

Running head: BISBENZOTHIOPHENE (BBT) BASED ORGANIC  
SEMICONDUCTORS

The Synthesis of a Bisbenzothiophene (BBT) Based Organic Semiconductor with  
Increased Function and Increased Solubility

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A Senior Thesis submitted in partial fulfillment  
of the requirements for graduation  
in the Honors Program  
Liberty University  
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## BISBENZOTHIOPHENE (BBT) BASED ORGANIC SEMICONDUCTORS

## Acceptance of Senior Honors Thesis

This Senior Honors Thesis is accepted in partial fulfillment of the requirements for graduation from the Honors Program of Liberty University.

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## BISBENZOTHIOPHENE (BBT) BASED ORGANIC SEMICONDUCTORS

**ABSTRACT**

Organic semiconductors are growing in applications for use in modern technology.<sup>1</sup> The main interest in these molecules can be attributed to their low cost (compared to silicon) and their ability to be used on flexible substrates. There are four features that make a good organic semiconductor. First, the molecule should be conjugated, having alternating single and double bonds (lone electron pairs act similarly to double bonds). Secondly, the molecule should be planar, or flat, in shape. Thirdly, the molecule should have a narrow band gap to increase the overall conductivity. Lastly, the molecule should be soluble to ease application. 3,4:3',4'-Bisbenzothiophene (BBT) **1** is a fairly unexplored molecule that is known to have semiconducting applications. BBT is conjugated and planar, but its band gap is large and it is highly insoluble. The aim of this research was to synthesize a malononitrile substituted BBT molecule in order to increase solubility and decrease the band gap. Theoretical modeling supports that this molecule will be highly conjugated, will be mostly planar, will have a narrow band gap, and will have increased solubility as a result of a high dipole moment.

## INTRODUCTION

**Organic Semiconductor Application and Properties.** Organic semiconductors are growing in application.<sup>1</sup> Although most of them are still being adjusted for use, organic semiconductors promise a more economic substitution for silicon in technology such as solar panels. Organic semiconductors also have the potential to allow the replacement of glass in liquid crystal displays, and have applications as fluorescence indicators and organic dyes.<sup>2,3</sup> The main attraction to these materials is due to their cost efficiency (in comparison to inorganic semiconductors like silicon) and their ability to be used on flexible substrates.<sup>1</sup> Further applications lie in increasing cell proliferation in vitro with thin films.<sup>4</sup> Organic field effect transistors (OFETs) also utilize organic semiconductors, but photooxidation is a problem.<sup>5</sup> Most of the technologies listed are still in experimental development, however, radio frequency identification (RFID) tags used in grocery stores and department stores currently utilize organic semiconductors.<sup>6</sup>

There are four molecular requirements that build a good organic semiconductor:

1. Planarity
2. Conjugation
3. Narrow band gap
4. Solubility.

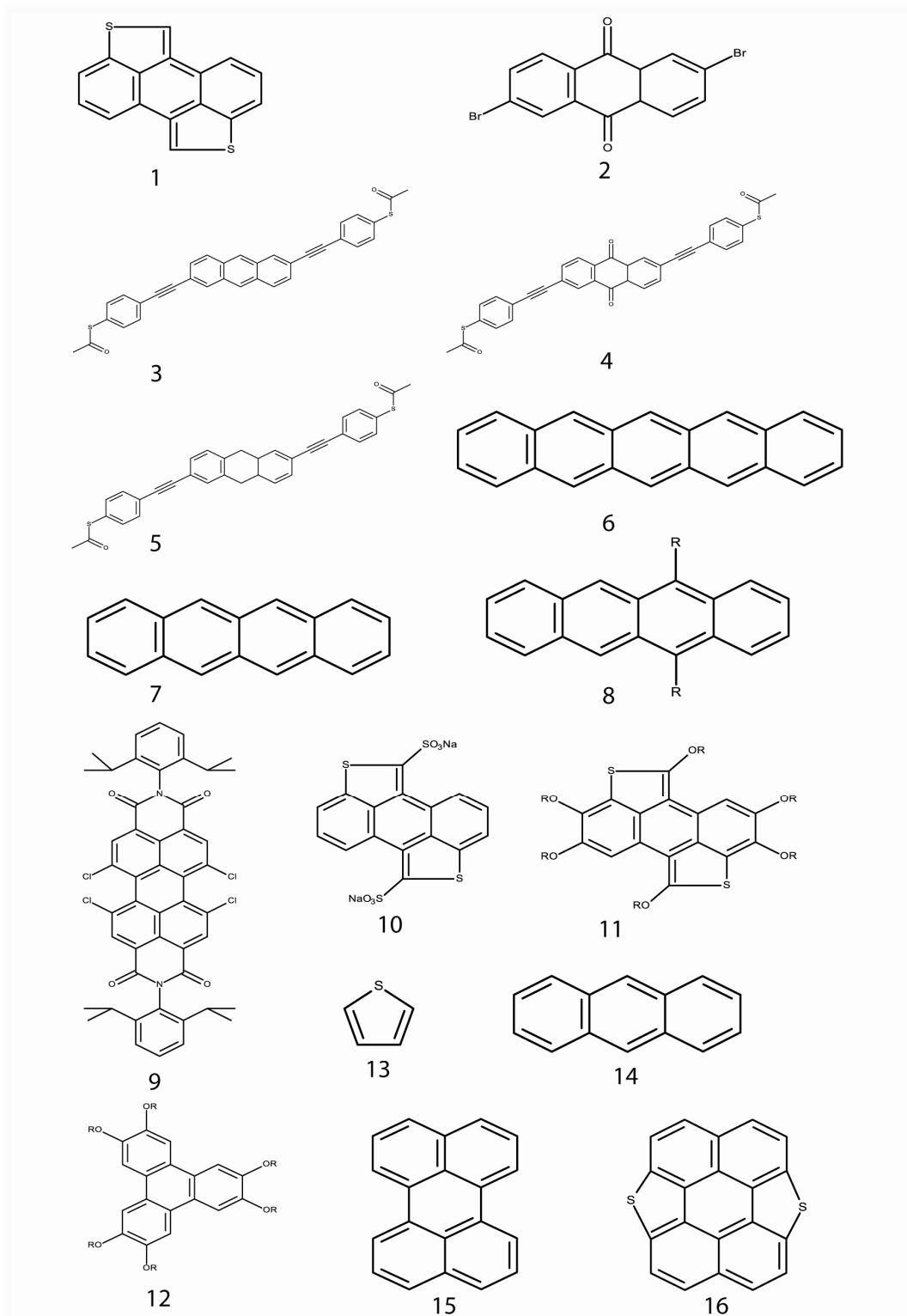
Organic semiconductor molecules should be planar, or flat, in shape.<sup>7</sup> The purpose behind this property is discussed more below. When a molecule contains a double bond, that bond forms a pi bond which has a highest occupied molecular orbital (HOMO) and a lowest unoccupied molecular orbital (LUMO).<sup>8</sup> The organic semiconductor molecule should be conjugated, having a maximum number of alternating single and double bonds,

## BISBENZOTHIOPHENE (BBT) BASED ORGANIC SEMICONDUCTORS

because this allows the electrons to move easily from the HOMO to the LUMO along the molecule generating semiconductivity.<sup>7-9</sup> Lone pairs on atoms also contribute to the conjugation of a molecule similarly to a double bond. If a molecule is not planar, the distance between HOMO and LUMO increases, so the electrons cannot jump from the HOMO to the LUMO as easily, which decreases its conductivity.<sup>9</sup> The band gap is an energy measurement between the HOMO and LUMO. A narrow band gap in organic semiconductor molecules is necessary because it also corresponds to the ease of electron movement. Organic semiconductor molecules need to be soluble because they can then be applied as thin films from a solution rather than through sublimation, which makes application easier.

**Literature Review.** Past research on organic semiconductors covers a wide range of areas including research in improving OFETs, thin film printing, and, especially, achieving a chemical structure that improves a semiconductor's function. The structure is important because it is essential to the conductivity of the molecule.<sup>7</sup> When derivatives of 2,6-dibromoanthracene-9,10-dione **2** (see Figure 1) were synthesized, it was found that larger donor-acceptor pi spacers, like alkenes or alkynes, that interrupt bond conjugation decrease the efficiency of the semiconductor.<sup>9</sup> Molecules with either linear conjugation **3**, cross conjugation **4**, or broken conjugation **5** were evaluated for conductivity in a different study, and it was found that the linearly conjugated molecule had the highest conducting capabilities, followed by the broken conjugation, and then the cross conjugation.<sup>7</sup> From the results of the latter two experiments, it can be concluded that consistent conjugation and linear form are the most efficient structures for organic semiconductors.<sup>7,9</sup>

## BISBENZOTHIOPHENE (BBT) BASED ORGANIC SEMICONDUCTORS



**Figure 1. Structures of various molecules.** These molecules are mentioned in the text. In molecule number 8, the R groups are equal to  $\text{CONHC}_6\text{H}_{13}$ .<sup>5</sup>

## BISBENZOTHIOPHENE (BBT) BASED ORGANIC SEMICONDUCTORS

Semiconductors have also shown better properties when band gaps are narrow.<sup>1</sup> This was achieved in research performed on thin layer printing that aimed to make it high-speed, low in cost, and highly flexible. Thin film transistors act as an on/off switch for individual pixels in active-matrix liquid-crystal displays (LCDs).<sup>2</sup> This type of screen is used in most technology, ranging from cell phones to laptop screens. The current problem with these screens is that the only material compatible with current semiconductors is glass, making this technology extremely fragile and somewhat heavy. The crystalline packing of organic molecules works well for liquid crystal screens. Organic semiconductors are also known for their flexibility, yet they are still lightweight and sturdy. In the near future, thin films could be used with plastic, instead of glass, making the screens flexible and lightweight. The application of organic semiconductors in this area is predicted to be wide ranging once it is perfected. In the experiment, the shelf-life of the semiconductors was also a concern, but it was found that when the molecule had a higher molecular weight (and therefore close pi-pi stacking) the shelf-life of the product increased and the molecule was a better field-effect transistor (FET).<sup>1</sup>

FETs and OFETs are devices used to control one electrical signal with a different signal.<sup>10, 11</sup> OFETs utilize organic semiconductors, but Liang found that when exposed to air and light, the semiconducting properties of compounds like pentacene **6** and tetracene **7** decrease because photooxidation causes instability.<sup>5</sup> Photooxidation occurs when a molecule becomes oxidized, or broken down by the removal of an electron, in the presence of light. The photooxidation observed in the study was attributed to hydrogen bonding with the oxygens available on tetracenediamide **8**. This reactive possibility should be apprehended when designing organic semiconductors.

## BISBENZOTHIOPHENE (BBT) BASED ORGANIC SEMICONDUCTORS

Human neural cells can be grown on organic semiconductors when they are used as thin films.<sup>4</sup> When a pentacene thin film was used, it was found that thicker film (up to fifteen monolayers—the upper limit-- where the proliferation began to decline) as well as longer incubation increased the cell proliferation (in vitro). Thin films are also used for applications with photovoltaic (PV) cells.<sup>12</sup> PV cells are able to convert sunlight into electricity.<sup>13</sup> Inorganic PV cells utilize silicon, but there is potential for organic semiconductors working in organic PV (OPV) cells.<sup>14</sup> This would save cost in solar panels and related technology because thin film manufacturing costs are much lower than the cost of current inorganic methods.<sup>15</sup> PV cells work through sunlight exciting electrons, which creates a current as a result of the electric field, direction, and momentum provided by the light.

**3,4:3',4'-Bisbenzothiophene Properties.** 3,4:3',4'-Bisbenzothiophene (BBT) **1** was first published in research in 1979 by Fred Wudl who synthesized this molecule as well as a few derivatives.<sup>16</sup> It was not investigated again until 2006 and still remains fairly unexplored. There are currently two patents on BBT by Christopher T. Brown (2012) and Jianmin Shi (2008). Both patents claim synthesis of BBT and many derivatives. Both researchers promote that the compound works well as an organic light emitting diode (OLED), as an OFET, and as an OPV.<sup>6,17</sup> Shi also lists that BBT can be used for thin film LCDs, electrophoretic display (similar to LCD), RFID tags, dyes, and sensor devices.<sup>6</sup>

BBT is mainly researched for its applications as an organic semiconductor. Qian researched heteroarenes in search of a high-performing organic semiconductor.<sup>18</sup> The researchers' main focus was to develop NN'-diisopropylphenyl-1,6,7,12-perylene-



## BISBENZOTHIOPHENE (BBT) BASED ORGANIC SEMICONDUCTORS

3,4:9,10-tetracarboxylbisimide (PBI) which features a BBT core in its structure **9**. This molecule was very twisted, so a Stille reaction was performed which created PBI with a BBT base **4** and flattened out the molecule. Crystal analysis of the achieved molecule revealed inversion symmetry and unique hydrogen bonding ribbons.<sup>18</sup>

In this current research, BBT and some of its derivatives have been fluorescent in certain solvents. Luisier worked with 3,4:3',4'-bibenzo-[*b*]thiophene-2,2'-disulfonate **10** when seeking a caffeine indicator because of its sulfur content (which makes it more polarizable) and the  $\pi$ -stacking on its surface.<sup>19</sup> It was found that the presence of caffeine caused a change in fluorescence from purple to yellow-green. Its success as an indicator was attributed to the caffeine interacting with  $\pi$ -stacking. The researchers developed a test strip with the BBT derivative that was able to distinguish between caffeinated and decaffeinated coffee with a color change visible to the naked eye.

García performed a theoretical analysis on electron and hole transport capabilities for several thiophene containing molecules, one of which had a BBT core **11**.<sup>20</sup> The thiophene containing molecules were compared to an alkoxy-triphenylene derivative **12** because this molecule is one normally used for liquid crystal discotic systems. The researchers wanted to test the possibility of using a sulfur containing molecule in discotic systems. Discotic systems rely on  $\pi$  stacking between the molecules which self-align into columns. This allows  $\pi$ - $\pi$  interaction and liquid crystalline formation. The BBT based molecule showed a narrower band gap and increased electron mobility, but the tetra-thiophene molecule exhibited the largest improvement in electron transport. It was concluded that thiophene rings **13** increase the distance between discs. Overall, the use of these molecules for electron transport was not recommended.

## BISBENZOTHIOPHENE (BBT) BASED ORGANIC SEMICONDUCTORS

BBT is a popular starting point for building organic semiconductors. It is both planar and conjugated. However, its calculated band gap was found to be 3.52eV, which is large, and it is insoluble. BBT's semiconducting properties are as follows:

1. Planar
2. Conjugated
3. Large band gap
4. Insoluble.

It possesses some of the qualities of an organic semiconductor, however, it lacks others. BBT is made up of two basic subunit molecules: anthracene and thiophene.

**Anthracene Properties.** Anthracene **14** is often the foundational structure of organic semiconductors because of its conjugation and planarity. It has great pi-pi stacking ability and is shorter than tetracene and pentacene.<sup>21</sup> Anthracene is also the base molecule of BBT. More specifically, BBT is made from an anthraquinone. Possibilities for adding to and modifying anthracene are broad.

**Thiophene Properties.** Thiophene **13** is the other foundational molecule of BBT. BBT contains two thiophene rings on either side of the anthracene. Similarly to anthracene, thiophene molecules perform pi-pi stacking well and are a common piece of successful organic semiconductors.<sup>22</sup> It is also aromatic, which contributes to the pi conjugation of the molecule containing it.

Much research aims to use thiophene alone in semiconductor design. One article, already discussed, used thiophene in a fluorescent indicator of caffeine.<sup>19</sup> Jiang performed research on perylene **15** to look at its derivatives' OFET and crystallinity properties.<sup>23</sup> Specifically, the research focused on synthesizing dithioperylene **16**, which

## BISBENZOTHIOPHENE (BBT) BASED ORGANIC SEMICONDUCTORS

has a BBT core. Dithioperylene exhibited good thermal and chemical stability, and was found to be very compact. The extra sulfur atom introduced in the synthesis allowed for ordered packing and symmetry in the molecule. García experimented with polythiophenes and recognized their pi stacking capabilities in discotic systems.<sup>20</sup>

**Importance of Sulfur Content.** Sulfur is often found in organic semiconductors because it makes molecules more polarizable which contributes to solubility.<sup>19</sup> Within BBT, the lone pair of the sulfur atom is what makes the molecule aromatic and continues the conjugation.

**Importance of Nitrile (CN) Presence.** Nitrile groups are often used in semiconductor structures because they contain a triple bond which forces a planar shape and adds to the conjugation. Nitrile addition also contributes to polarity, and therefore solubility. Opatkiewicz used nitrile groups in place of amines to terminate monolayers.<sup>24</sup> Self-assembling monolayers add to the molecular packing structure of organic semiconductors. It was found that the nitrile containing molecules made higher quality devices (like thin film transistors) and that the molecules were more accurate at self-assembly into monolayers. These properties make nitrile groups a favorable side group for organic semiconductors.

**Fluorescence and dye capabilities.** Fluorescence is useful because it opens up the possibility of organic semiconductors being used as fluorescent tags or probes. Bruchez reported using semiconductor nanocrystals as fluorescent probes on mouse fibroblasts.<sup>3</sup> It was particularly noted that the excitation spectrum, or the range of wavelengths that can excite the electrons, of the fluorescence was very broad which allowed for wide-ranging applications.

## BISBENZOTHIOPHENE (BBT) BASED ORGANIC SEMICONDUCTORS

Organic semiconductors also may be used as a dye. Conjugation as well as nitrogen content benefit dye capabilities. The dyes used with dye-sensitized solar cells are often not organic semiconductors. Semiconductors are needed for the application of these cells, though.<sup>12</sup> Westermarck indicates that usually dyes are absorbed into semiconductors. If a semiconductor were designed that could be used both for the dye and the semiconducting, it would save the need of bridging the two for application.

**The Proposed Research.** BBT possesses two of the four requirements of a semiconducting molecule (see Table 1). It is planar and it is conjugated, however, it has a large band gap and it is quite insoluble. The main goals of this research group have been to increase solubility, narrow the HOMO/LUMO band gap, and investigate fluorescence by modifying the BBT molecule. A peer is currently working on the synthesis of a different BBT derivative. In the current research, malononitrile groups will be added to BBT in hopes of increasing its solubility and semiconducting capabilities **20** (see Scheme 1). The further conjugation will help to narrow the band gap and the malononitrile group, which has an extremely high dipole moment, is expected to increase solubility. Throughout the work of the research group, many intermediate and product molecules have fluoresced at various wavelengths. If the product of this experiment fluoresces, its application as a fluorescence indicator and as a fluorescent dye will be investigated as well.

**Computational Modeling.** Computational modeling is used to theoretically predict properties of molecules. Figure 2 A shows the relative band gap of BBT compared to the estimated HOMO-LUMO band gap for the goal molecule. These values were calculated theoretically using density functional theory (DFT) on a computer.

## BISBENZOTHIOPHENE (BBT) BASED ORGANIC SEMICONDUCTORS

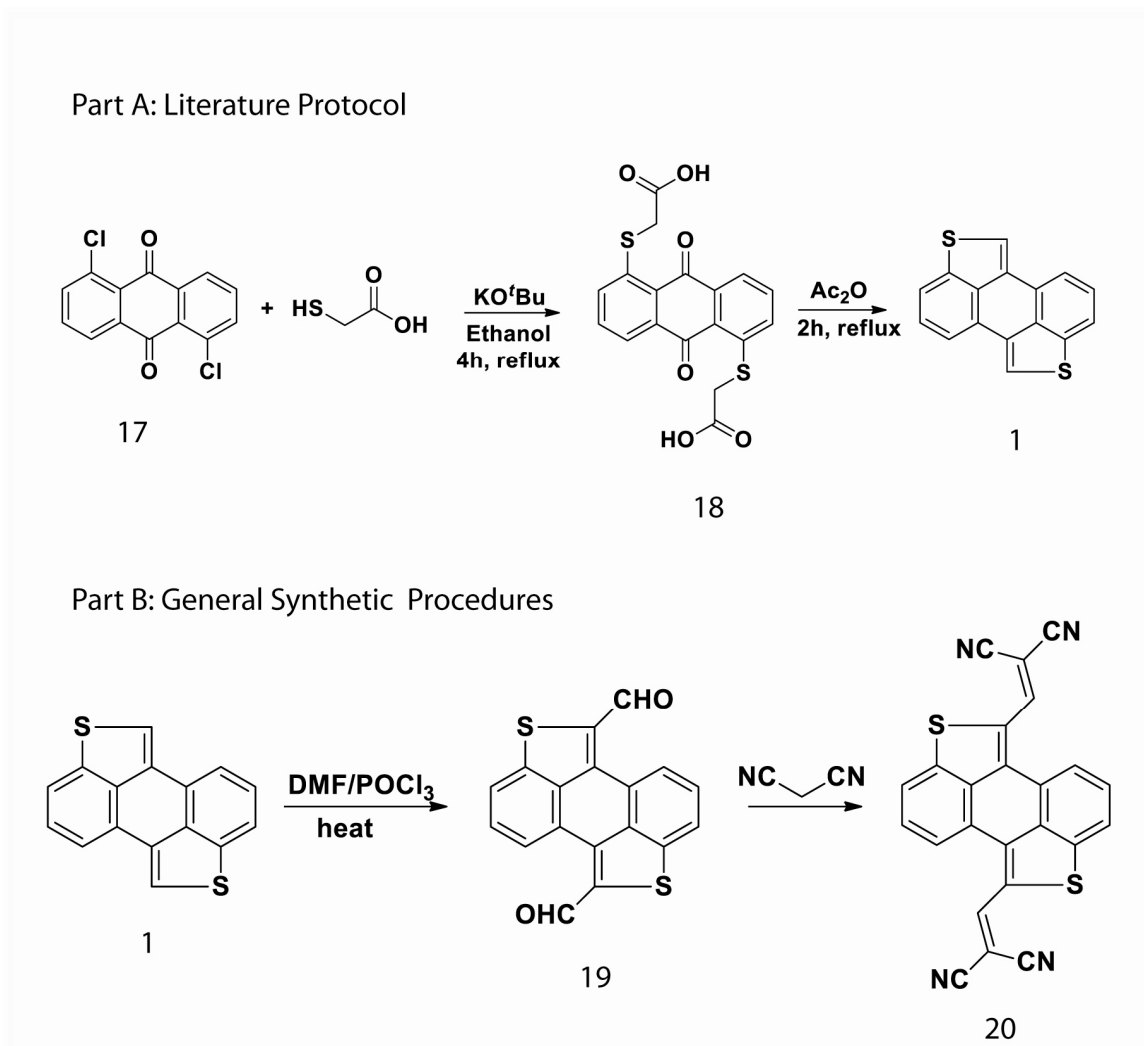
Requirements	BBT	Proposed compound
1. Planar	✓	≈
2. Conjugated	✓	✓
3. Narrow Band Gap	×	✓
4. Soluble	×	✓

**Table 1. Requirements of a good organic semiconductor.** The table displays the four main properties a good organic semiconductor possesses. BBT is planar and conjugated, but it has a large band gap and is insoluble. The proposed compound, 1,5-dimalononitrilebisbenzothiophene, twists slightly out of plane (by  $4.34^\circ$ ), but it still has a narrow band gap, it extends the conjugation (compared to BBT), and it has a greater dipole moment than BBT, supporting that it will be more soluble in water.

Unlike density functional based tight binding (DFTB), DFT can be used to more accurately predict the band gaps of sulfur containing molecules.<sup>25</sup> Adding the malononitrile groups, through increased conjugation, will significantly narrow the band gap from 3.52eV to 2.25eV, according to this model, supporting that this molecule should improve semiconductivity (in comparison to BBT). The gap is also shifted into a more favorable energy level for the electrodes required for function.

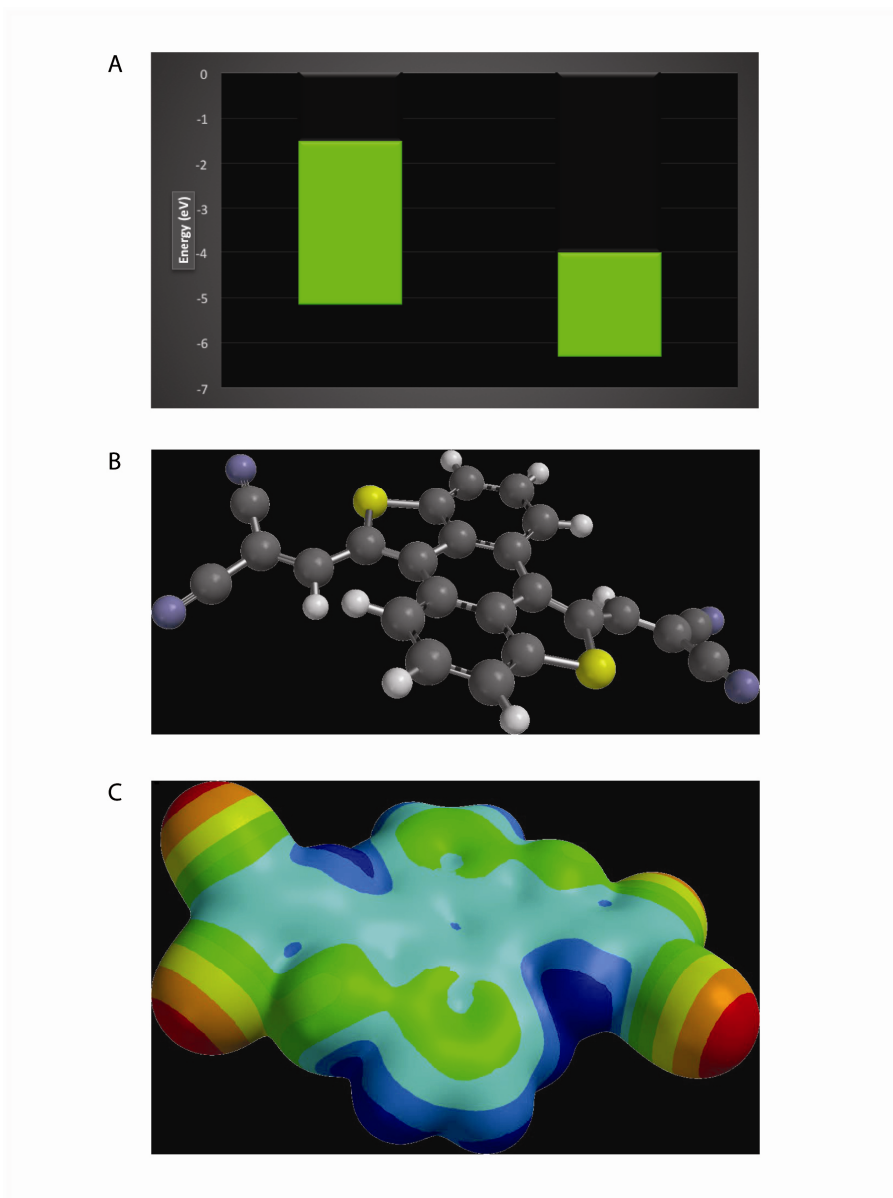
In order to estimate the level of planarity of the desired molecule, the malononitrile substituted BBT molecule was modeled using the computational software SPARTAN 08 (see Figure 2 B). The addition of the malononitrile substituents will likely cause the molecule to turn out of plane by  $4.34^\circ$ . The molecule was designed with two extra carbons in between BBT and the malononitrile in order to attempt to avoid twisting.

## BISBENZOTHIOPHENE (BBT) BASED ORGANIC SEMICONDUCTORS



**Scheme 1.** The synthesis of Bisbenzothiophene (BBT) with malononitrile side groups. Part A of the synthesis is completely reported in literature by Shi.<sup>6</sup> The reaction starts with 1,5-Dichloroanthraquinone and exists as a diacid in the intermediate. This piece of the synthesis will yield BBT. Part B of the synthesis involves two reactions on this molecule that have never been reported in literature. The first step uses the Vilsmeier reaction to substitute BBT with aldehyde groups. The second step utilizes the Knoevenagel condensation to replace the aldehyde groups with malononitrile groups. The two reactions have been reported on thiophene, but not on BBT.

## BISBENZOTHIOPHENE (BBT) BASED ORGANIC SEMICONDUCTORS



**Figure 2.** Computational analysis of 1,5-dimalononitrilebisbenzothiophene using DFT and SPARTAN 08. A) DFT calculations showing the HOMO to LUMO gap difference between BBT (left) and 1,5-dimalononitrilebisbenzothiophene (right). The new molecule is expected to narrow the band gap from 3.52eV to 2.25eV. It also moves the energy into a different range which will be much more conducive to the electrodes used for semiconducting function. B) SPARTAN 08 molecular modeling of 1,5-dimalononitrilebisbenzothiophene. This model reveals that the malononitrile groups will most likely twist slightly out of plane by a total of 4.34°. C) The SPARTAN 08 polarity modeling of the malononitrile substituted BBT. The red areas on the ends of the molecule reveal polarity hot spots which should increase solubility.

## BISBENZOTHIOPHENE (BBT) BASED ORGANIC SEMICONDUCTORS

However, the malononitrile groups are still very large substituents. The twisting is probably a result of the large side groups trying to avoid Van der Waals strain. Van der Waals strain is the repulsion between molecules resulting from large electron clouds. The negative charge of each cloud repulses the other. In this case, the nitrile group (CN) is too close to the thiophene ring to comfortably be planar. It could also be that the molecule has steric hindrance. Similarly, this arises from the molecules being too nearby each other. While the goal molecule is out of plain, it is not an extremely twisted molecule and it could still work well as an organic semiconductor. This is supported by the fact that the band gap did decrease compared to BBT, even though BBT is more planar.

Solubility is also an important aim of the current research because current application requires sublimation which can be time consuming. Sublimation is the direct conversion of a solid to a gas. In order to sublime, there must be heat and very low pressure (vacuum conditions). To collect the sublimed product, the gas is condensed and collected as a solid. BBT and other organic semiconductors would be much easier to utilize if they could simply be dissolved in solvent. The addition of malononitrile groups to BBT is expected to increase solubility because this substituent has a very large dipole moment of 3.57D. SPARTAN 08 was used to model the polarity of the desired molecule (see Figure 2 C). The red areas in this figure correspond to the locations of high polarity in the molecule. Polarity depends on the dipole moments interacting in a molecule. BBT has an overall estimated dipole of zero. Contrarily, the estimated dipole of 1,5-dimalononitrilebisbenzothiophene is 1.36D. This supports the synthesis of the latter molecule for the purpose of increasing solubility.



## BISBENZOTHIOPHENE (BBT) BASED ORGANIC SEMICONDUCTORS

**Proposed Synthesis.** BBT synthesis is defined in literature, but the last two reactions (Scheme 1 B) have not been reported in literature. However, BBT is expected to react similarly to thiophene since they have the same active sites, and the two reactions have been performed on thiophene.

BBT will be synthesized by reacting a 1,5-Dichloroanthraquinone **17** with thioglycolic acid (manganese dioxide, 18-Crown-6, and *tert*-butyl potassium oxide) in ethanol (see Scheme 1 Part A).<sup>6</sup> HCl will then be added to make a diacid intermediate **18** (1,5-dithiocarboxylic acid BBT) to BBT. The intermediate structure features cross conjugation which was discovered to have weaker conductivity than the linear conjugation seen in BBT.<sup>7</sup> BBT will be produced when the diacid is reacted with acetic anhydride. In order to use BBT further, it is presently sublimed from insoluble impurities. This makes application particularly difficult. A Vilsmeier reaction will be performed on the BBT next in order to attach aldehyde groups onto the BBT molecule **19** (see Scheme 1 Part B).<sup>26</sup> DMF and POCl<sub>3</sub> react to form an immonium cation intermediate. Then, the charged DMF undergoes nucleophilic substitution with BBT. The product is obtained upon hydrolysis of the immonium salt. Malononitrile groups will then replace the aldehyde groups on the BBT **20** molecule using a Knoevenagel condensation.<sup>27</sup> This condensation only requires malononitrile and water to react. It works by first forming an enol intermediate which reacts with the aldehyde of the substrate. The product undergoes base-induced elimination. If these goals are met, ease of application and efficiency will be increased. 1,5-dimalononitrilebisbenzothiophene **20** is predicted to possess the following semiconductor properties:

1. Fairly planar

## BISBENZOTHIOPHENE (BBT) BASED ORGANIC SEMICONDUCTORS

2. Extended conjugation
3. Narrow band gap
4. Soluble.

**METHODS**

**Reagents.** The reagents used in this experiment are as follows: 1,5-dichloroanthraquinone (Lot #: A010847201), potassium *tert*-butoxide (Lot #: A0321985), and dimethylformamide (DMF; Lot #: 1134969) from Acros Organics; 200 proof ethanol from Quantum Chemical Corporation; thioglycolic acid (Lot #: MKBH0417V) and phosphorus oxychloride (Lot #: 29797HJ) from Sigma-Aldrich; manganese dioxide (Lot #: 723291) and acetic anhydride (Lot #: 113625) from Fisher; 18-crown-6 (Lot #: 1710TD) from Aldrich; argon gas from Arcet; diethyl ether (Lot #: X37477) from J.T. Baker; thiophene (Lot #: MPYFMHK) from TCI.

**1,5-Dithiocarboxylic Acid Anthraquinone 18.** This procedure was performed in proportional quantities to the research of Shi (see Figure 1 A).<sup>6</sup> 8.31g (30.0mmol) of 1,5-dichloroanthraquinone **17** were added to a 500mL round bottom flask (RBF). Then, 50mL of 200 proof ethanol were added and stirred. After that, 5mL (72.0mmol) of thioglycolic acid were added with 25mL more of ethanol. Then, 448mg (5.00mmol) of manganese dioxide were added followed by 11.0mg of 18-Crown-6. Next, 18.1g (161mmol) of potassium *tert*-butoxide were added with 120mL of ethanol.

A reflux apparatus was set up and a balloon filled with Argon gas was used to close the system. The reaction was then allowed to run for 4.5 hours in a 73°C water bath. During this reaction, the mixture changed from light yellow to a dark orange-brown

## BISBENZOTHIOPHENE (BBT) BASED ORGANIC SEMICONDUCTORS

color. The mixture was allowed to cool, then 650mL of water were added to the product and the mixture was vacuum filtered.

60.0mL (159mmol) of 2M HCl were added to the filtered solution. The mixture turned from dark orange-brown to bright yellow-orange as the HCl was stirred into it. It was filtered and washed with water until the pH reached pH 5. The solid was then washed with ice cold ethanol (95%) and allowed to dry for 24 hours. The dry product was collected and weighed (6.12g; 52.6% yield).

**3,4:3',4'-Bisbenzothiophene (BBT) 1.** 5.82g (16.0mmol) of the solid diacid product **18** were mixed with 200mL of acetic anhydride, which made the mixture a deep orange, and refluxed for 2 hours. The product was black, but its solution fluoresced bright green-yellow at 365nm (see Figure 3). The mixture was cooled, then filtered to collect the solid products (1.00g). The filtrate was then distilled until half of the initial liquid had been distilled off. The remaining liquid was then filtered again and the black, solid product was collected (1.60g). This was allowed to settle in a refrigerator and black, solid product was collected again as previously described (1.40g). The liquid product fluoresced yellow at 365nm and, when in acetone, fluoresced purple at 254nm. The total amount of solids collected was 3.00g (63.3% yield). This process was repeated to attain more BBT.

The products were sublimed to prepare for the next reaction. This was first attempted using an Erlenmeyer flask over a heating plate and attaching it to a vacuum, but the heat was too uncontrolled and the product melted. In order to encourage the BBT to rise and condense during sublimation, a new apparatus was set up that incorporated a minute pathway of air on the opposite end of the vacuum attachment site. This method

## BISBENZOTHIOPHENE (BBT) BASED ORGANIC SEMICONDUCTORS

worked better than the first, but still did not ease the collection process. A legitimate sublimation apparatus was utilized for the next attempt, but the vacuum was not strong enough, so the method using a pathway of air was utilized for all future attempts.

**1,5-Diformylbisbenzothiophene 19.** A Vilsmeier reaction was performed in order to attach two aldehyde groups to BBT.<sup>28</sup> 125mg (0.0500mmol) of sublimed BBT were first combined with 1.00mL of DMF (11.0mmol) and 100 $\mu$ L (1.00mmol) of phosphorus oxychloride at room temperature for one week (see Figure 2 B).<sup>26a</sup> The mixture changed in color from orange-brown to slightly green. Some of the mixture was aliquoted into 2mL of water and the pH was brought up to 6 using 1M NaOH. The aliquot was then filtered, solids were collected, and a small amount was dissolved in acetone. Thin layer chromatography (TLC) with dichloromethane was used to determine the presence of product (see Figure 4). The remaining BBT mixture was heated at 100°C for 3 hours, then the aliquot procedure was repeated. Infrared spectroscopy (IR) was performed on the second sample, but it revealed no difference between BBT and the product collected (see Figure 5 A).

In an attempt to force the reaction, 100 $\mu$ L more of phosphorus oxychloride were then added to the left over BBT mixture. The mixture heated up by itself with this addition, but the aliquot procedure was repeated and TLC showed no new results. The remaining solids from the three aliquots were combined. The remainder of the BBT mixture was mixed with water, brought to pH 6, and filtered.

**2-Formylthiophene.** In order to further evaluate the reaction conditions of the synthesis of 1,5-diformylbisbenzothiophene, the Vilsmeier reaction was performed on

## BISBENZOTHIOPHENE (BBT) BASED ORGANIC SEMICONDUCTORS

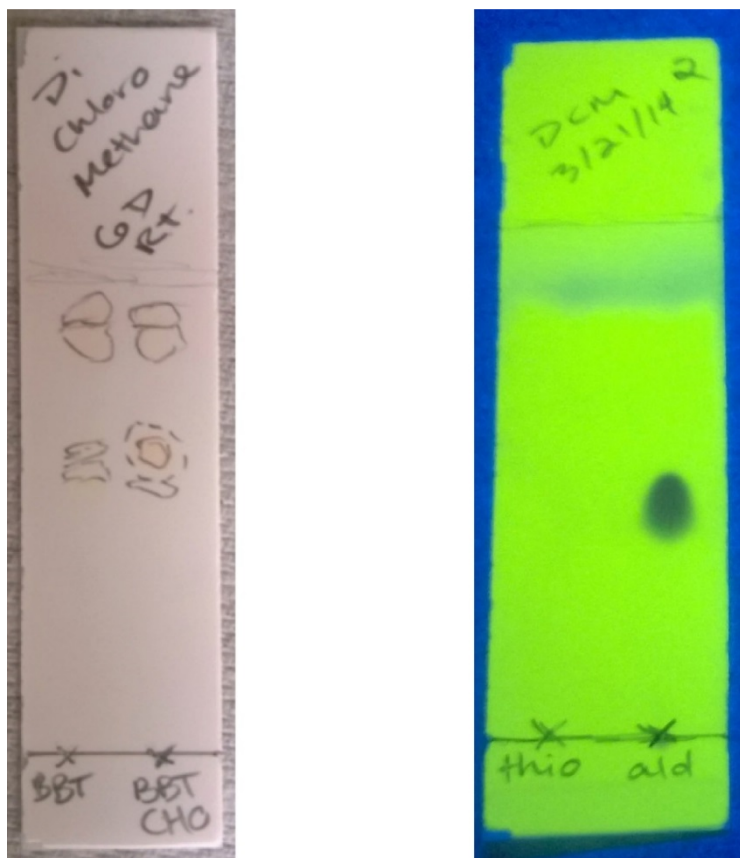


**Figure 3.** The observed fluorescence in the synthesis of Bisbenzothiophene (BBT). The image on the left displays BBT dissolved in acetone. This was apparent at 365nm (a long wavelength). The right picture exhibits the fluorescence of BBT that arose after the addition of acetic anhydride. This was captured at 254nm (a short wavelength). Fluorescence demonstrates the ability of the molecule to absorb and reemit light. These fluorescent molecules have applications in biological fluorescent probes and tags.<sup>3</sup>

thiophene as reported in literature.<sup>29</sup> 3.86mL (50.0mmol) of thiophene were mixed with 4.80mL (150mmolmol) DMF and 16.0mL 1,2-dichloroethane (a solvent) in an ice bath.

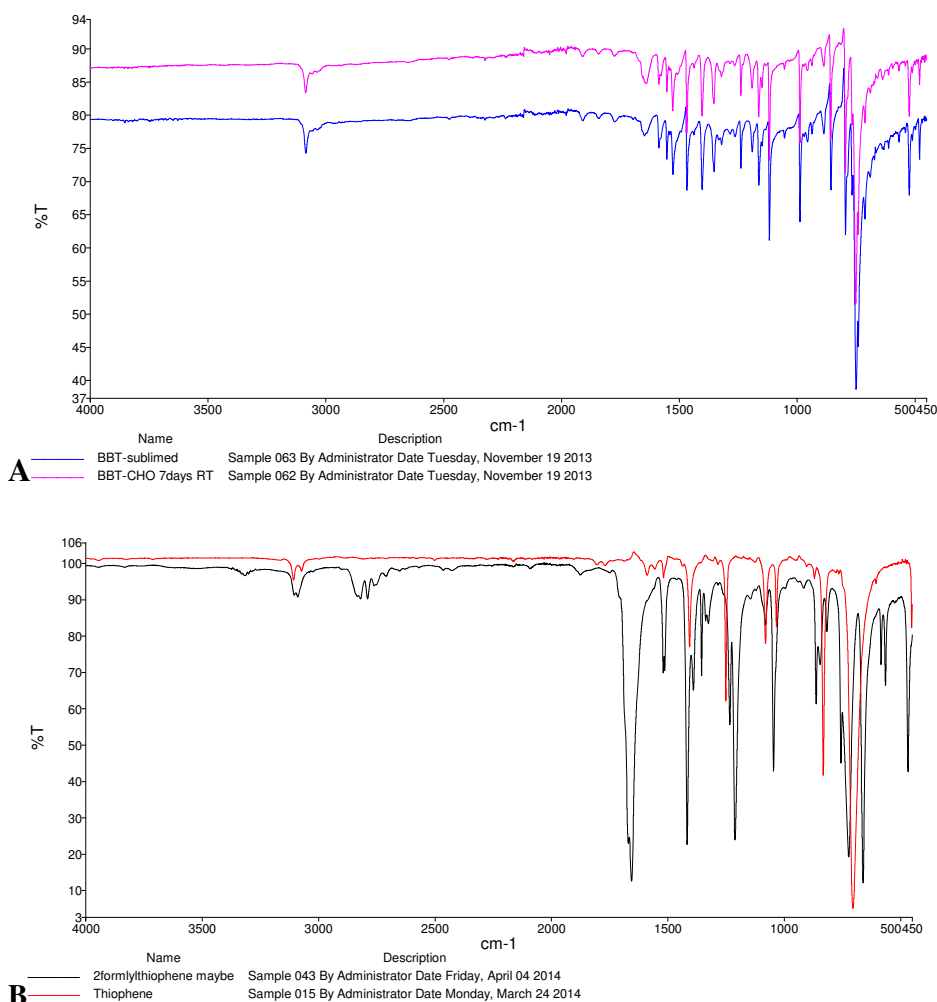
The mixture was allowed to chill, then 5.80mL (60.0mmol) of phosphorus oxychloride were added. The ice was removed and the mixture became cloudy. After it had reached room temperature, it was placed in a hot water bath and refluxed for 2 hours. The mixture turned yellow about 10 minutes after heat was added, then turned a

## BISBENZOTHIOPHENE (BBT) BASED ORGANIC SEMICONDUCTORS



**Figure 4.** The Thin Layer Chromatography (TLC) data of the Vilsmeier reactions. TLC is a method used to separate components of a substance or to compare two substances to find identity. In this case, TLC was used to verify that the Vilsmeier reaction produced a new product.<sup>30</sup> The left image shows the TLC data for bisbenzothiophene (“BBT”) and the attempted Vilsmeier reaction to make 1,5-diformylbisbenzothiophene (“BBT CHO”) in dichloromethane. The TLC is in regular lighting and the results have been outlined using ultraviolet (UV) light. There is an apparent difference between BBT and the attempted Vilsmeier product in the lower outlined spots. The Vilsmeier product revealed a small pink spot that was not existent in the BBT analysis. This supports that there is a difference between BBT and the Vilsmeier product. However, the infrared spectroscopy (IR) data reveals no difference between the two molecules. The right image shows the TLC data for thiophene (“thio”) and 2-formylthiophene (“ald”) in dichloromethane. The TLC is under UV light (365nm) and there is an apparent difference (the dark spot) between thiophene and 2-formylthiophene. This difference was seen in IR analysis as well.

## BISBENZOTHIOPHENE (BBT) BASED ORGANIC SEMICONDUCTORS



**Figure 5.** Infrared spectroscopy (IR) data for Vilsmeier reaction results. IR is utilized to determine molecular identity by using infrared light.<sup>31</sup> The peaks on the graph indicate where certain functional groups of a molecule are absorbed by the infrared light. The Y-axis is the percentage of transmission, and the X-axis is the frequency. After IR has been completed, values are compared with known data for functional groups to determine the identity of the molecule. A) The IR data for Bisbenzothiophene (BBT) (blue) and the attempted 1,5-diformylbisbenzothiophene (pink). Because the two lines are identical, it is supported that the Vilsmeier reaction did not synthesize a new product. B) The IR data for thiophene (red) and 2-formylthiophene (black). This spectrum supports that 2-formylthiophene was successfully synthesized. The thiophene and 2-formylthiophene have very different spectrums and 2-formylthiophene contains a strong peak at  $1656\text{cm}^{-1}$  which is lower than the absorbance normally associated with conjugated aldehydes, but is expected to result from the high conjugation and aromaticity of thiophene.

## BISBENZOTHIOPHENE (BBT) BASED ORGANIC SEMICONDUCTORS

red/brown color after 10 more minutes. After the reflux had run for an hour, the mixture was completely black. It appeared green as it was poured onto ice. 40.0g of sodium acetate dissolved in 70.0mL of water and 4.00g of pure sodium acetate were added to the mixture to neutralize it. 30.0mL of diethyl ether were used to extract the aqueous phase from the organic phase three times. The combined organic phases were washed with 20.0mL of saturated sodium bicarbonate two times, then washed with water. The mixture was dried over magnesium sulfate. TLC with dichloromethane was used to distinguish between thiophene and 2-formylthiophene (see Figure 4). Then the magnesium sulfate was filtered off and the mixture was distilled. The product was collected at 157°C and was deep yellow in color. IR was run on the product to confirm the outcome of the reaction (see Figure 5 B).

## RESULTS AND DISCUSSION

**Fluorescence.** During the experiment, BBT (before being sublimed) fluoresced when dissolved in acetic anhydride and when dissolved in acetone (see Figure 3). A neon yellow-green color was observed in the acetic anhydride. However, when in acetone, the BBT fluoresced purple. The final products will also be monitored for fluorescence and their potential use as a fluorescent probe or indicator will be considered.

**BBT Synthesis and Analysis.** The BBT synthesis was completely reported in literature. It was successfully repeated in this research as a precursor for new chemistry. IR analysis was performed and was consistent with the known spectrum of BBT (see Figure 5 A).



**1,5-Diformylbisbenzothiophene Synthesis and Analysis.** The Vilsmeier reaction was conducted in order to achieve the aldehyde precursor for placing malononitrile groups onto BBT.<sup>26</sup> The first attempt showed a slight variation from BBT in TLC analysis (see Figure 4), however, upon inspection with IR, it was found that the reaction did not alter BBT (see Figure 5 A). The TLC (in dichloromethane) revealed a spot for the Vilsmeier product that was not present for BBT. IR of the Vilsmeier product was run against BBT and the same peaks were present on the spectrum.

It is unclear as to why the Vilsmeier reaction was unsuccessful. It is possible that the chemicals used were too old and unreactive, but when extra reagents were added, the mixture heated up indicating some sort of reaction. There was also a color change present in the first attempt of the reaction, supporting the presence of a reaction. It could be that only a very small portion of the reagent was converted to product. TLC is a more sensitive procedure than IR, so a very small yield of product could account for the different conclusions drawn from the TLC and the IR. The protocol claimed a high yield, though, and the reaction was done in small aliquots with excess reagents making this unlikely.

**2-Formylthiophene Synthesis and Analysis.** The synthesis of 2-formylthiophene was performed in order to test the method reported in literature before trying to synthesize 1,5-diformylbisbenzothiophene again.<sup>29</sup> The Vilsmeier reaction used here was a little different than the one originally performed to make the BBT derivative. TLC analysis revealed a difference in thiophene and the product, 2-formylthiophene (see Figure 4). The Vilsmeier product contained a spot on the TLC plate that was not present in the TLC of thiophene. IR analysis also revealed a difference between the two. Figure 5

## BISBENZOTHIOPHENE (BBT) BASED ORGANIC SEMICONDUCTORS

B shows the IR spectrum of thiophene and 2-formylthiophene. The product, 2-formylthiophene, is represented by the black line and has a peak at  $1656\text{cm}^{-1}$ . The absorbance associated with conjugated aldehydes is  $1710\text{-}1685\text{cm}^{-1}$ .<sup>32</sup> However, thiophene is highly conjugated and aromatic which could lower the absorbance further. This supports that the synthesis of 2-formylthiophene was successful and this method will be performed on BBT to synthesize 1,5-diformylbisbenzothiophene in the future.

## CONCLUSIONS

**Main Goals.** There were four main goals of this experiment:

1. Synthesize BBT
2. Synthesize 1,5-diformylbisbenzothiophene
3. Synthesize 1,5-dimalononitrilebisbenzothiophene
4. Measure spectroscopic properties.

**This Current Research.** The first goal of this current research has been completed. BBT was synthesized and verified according to what is known by the research group. The second goal of the current research has been attempted and is underway. It is the first step that has not been reported in literature and is new chemistry. The first effort for the synthesis of 1,5-diformylbisbenzothiophene was unsuccessful. However, a slightly different Vilsmeier reaction method utilizing 1,2-dichloroethane and multiple wash steps was performed successfully on thiophene, so this will be attempted on BBT in the future. The third goal will be attempted by first performing the Knoevenagel condensation on a simpler molecule (thiophene). The reaction will then be performed on 1,5-

## BISBENZOTHIOPHENE (BBT) BASED ORGANIC SEMICONDUCTORS

diformylbisbenzothiophene to achieve 1,5-dimalononitrilebisbenzothiophene. At that point, the spectroscopic data (goal 4) will be attainable.

**Future Research Focus.** Based on the theoretical data for 1,5-dimalononitrilebisbenzothiophene, this molecule will be a good starting point for future research. Modifying BBT with groups similar, but smaller than, the malononitrile side chain may be beneficial to the band gap. Smaller side groups could make the molecule more planar and therefore narrow the band gap further. The target molecule could also be extended to explore further solubility. However, any additions would probably twist the molecule further out of plane. It would be interesting to study the molecular packing of 1,5-dimalononitrilebisbenzothiophene, as well. The procedure outlined in this research could also be performed on a monothiophene derivative of BBT to relate to the current research. The molecule would be asymmetrical and could provide an interesting comparison. Once 1,5-dimalononitrilebisbenzothiophene is developed and characterized, its spectroscopic properties will be known and further research will be planned.

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