain promoted more 1-D packing and decreased the intermolecular distance between the molecules. However, steric appears to play a large role in the packing orientation and distance.

4.3. Crystallography

Acenes used as organic semiconductors exhibit typical crystal packing motifs, which orient in a face-to-face arrangement or a face-to-edge herringbone. These ADT quinones tended to assemble in a 1D pi-stacking arrangement. The derivatives with short alkyl chains, as well as the slightly branched chains tended to arrange in a slipped stack arrangement (Table 2). Bulky groups, such as the octyl chain and phenyl substituent promoted a herringbone arrangement with the face-to-edge contact (Table 2). The dimethyl-trifluoropropyl (DMP3F) derivative appeared to pack more compactly in a 1D slipped stack arrangement (Table 2).

<table>
<thead>
<tr>
<th>Acceptor</th>
<th>Stacking</th>
</tr>
</thead>
<tbody>
<tr>
<td>TIPS</td>
<td>1D “slipped stack”</td>
</tr>
<tr>
<td>DMOct</td>
<td>1D “coplanar arrangement”</td>
</tr>
<tr>
<td>DMBu</td>
<td>1D “slipped stack”</td>
</tr>
<tr>
<td>DMBuCl</td>
<td>1D “slipped stack”</td>
</tr>
<tr>
<td>DMP</td>
<td>1D “slipped stack”</td>
</tr>
<tr>
<td>DMPh</td>
<td>1D “face to face”</td>
</tr>
<tr>
<td>DMisoBu</td>
<td>1D “slipped stack”</td>
</tr>
<tr>
<td>DMCyc</td>
<td>1D “slipped stack”</td>
</tr>
<tr>
<td>DMP3F</td>
<td>1D “slipped stack”</td>
</tr>
<tr>
<td>DMBuDM</td>
<td>1D “slipped stack”</td>
</tr>
</tbody>
</table>

Table 2. Crystal packing of the ADT quinone acceptors.
The first synthesized derivative, TIPS ADT quinone, exhibited pi-pi overlap among the large lattice (Fig. 23). The small branching of the three triisopropyl groups provided minimal steric crowding, causing the quinone molecules to pack with the outer quinoid rings in a 1D slipped stack arrangement. The TIPS group on the ADT quinone core appeared to easily fit between the open space of neighboring molecules.
Figure 25. Top View of the DMBu derivative.

The dimethyl-butyl derivative may have a smaller packing distance, but the large butyl chains created steric issues among the molecules. Figure 24 exhibits how the butyl chain and dimethyl substituents align in the same orientation, providing the 1D slipped stack. Figure 25 demonstrates the influence of the DMBu substituents in regards to the lack of pi-overlap among the quinone structures, which is caused by the quinones to shift 1.4-1.6 Å from each molecule.

Figure 26. DMBuCl ADT quinone.
The addition of the chlorine onto the butyl chain appeared to further upset the pi overlap among the ADT quinone molecules (Fig. 27). The sterics of the long chain, including the halogen, inhibited the pi stacking, which would in turn hurt the charge mobility of an organic photovoltaic. Similar to the DMBu derivative, the quinone molecules are shifted 1.92-1.95 Å to the side of the neighboring structures.
The packing of dimethyl-propyl derivative 21 displayed better pi overlap than the previous butyl derivatives. Similar with the butyl chains in the DMBu and DMBuCl, the propyl chain within the DMP ADT quinone aligns in the same direction (Fig. 28). However, the shorter propyl chain allows the molecules to pack together more compactly (Fig. 29).
Similar to the TIPS analog, the dimethyl-isobutyl ADT quinone has adequate pi overlap (Fig. 31). The isobutyl chains appear to align with each other, enabling the structures to adopt a dense packing. The iso-branching, similar to the TIPS derivative, packs the branched, alkyl carbons above the adjacent core and increases the pi-pi overlap of the molecules (Figure 31).

Figure 32. DMCyclohex ADT quinone slip stack.

Figure 33. DMCyclohex ADT quinone top view.

The dimethyl-cyclohexyl derivative appears have some pi stacking interactions. When looking at Figure 32, the slipped stack arrangement seems to be promoted by the slight overlap of the cyclohexyl substituents. The cyclohexyl groups exist as a chair conformer and align in alternate directions in comparison to the other substituents (Fig. 33).
Terminal branching, similar to the substitution of chlorine (Fig. 27), eliminates the pi overlap among the heteroacene core of the 3, 3-dimethylbutyl-dimethyl derivative. Neighboring quinone molecules are offset by 2.3-2.4 Å, as a result of the dimethyl substitution on the third carbon on the butyl chain (Fig. 35).
With larger alkyl chains, the stacking arrangement was modified slightly. The octyl chain caused the molecules to arrange in a coplanar motif. The large alkyl chains prohibit pi-stacking, creating sections of 1-D pi stacks (Fig. 36). When looking at Fig. 38, there was no pi-overlap of the core in the octyl derivative.
When the solubilizing group on the ADT quinone was the dimethyl-phenyl, the derivative had overlap among the molecular structures; however, the overlap was seen within sections (Fig. 40). The quinone structures were arranged in a 1-D pi stack.

Figure 41. DMP3F ADT quinone.
Figure 42. DMP3F ADT quinone top view.

Surprisingly, the three fluorines attached on the terminal carbon of the propyl chain (Fig. 41, Fig. 42) did not disrupt the crystal packing as compared to the branched and ring systems. The derivative was packed in a quite compact arrangement, 1D “slipped stack” (Fig. 41). The shortened alkyl chain aided in creating strong pi-overlap between the quinone molecules (Fig. 42).

4.4. Electrochemistry

Differential pulse voltammetry was performed with a BAS CV-50W voltammetric analyzer at room temperature with a platinum button working electrode, a platinum wire counter electrode and a silver wire pseudo-reference electrode, in nitrogen purged 0.1M Bu₄NPF₆ solution in dichloromethane, using ferrocene/ferrocenium as an internal standard at a scan rate of 20 mVs⁻¹. All values quoted are relative to Fc/Fc⁺ (Table 3).

<table>
<thead>
<tr>
<th>Acceptors</th>
<th>LUMO (eV)</th>
<th>E gap (eV)</th>
<th>HOMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TIPS</td>
<td>-3.39 (+/-0.036 eV)</td>
<td>2.58</td>
<td>-5.97</td>
</tr>
<tr>
<td>DMOct</td>
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<td>-6.01</td>
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<td>DMBu</td>
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<td>-3.49 (+/-0.036 eV)</td>
<td>2.59</td>
<td>-6.08</td>
</tr>
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<td>-6.08</td>
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</tr>
<tr>
<td>DMisoBu</td>
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<td>2.59</td>
<td>-6.04</td>
</tr>
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<td>DMCyc</td>
<td>-3.38 (+/-0.018 eV)</td>
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</tr>
<tr>
<td>DMBuDM</td>
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<td>2.60</td>
<td>-6.02</td>
</tr>
</tbody>
</table>

Table 3. Electrochemical Data of the ADT quinones.

The HOMO/LUMO energies, as shown by Table 3, are influenced by the differences between various substituted silylethynyl groups. When comparing TIPS pentacene to another TIPS analog, 1,3,7,9-tetraakis(trisopropylsilylethynyl)-anthra[2,3-c;6,7-c’]dithiophene-5,11-dione, the HOMO/LUMO energies differ dramatically (Fig.
The TIPS ADT quinone has two additional functionalized positions on the heteroacene core, as compared to the pentacene. Additionally, the fused aromatic core contains two sulfurs and two carbonyls, while the pentacene consists of five fused benzene rings. The deviation in functionalization caused the HOMO and LUMO energies to decrease in comparison to the TIPS pentacene (Fig. 43). Moreover, the energy gap ($E_g$) also increased by 0.77 eV (Fig. 43).

The HOMO and LUMO energies of the synthesized quinones ranged from -5.96 eV to 6.08 eV and -3.38 eV to -3.49 eV, respectively (Fig. 43; Table 3). The HOMO energy level decreased by 0.04 eV, while the LUMO energies were decreased by 0.02 eV when the ADT quinone was functionalized with butyl-dimethyl (DMBu) silylethynyl group, when compared to the TIPS ADT derivative (Fig. 43). The energies butyl chain, attached to the silyl atom, was further explored with the DMBuCl, DMBuDM and DMIsoBu derivatives (Table 3; Fig. 43). In regards to DMBuCl, the addition of the chlorine, at the 4 position of the butyl chain, decreased the HOMO and LUMO energies by ~0.1 eV (Fig. 43). Furthermore, substitution of methyl groups and inclusion of slight branching aided in decreasing both the HOMO and LUMO energies (Fig. 43; Table 3).

The effect of the halogen on the HOMO/LUMO energies was further explored with the DMP and DMP3F derivatives. The DMP3F ADT derivative consisted of three fluorine atoms substituted at the 3 position on the propyl chain and had a slightly similar HOMO energy to the n-propyl derivative (Fig. 42). The presence of the fluorine atoms, however, shifted the LUMO to -3.49 eV (Table 3), with an $E_g$ of 2.66 eV (Fig. 43). In comparison to n-Propyl, the DMP3F had a lower LUMO energy, but the DMP3F had a slightly larger energy gap (Fig. 43).

Cyclic substituents, such as the DMPh and DMCyclohex, were also examined. The DMPh and DMCyc derivatives had a similar energy gaps, deviating by roughly 0.04 eV. The presence of the phenyl substituent yielded a lower LUMO than the DMCyc LUMO energies (Fig. 43). Unlike the DMCyclohex ADT, the increased conjugation allowed better stabilization of resonance through the DMPh ADT derivative.
Figure 43. HOMO-LUMO energy levels calculated from electrochemical data.

The large deviation of the LUMO and HOMO energy levels could be a result of systematic error. The potentiostat was replaced with a new model and possibly interfering with the measurement process of the energy levels of the synthesized ADT quinones. An alternate source of deviation, among the data collected from the electrochemical experiments, could be due to the inability of estimating the HOMO directly from the potentiostat. Theoretically, a molecule should be able to accept and donate electrons. However, the quinone molecules were quite electron deficient, due to the structural components of the two carbonyls and fused aromatic rings.

4.5. UV-vis absorption & Solar Cell device data

UV-vis absorption spectra were obtained using a Shimadzu UV-3101PC UV/vis/Near IR Spectrophotometer. The absorption of TIPS ADT quinone and DMisoBu quinone were recorded up to 600nm. The anthradithiophene quinones, 1,3,7,9-tetrakis(triisopropylsilylethynyl)anthra[2,3-c;6,7-c’]dithiophene-5,11-dione (TIPS) and 1,3,7,9-tetrakis(isobutyl-dimethylsilylethynyl)anthra[2,3-c;6,7-c’]dithiophene-5,11-dione (DMisoBu), appear to absorb into the blue region when compared to TIPS pentacene, with the ADT quinones displaying absorption peaks at 481 nm (Fig. 44) and 479.5 nm (Fig. 45), respectively. UV-vis absorptions were taken for the other seven quinones in order to calculate the molecule’s HOMO energy levels. The optical energy gaps ranged from 2.58 eV to 2.66 eV, with maximum absorption wavelengths of 467 to 481 nm.

The half lives of the TIPS and DMisoBu ADT quinones were observed in dilute toluene solutions as 118.47 hrs and 56.84 hrs, respectively. These ADT quinone analogs appeared to have a longer half life than TIPS pentacene ($t_{1/2} = 4.93$ hrs).
The solar cell performance for the TIPS ADT quinone is found in Table 4. The following devices were made with AI 4083 PEDOT, at 10:10 concentration ratio of P3HT:TIPS ADT quinone in various solvents. The open-circuit voltage ($V_{oc}$), short circuit current ($J_{sc}$), fill factor (FF) and power conversion efficiency (PCE) are reported, together with the solvent used in device fabrication. The $V_{oc}$ values appear to be low, demonstrating that there was poor light absorption and poor alignment between the donor and acceptor orbital levels; even though, the
LUMO level of the TIPS ADT is slightly lower than the LUMO of P3HT (-3.0 eV). The values noted for the FF reveal that the devices may have experienced unbalanced charge transport. Yet, the TIPS ADT quinone FF exhibited an increase of ~10%, when compared to the device fabricated by Deng et al. utilizing DBBQ as the acceptor material. Additionally, a PCE of 32% was achieved when dissolved in toluene: 30% dichloromethane. Upon optimization of the n-type acceptor material and tuning of the crystal packing, a higher PCE could be a possibility for these ADT quinones.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Voc</th>
<th>Jsc</th>
<th>FF</th>
<th>PCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorobenzene</td>
<td>0.82V</td>
<td>0.90mA/cm²</td>
<td>29%</td>
<td>0.22%</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.86V</td>
<td>0.76mA/cm²</td>
<td>30%</td>
<td>0.19%</td>
</tr>
<tr>
<td>Toluene: 30% Dichlorobenzene</td>
<td>0.82V</td>
<td>1.16mA/cm²</td>
<td>33%</td>
<td>0.32%</td>
</tr>
<tr>
<td>PH 500 PEDOT/Toluene:30% Dichlorobenzene</td>
<td>0.64V</td>
<td>1.58mA/cm²</td>
<td>36%</td>
<td>0.37%</td>
</tr>
</tbody>
</table>

Table 4. Solar cell data for TIPS ADT quinone.

Chapter 5: Future Work

The ADT quinones tend to exhibit success with the dimethylalkyl silyl arrangement. The interesting aspect was how the quinone framework demonstrated the strong electron affinity and their potential as electron acceptors. It is necessary to gain a better understanding of what could force the ADT quinone to adopt the sandwich herringbone motif and why the sandwich herringbone packing aids in the efficiency of the BHJ in the solar cell device. Future work could provide insight about determining the specific requirements, such as solubilizing groups, for tuning the ADT quinones’ HOMO and LUMO energy levels. It would also be useful in determining the possible influence of the varied chalcogen on the crystal packing and HOMO LUMO energy levels. Synthesis of anthradifuran and anthradiselenophene quinones could aid in explaining the effect of varying the heteroatoms in the terminal rings of the quinone chromophore.

Chapter 6: Conclusions

Anthradithiophene quinones have demonstrated potential as a new class of acceptors for OPVs. It is possible to tune the crystal packing and HOMO-LUMO energy levels, by interchanging the solubilizing groups around the heteroacene core. However, to increase the pi overlap and promote the formation of crystalline material, the substituent arrangement on the silyl-ethynyl groups needs to be restricted to a dimethyl-alkyl arrangement. The alkyl chains substituted to the silylacetylene of the functionalized ADT quinones require minimal branching while maintaining a short carbon chain.
References

(8) 280w, D. S. P. Solar Module 280w Item#: DM280M2-36.
(10) Dennler, G.; Sariciftci, N. S. P Ieee 2005, 93, 1429.
(22) Gregg, B. A.; Hanna, M. C. J Appl Phys 2003, 93, 3605.
Appendix I. Commonly used Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>Å</td>
<td>Angstroms</td>
</tr>
<tr>
<td>Al</td>
<td>Aluminum</td>
</tr>
<tr>
<td>Ca</td>
<td>Calcium</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>DPV</td>
<td>Differential pulse voltammetry</td>
</tr>
<tr>
<td>EA</td>
<td>Electron affinity</td>
</tr>
<tr>
<td>EQE</td>
<td>External quantum efficiency</td>
</tr>
<tr>
<td>Fc</td>
<td>Ferrocene</td>
</tr>
<tr>
<td>FF</td>
<td>Fill Factor</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>IP</td>
<td>Ionization potential</td>
</tr>
<tr>
<td>IPCE</td>
<td>Incident photon-to-current conversion efficiency</td>
</tr>
<tr>
<td>IQE</td>
<td>Internal Quantum Efficiency</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium Tin Oxide</td>
</tr>
<tr>
<td>Jsc</td>
<td>Short circuit current density</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>PCE</td>
<td>Power conversion efficiency</td>
</tr>
<tr>
<td>Pmax</td>
<td>Maximum power point</td>
</tr>
<tr>
<td>Voc</td>
<td>Open circuit voltage</td>
</tr>
</tbody>
</table>
Vita

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