Final Report: Enhanced Internal Electric Field of Organic Photovoltaics by Anode Surface Modification by an Organic Self-Assembled Monolayer
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Over the course of this summer, my goal was to synthesize a series of molecules for use in an organic self-assembled monolayer (SAM) on the anode surface of an organic photovoltaic (OPV) device. I wanted to investigate the hypothesis that an organic SAM on the anode would induce a stronger electric field in favor of charge collection in an OPV. Originally, the proposal included n-propylaniline, diphenyl-n-propylaniline, and dipentafluorophenyl-n-propylaniline (Figure 1) as the molecules for study. After consideration that n-propylaniline’s structure was too dissimilar to the other molecules, it was replaced with 3-dipyridinamine-n-propylaniline. Therefore, diphenyl-n-propylaniline (PAPSi), dipentafluorophenyl-n-propylaniline (F10PAPSi), and 3-dipyridinamine-n-propylaniline (Figure 2) were the focus of investigation. This series of molecules has a range of dipole moments from 1.48 D to 6.51 D (Figure 3). It was hypothesized that the molecule with the largest dipole moment would make a device with the best performance.

Molecule 1 had a 2-step synthetic pathway, and Molecules 2 and 3 had 3-step pathways (Figure 4). For Molecule 1, the first step alkenylated a diphenylamine. The second step hydrosilylated the alkene chain. For Molecules 2 and 3, the first step coupled the aromatic rings with an amine, the second step added the alkyl group, and the third step hydrosilylated the terminal alkyl carbon.

In Step 1 of Molecule 1, diphenylamine was coupled to allyl bromide using potassium carbonate, tetrabutylammonium iodide, and acetonitrile. \(^1\) \(^1\)H NMR showed that the reaction was successful. It had a yield of 70.1%. Step 2, the hydrosilylation, was performed using trichlorosilane and chloroplatinic acid. This reaction occurred under a nitrogen atmosphere, and was heated under vacuum to dry and purify. This resulted in a yield of 59.0%.

In Step 1 of Molecule 2, hexafluorobenzene was coupled with lithium amide. \(^2\) \(^1\)H NMR confirmed the success of this reaction, which was purified by extraction and concentrated under vacuum. It had a percent yield of 20.97%. Step 2, the alkenylation, was performed using allyl bromide, potassium carbonate, tetrabutylammonium iodide, and acetonitrile. \(^3\) It was purified by extraction and dried with magnesium sulfate and vacuum. \(^1\)H NMR also confirmed this reaction. This reaction’s yield was 38.68%. Step 3, the hydrosilylation, was performed as for Molecule 1. It had a yield of 88.4%.

Molecule 3 was much more difficult to obtain than Molecule 1 and Molecule 2. Several different methods were attempted before successfully completing the first step. First, a synthetic scheme from a 2007 Merck patent \(^4\) was used, but with a different catalyst because the original catalyst had not yet been shipped. This reaction would have coupled 3-aminopyridine and 3-

bromopyridine by using a tri(t-buty1)phosphine catalyst, tris(dibenzylideneacetone)dipalladium(0), and sodium tert-butoxide in hexane. After \(^1\)H NMR indicated that no product had formed, the same reaction was run in toluene at a higher temperature. Thin-layer chromatography and a silica gel column were used to separate the reagents from the product; however, the product was determined by \(^1\)H NMR not to be the desired compound. The third method used would have coupled 3-bromopyridine by using lithium amide in a solution of tetrahydrofuran. \(^1\)H NMR was inconclusive, so the subsequent alkenylation reaction was attempted using this product. \(^1\)H NMR, COSY, and HSQC indicated that only a single substitution had occurred in the previous step, thus giving 3-pyridinamine as the product. The lithium amide reaction was run for a second time overnight, rather than only 2 hours. \(^1\)H NMR showed that the product was still not formed. The fourth method used to produce the product was a modified synthetic scheme from Zhang, et al. Potassium phosphate, copper (I) bromide, and L-proline in DMSO. Thin layer chromatography and a silica gel column were used to separate the reagents. \(^1\)H NMR demonstrated that the reaction did not proceed, as only the starting materials were present. The final synthetic scheme for this molecule was the Bilodeau patent, with the indicated catalyst. 3-aminopyridine and 3-bromopyridine were coupled by using Xantphos, tris(dibenzylideneacetone)dipalladium(0), and sodium tert-butoxide. \(^1\)H NMR of the crude reaction mixture showed evidence of the desired product. After purification using a silica gel column, however, the product no longer appeared in the \(^1\)H NMR spectra. The appearance of additional hydrocarbon peaks indicated that the acidic nature of the silica gel had decomposed the product. A second, scaled up reaction was run and purified using a short layer of aluminum oxide. While concentrating the product under vacuum, it crystallized and became insoluble in the solvent, acetone, providing an easy method for purification. \(^1\)H NMR and \(^13\)C NMR confirmed that the product had been made. It had a 41.05% yield.

Step 2 of Molecule 3, the alkenylation, was performed as for the other molecules. It ran over a period of three days. \(^1\)H NMR of the crude product indicated the successful formation of the product. After an aqueous workup and concentration, however, successive \(^1\)H NMR spectra indicated that the product was decomposing over time and exposure to air and water. The signal to noise ratio of the post-workup samples became noisier over time, while the crude sample remained the same. This indicates that the product of Step 2 is air- and water-sensitive and will decompose in protic solvents. Although the molecule was successfully synthesized, due to time constraints on this project, the molecule was unable to be purified in an air-free system.

As the final step of Molecule 3 has not been synthesized yet, no devices were created with it. Devices were made and tested for Molecules 1 and 2, however. (Figures 5 and 6.) A device made with Molecule 1 had a \(V_{oc}\) of 0.5181 V and a \(J_{sc}\) of -7.594 mA/cm\(^2\). A device made with Molecule 2 had a \(V_{oc}\) of 0.578 V and a \(J_{sc}\) of -8.96 mA/cm\(^2\). In comparison, a device made with PEDOT:PSS had a \(V_{oc}\) of 0.58 V and a \(J_{sc}\) of -9.84 mA/cm\(^2\). Molecule 2 achieved an efficiency of 2.6%, compared to 3.66% for PEDOT:PSS. Despite this smaller efficiency, Molecule 2 had a smaller fill factor (54.6%) than PEDOT:PSS (63.3%), indicating that with more optimization, Molecule 2 could achieve a higher efficiency. These preliminary results show that Molecule 2 has the potential to achieve performance efficiency as good as PEDOT:PSS.

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Additionally, according to the trend of Molecules 1 and 2, a device made with Molecule 3 is likely to result in an efficiency higher than PEDOT:PSS.
Figures:

Figure 1. The original molecule series.

Figure 2. The modified molecule series.
Figure 3. A comparison of the dipole moments of IFL materials, including F10PAPSi and PAPSi. (Figure provided by Charles Song.)
1.

\[
\begin{align*}
\text{NH} & \quad \rightarrow \quad \text{N} & \quad \rightarrow \quad \text{N} \\
\text{Si(OMe)}_3 & 
\end{align*}
\]

2.

\[
\begin{align*}
\text{F} & \quad \rightarrow \quad \text{F} & \quad \rightarrow \quad \text{F} \\
\text{(MeO)}_3\text{Si} & 
\end{align*}
\]

3.

\[
\begin{align*}
\text{NNH}_2 & + \quad \text{NNBr} & \quad \rightarrow \quad \text{NN} & \quad \rightarrow \quad \text{NN} \\
\text{Si(OMe)}_3 & 
\end{align*}
\]

**Figure 4.** The synthetic scheme for the molecular series.
**Figure 5.** A comparison of device efficiencies.

<table>
<thead>
<tr>
<th>IFL</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>FF (%)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0.46</td>
<td>8.54</td>
<td>48.4</td>
<td>1.93</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>0.58</td>
<td>9.84</td>
<td>63.3</td>
<td>3.66</td>
</tr>
<tr>
<td>PABTSi$_2$:P3HT (1:2)</td>
<td>0.55</td>
<td>9.6</td>
<td>53.8</td>
<td>2.77</td>
</tr>
<tr>
<td>F$_{10}$PAPSi (SAM)</td>
<td>0.578</td>
<td>8.96</td>
<td>54.6</td>
<td>2.6</td>
</tr>
</tbody>
</table>

**Figure 6.** A comparison of the open circuit voltage ($V_{oc}$), short circuit current density ($J_{sc}$), fill factor (FF), and power conversion efficiency ($\eta$).