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vi. Introduction

Inorganic semiconductor materials such as silicon have been traditionally used in the advancing electronics industry for items such as memory cards, CPUs, etc. Recent progress in organic semiconductor material processing has increased attention to a potentially less expensive and more beneficial option that could produce things like flexible "smart" cards and paper. Interest has also arisen in hybrid organic/inorganic semiconductor materials for use in solar energy conversion and sensors.

Molecular orientation and ordered packing are very important for determining the overall efficiency of organic semiconductor films. Control over the molecular order at interfaces, especially, is critical for good electrical behavior. Several commonly used organic semiconductor materials contain naphthalene and perylene conjugated core molecules that have been randomly deposited onto a substrate in a device preparation step. These films can suffer from discontinuities and interface problems due to a lack of control over the molecular ordering in the films. Covalent bonding to an ordered substrate may be used to alleviate this problem.

Perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) and naphthalene-1,4,5,8-tetracarboxylic dianhydride (NTCDA) (Figure 1) are both commercially available.
available and can be relatively easily converted into diimides (PTCDI or NTCDI) via condensation reactions (Figure 2) with readily available primary amines. In order to provide a spot on the imide side-chain arm for linking to a silicon surface, an additional organic functional group must be present at the opposite end of the amine chain (the "R" group).

Functional groups of interest for potential linking reactions to silicon, silicon oxide, or metal surfaces or nanoparticles include alkene groups (from precursor amines such as allyl amine), amine groups (from precursors such as p-phenylene diamine and ethylene diamine), thiols (cysteamine and 4-aminothiophenol), alcohols (4-aminophenol and aminopropanol), and carboxylic acids (5-aminovaleric acid and p-aminobenzoic acid). These differing terminal groups allow for variation of the linking chemistry during attachment of the NTCDI or PTCDI to the surface.

Imide synthesis products can be characterized by infrared (IR) spectroscopy (to probe characteristic molecular vibrations), ultraviolet/visible (uv-vis) spectroscopy (to probe molecular electronic structure), nuclear magnetic resonance (NMR) spectroscopy (to probe chemical connectivity along the molecular backbone), and by X-ray diffraction (to probe molecular geometries in products that form crystals), in cases where single crystals could be obtained.

After characterization, product imides will be reacted with hydrogen terminated single crystal silicon surfaces (the Si(111)-(1x1):H surface) that are prepared by etching
in a buffer solution. The imide reactions will be initiated by ultraviolet irradiation in solution, and the surfaces will be characterized by surface IR vibrational spectroscopy. In addition to providing evidence of molecular attachment to the surface, the IR spectroscopy can provide molecular orientation information. Lastly, the films will be examined using electrochemistry to probe the relative ease of electron transfer through the modified surfaces, as compared to the hydrogen terminated surfaces.

vii. Methods

Symmetric NTCDI molecules were synthesized using two methods:

1. Toluene Reflux
a. NTCDA (0.2g) was mixed with selected amines (see table 1) in a 1:20 molar ratio in 50 mL toluene. The mixture was then refluxed for 3 hours at 110°C. The products were separated by vacuum filtration and washed with 100 mL 1% KOH, 50 mL acetone, and 50 mL diethyl ether.

Table 1. Functional Side Chains attached symmetrically via toluene reflux

<table>
<thead>
<tr>
<th>Molecule Number</th>
<th>Functional Side Chain</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ethylene diamine (H₂NCH₂CH₂NH₂)</td>
</tr>
<tr>
<td>5</td>
<td>Cysteamine (HSCH₂CH₂NH₂)</td>
</tr>
<tr>
<td>11</td>
<td>3-amino-1-propanol (HO(CH₂)₃NH₂)</td>
</tr>
</tbody>
</table>

2. Directed Microwave Synthesis

a. Selected amines (see table 2) were reacted in a 4:1 molar ratio with 0.746 millimoles of NTCDA (0.2g). The reaction took place in 8 mL dimethylformamide (DMF), with 0.2 mL of triethylamine added, in a dedicated microwave synthesizer (CEM Discover) at 300 Watts, 140°C, 150 Psi for 5 minutes.

Table 2. Functional Side Chains attached symmetrically via directed microwave synthesis
Asymmetric NTCDI molecules were synthesized using the following two methods:

1. Directed Microwave Synthesis
   a. The first selected amine (see table 3) was reacted in a 1:1 molar ratio with 0.746 millimoles of NTCDA (0.2g). The reaction took place in 8 mL DMF, with 0.1mL of triethylamine added, in a dedicated microwave system at 300 Watts, 135°C, 150 Psi for 5 minutes. The second selected amine was then added to this unpurified mixture in a 1:1 molar ratio with the previously added NTCDA, with an additional 0.1mL of triethylamine added, sonicated for 30 minutes, and ultimately microwaved under the above conditions.
   b. The overall product was then taken up in 100 mL acetonitrile, and added to 75 mL 1 N hydrochloric acid. This was allowed to coagulate for 1-4 days. Vacuum filtration was applied, and the product dried overnight.

2. Simultaneous microwave synthesis for 5-aminovaleric acid and ethylene diamine
a. 0.746 millimoles of NTCDA were added to 10mL of DMF with 0.1mL of triethylamine. 0.746 millimoles of aminovaleric acid were added to the mixture, which was then sonicated for 5 minutes. 0.1mL of triethylamine and 0.746 millimoles of ethylene diamine were added to the resulting dark brown solution, and ultimately microwaved for 45 minutes at the above conditions. 

b. The black product was then taken up into 20mL of acetonitrile and added to 75mL of 1 N hydrochloric acid. The product was allowed to coagulate for 4 days, vacuum filtered, and dried overnight.

Table 3. Functional side chains attached asymmetrically via directed microwave synthesis

<table>
<thead>
<tr>
<th>Molecule Number</th>
<th>1st Functional Side Chain Attached</th>
<th>2nd Functional Side Chain Attached</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>4-aminothiophenol (HSC₆H₄NH₂)</td>
<td>Propylamine (CH₃CH₂CH₂NH₂)</td>
</tr>
<tr>
<td>7</td>
<td>Propylamine (CH₃CH₂CH₂NH₂)</td>
<td>4-aminothiophenol (HSC₆H₄NH₂)</td>
</tr>
<tr>
<td>8</td>
<td>4-aminothiophenol (HSC₆H₄NH₂)</td>
<td>Allylamine (H₂C=CHCH₂NH₂)</td>
</tr>
<tr>
<td>9</td>
<td>Propylamine (CH₃CH₂CH₂NH₂)</td>
<td>Cysteamine (HSCH₂CH₂NH₂)</td>
</tr>
<tr>
<td>10</td>
<td>5-aminovaleric acid (H₂N(CH₂)₄CO₂H)</td>
<td>Ethylene diamine (H₂NCH₂CH₂NH₂)</td>
</tr>
</tbody>
</table>

Simultaneous addition:
5-aminovaleric acid (H₂N(CH₂)₄CO₂H) with ethylene diamine
3. Analysis:

   a. Varian 400 MHz Automated NMR: Number of scans: 512, relaxation delay: 1, spin: 20 Hz, auto lock and auto shimming.

   b. Shimadzu UV-VIS Spectrophotometer: (Model: UV-2550 (PC)), Scan speed: very slow, wavelength range: 200-800nm, sampling interval: 0.5 nm, path length: 1.0cm, slit width: 5nm.

   c. Thermo Nicolet Nexus 670 FT-IR: Attenuated total reflectance (ATR), Number of scans: 512, resolution: 1cm, window material: Ge, Air background.

vii. Results

Symmetric Molecule Synthesis Results (a):

Molecule 1 (symmetric, ethylene diamine side chains) was synthesized via the microwave method outlined above and was analyzed using $^1$H-NMR (Figure 3), UV/VIS (Figure 4), and IR (Figure 5) spectroscopies. The $^1$H-NMR in deuterated chloroform has three characteristic peaks occurring at chemical shifts of 8.77ppm (singlet, 4 hydrogens), 4.31ppm (triplet, 5.03 hydrogens), and 3.11ppm (triplet, 5.11 hydrogens), each corresponding to the three types of hydrogens (bonded to carbon) on the ethylene diamine product (see figure 3). The UV/VIS spectrum of 1 in chloroform has the three distinctive peaks (377nm, 357nm and 340nm) characteristic of naphthalene diimides (see
The IR spectrum confirms the presence of a primary amine side chain with a characteristic peak at 3415 cm\(^{-1}\), aromatic CH stretches at 3080 cm\(^{-1}\), the methylene side chains at 2950 cm\(^{-1}\) and 2875 cm\(^{-1}\), and the “imide” like CO stretches at 1700 cm\(^{-1}\) and 1660 cm\(^{-1}\).

**Figure 3.** This proton NMR shows the product of NTCDA and ethylene diamine through microwave synthesis in deuterated chloroform.
Figure 4. This spectrum reflects the UV-VIS for the microwave Ethylene Diamine and NTCDA product.
Molecule 2 (symmetric, 4-aminophenol) was analyzed using three various techniques; Hydrogen NMR (See Figure 6), UV/VIS (Figure 7), and Infrared (Figure 8) spectrosopies. The $^1$H NMR spectrum in chloroform matches the predicted HNMR Razorix. This should be confirmed by running the product with DMSO as the solvent. The UV/VIS spectra has the three distinctive peaks (337nm, 352nm and 395nm) for naphthalene diimides (see figure 7), and the IR spectrum confirms the presence of a phenol hydroxyl broad stretch with a characteristic peak at ~3300cm$^{-1}$ and aromatic CH stretches at 3070 cm$^{-1}$.

Figure 5. The IR spectrum provides verification for the primary amine side chain at 3415cm$^{-1}$. 
Figure 6. Hydrogen NMR of microwave synthesized symmetric 4-aminophenol in deuterated chloroform.
Figure 7. UV/VIS of microwave synthesized symmetric 4-aminophenol.
Molecule 3 (symmetric, 4-aminobenzoic acid) was analyzed using three various techniques; Hydrogen NMR (See Figure 9), UV/VIS (Figure 10), and Infrared (Figure 11) spectroscopies. The $^1$H-NMR has four characteristic peaks occurring at chemical shifts of 8.71 ppm (singlet, 4 hydrogens), 8.08 ppm (triplet, 4.06 hydrogens), 7.92 ppm (singlet, 0.48 hydrogens) and 7.56 ppm (triplet, 3.83 hydrogens), each corresponding to the four types of hydrogens (bonded to carbon) on the 4-aminobenzoic acid product (see figure 9). This NMR has poor splitting. The UV/VIS spectra has three distinctive peaks (338 nm, 358 nm and 380 nm) for naphthalene diimides (see figure 10), and the IR spectrum confirms the presence of the carboxylic acid carbonyl group at ~1745 cm$^{-1}$ and a broad OH at ~3300 cm$^{-1}$.

Figure 8: IR of microwave synthesized symmetric 4-aminophenol with a peak at ~3300 confirming the presence of the phenol hydroxyl functional group.
Figure 9. Hydrogen NMR of microwave synthesized symmetric 4-aminobenzoic acid in deuterated DMSO.
Figure 10. UV/VIS of microwave synthesized symmetric 4-aminobenzoic acid.
Molecule 4 (symmetric, 5-aminovaleric acid) was analyzed using three various techniques; Hydrogen NMR (See Figure 12), UV/VIS (Figure 13), and Infrared (Figure 14) spectroscopies. The $^1$H-NMR has 6 characteristic peaks occurring at chemical shifts of 11.96ppm (singlet, 1.86 hydrogens), 8.69ppm (singlet, 4 hydrogens), 4.03ppm (triplet, 4.99 hydrogens), 2.25ppm (triplet, 4.71 hydrogens), 1.68ppm (quintet, 5.62 hydrogens), and 1.58ppm (quintet, 5.74 hydrogens), each corresponding to the six types of hydrogens (bonded to carbons) on the 5-aminovaleric acid product (see figure 12). The UV/VIS spectra has the three distinctive peaks (337nm, 358nm and 385nm) for naphthalene diimides (see figure 13), and the IR spectrum confirms the presence of the carboxylic acid with characteristic peaks of the carboxylic acid carbonyl group at $\sim$1710 cm$^{-1}$, a
small broad peak at ~3350 cm$^{-1}$ confirming the hydroxyl group, and the characteristic methylene stretches.

Figure 12. Hydrogen NMR of microwave synthesized symmetric 5-aminovaleric acid in deuterated DMSO.
Figure 13. UV/VIS of microwave synthesized symmetric 5-aminovaleric acid.
Molecule 5 (symmetric, cysteamine) was analyzed using three various techniques; Hydrogen NMR (Figure 15), UV/VIS (Figure 16), and Infrared (Figure 17) spectroscopies. The hydrogen NMR matches the predicted hydrogen NMR from HNMR Razor program\textsuperscript{ix}. This product should be rerun with DMSO as the solvent. The UV/VIS spectra has the three distinctive peaks (340nm, 360nm and 380nm)\textsubscript{i} for naphthalene diimides (see figure 16), and the IR spectrum tentatively confirms the presence of a thiol side chain with a broad weak peak at ~2600 cm\textsuperscript{-1} and the characteristic methylene groups. There could possibly be unreacted cysteamine starting material contaminating the product.

Figure 14. IR of microwave synthesized symmetric 5-aminovaleric acid confirming the presence of the carboxylic acid carbonyl group at ~1710 cm\textsuperscript{-1} and a small broad peak at ~3350 cm\textsuperscript{-1} confirming the hydroxyl group.
Figure 15. Hydrogen NMR of microwave synthesized symmetric cysteamine in deuterated chloroform.
Figure 16. UV/VIS of microwave synthesized symmetric cysteamine.
Molecule 6 (symmetric, vinylaniline) did not coagulate during chloroform extraction. No product was obtained.

Asymmetric Synthesis Results (b):

Molecule 7 (asymmetric, stepwise 4-aminothiophenol with propylamine) did not yield a product. Further extraction yielded no product.

Molecule 7 (asymmetric, stepwise propylamine with 4-aminothiophenol) was analyzed using three various techniques; Hydrogen NMR (Figure 18), UV/VIS (Figure 19), and Infrared (Figure 20) spectroscopies. The hydrogen NMR provides evidence that this
product could possibly be symmetric propylamine. The $^1$H-NMR has only 4 characteristic peaks occurring at chemical shifts of 8.76ppm (singlet, 4 hydrogens), 4.18ppm (triplet, 2.5 hydrogens), 1.78ppm (triplet of quartets, 6.07 hydrogens), 1.01ppm (triplet, 8.3 hydrogens), each weakly corresponding to the four types of hydrogens (bonded to carbons) on symmetric propylamine (see figure 18). The UV/VIS spectra has the three distinctive peaks (343nm, 359nm and 379nm), for naphthalene diimides (see figure 19), and the IR spectrum is also consistent with the assumption that this molecule is symmetric propylamine, as it does not display a characteristic thiol group at ~2700cm$^{-1}$.

Figure 18. Hydrogen NMR of microwave synthesized asymmetric propylamine and 4-aminothiophenol in deuterated chloroform.
Figure 19. UV/VIS of microwave synthesized asymmetric propylamine and 4-aminothiophenol.
Molecule 8 (asymmetric, stepwise 4-aminothiophenol with allylamine) was analyzed using three various techniques; Hydrogen NMR (Figure 21), UV/VIS (Figure 22), and Infrared (Figure 23) spectroscopies. Initially, the hydrogen NMR provided evidence that this product could possibly be symmetric allylamine. The $^1$H-NMR has 4 characteristic peaks occurring at chemical shifts of 8.76ppm (singlet, 4 hydrogens), 4.17ppm (triplet, 2.41 hydrogens), 1.78ppm (triplet of quartets, 5.15 hydrogens), and 1.034ppm (triplet, 7.44) (see figure 21). But after further integration and evaluation, these peaks do not translate well for a symmetric allylamine molecule either. Therefore, it is possible that the alkene group was protonated and/or chlorinated through the extraction method with HCl. This appears to be so, since the hydrogen NMR is near equivalent to a predicted
hydrogen NMR and the hydrogen NMR for molecule 7 (propylamine)\textsubscript{x}. The UV/VIS spectrum has the three distinctive peaks (379nm, 359nm and 343nm), for naphthalene diimides (see figure 23), and the IR spectrum is consistent with the assumption that this molecule is symmetric allylamine.

**Figure 21.** Hydrogen NMR of microwave synthesized asymmetric 4-aminothiophenol and allylamine in deuterated chloroform.
Figure 22. UV/VIS of microwave synthesized asymmetric 4-aminothiophenol and allylamine.
Figure 23. IR of microwave synthesized asymmetric 4-aminothiophenol and allylamine.

**Molecule 9** (asymmetric, stepwise propylamine with cysteamine) was analyzed using three various techniques; Hydrogen NMR (Figure 24), UV/VIS (Figure 25), and Infrared (Figure 26) spectroscopies. The hydrogen NMR is consistent with the HNMR Razor prediction for the asymmetric molecule, but due to the additional peaks, it appears to be contaminated with unreacted starting material. The UV/VIS spectra has the three distinctive peaks (343nm, 359nm and 380nm) for naphthalene diimides (see figure 25), and the IR spectrum tentatively confirms the presence of the thiol group for cysteamine with a broad weak peak at ~2600cm⁻¹.
Figure 24. Hydrogen NMR of microwave synthesized asymmetric propylamine and cysteamine in deuterated chloroform.
Figure 25. UV/VIS of microwave synthesized asymmetric propylamine and cysteamine.
Molecule 10 (asymmetric, stepwise aminovaleric acid with ethylene diamine) was analyzed using three various techniques; Hydrogen NMR (Figure 27), UV/VIS (Figure 28), and Infrared (Figure 29) spectroscopies. The hydrogen NMR corresponds to the predicted hydrogen NMR from HNMR Razorix. The product should be run in chloroform for additional confirmation. The UV/VIS spectra has the three distinctive peaks (352nm, 361nm and 381nm) for naphthalene diimides (see figure 28), and the IR spectrum confirms the presence of the aminovaleric acid with the carboxylic acid carbonyl group at ~1710 cm$^{-1}$ and a relatively large broad peak at ~2950 cm$^{-1}$ confirming the methylene

Figure 26. IR of microwave synthesized asymmetric propylamine and cysteamine.
chains, and broad peaks ranging from 3200cm$^{-1}$ to 3350cm$^{-1}$ for the amino and hydroxyl group portions.

Figure 27. Hydrogen NMR of stepwise microwave synthesized asymmetric 5-aminovaleric acid and ethylene diamine in deuterated DMSO.
Figure 28. UV/VIS of stepwise microwave synthesized asymmetric 5-aminovaleric acid and ethylene diamine.
Molecule 10 (asymmetric, same time microwave synthesis of aminovaleric acid with ethylene diamine) yielded a poor amount of product. No promising results were obtained with this method.
xi. Discussion and Conclusions

Much attention has been placed on creating more beneficial and less expensive semiconductor materials. Exploration of organic materials has therefore increased tremendously. By creating various naphthalene tetracarboxylic diimides, and interacting the terminal functional groups on the linker side chains with metals and semiconductors, there is hope to use these molecules as hybrid organic/inorganic semiconductor materials.

Creating the various naphthalene tetracarboxylic diimides is the primary focus of this thesis. Syntheses of molecules containing numerous functional groups were attempted including alcohols, carboxylic acids, primary amines, alkenes, thiols, and alkyl groups. The successful synthesis of these molecules was then verified using mainly three techniques: proton NMR, UV/VIS, and IR spectroscopy.

Two different synthetic methods were used to attach the various linker groups. The toluene reflux method proved to be lengthy and not efficient. Therefore, the synthesis process immediately changed to directed microwave synthesis only. Directed microwave synthesis produced consistent results and proved to be drastically more efficient than the toluene reflux method.

Attaching linker groups in a symmetric manner to the NTCDA core was first attempted. The precursor amine molecules attempted included: ethylene diamine (1), 4-aminophenol (2), 4-aminobenzoic acid (3), 5-aminovaleric acid (4), cysteamine (5), and vinylaniline (6). The only attempted molecule that did not yield coagulation and therefore lacked an isolable product was vinylaniline. Attempted extraction with chloroform and acetonitrile failed to yield any solid products, which was a marked
departure from the syntheses for the other molecules.

Formation of asymmetric NTCDI molecules then became the primary focus in order to manipulate the attachment to silver nanoclusters and silicon surfaces. The synthesis of the asymmetric molecules initially followed a stepwise addition procedure. The only synthetic target that involved both a stepwise procedure as well as a simultaneous attachment procedure was the 5-aminovaleric acid and ethylene diamine adduct. The simultaneous method produced little coagulation and with the small amount of product formed, the results were deemed as unfavorable. The stepwise procedure seemed to require specific attachment sequences. The following molecules were attempted in order of attachment respectively: (7) 4-aminothiophenol & propylamine, (7) propylamine & 4-aminothiophenol, (8) 4-aminothiophenol & allylamine, (9) propylamine & cysteamine, (10) aminovaleric acid & ethylene diamine, (10) sametime aminovaleric acid and ethylene diamine.

The ones that appeared to give asymmetric products were molecules 9 and 10. As for the other asymmetric attempts, it appears that the aryl amines are not as reactive as the alkyl amines. Therefore molecules 7 and 8, both of which had aryl and alkyl amines, produced symmetric molecules with the alkyl amines. The order of attachment was also ruled out as a factor since the creation of molecule 7 was attempted twice, through stepwise synthesis with both orders of attachment. If the aryl group is desired, one could attempt the asymmetric molecule with an additional aryl group such as 4-amintoluene.

In summary, the analytical probes used point to the succesfull synthesis of symmetric ethylene diamine, symmetric 4-aminobenzoic acid, symmetric 5-aminovaleric
acid, and asymmetric ethylene diamine & 5-aminovaleric acid using the microwave-directed technique. Mass spectrometry, $^{13}$C NMR, and elemental analysis should be pursued to confirm the successful synthesis of these molecule.
x. Literature Cited


