Alignment of Organic Small Molecules
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Introduction
A bulk-heterojunction solar cell, used in organic photovoltaics (OPVs), consists of an active layer with a mixture of donor and acceptor phases, whose morphology greatly impacts the performance of the cell [1]. Determining the crystal structures of small molecules used in OPVs aids in understanding their morphology. However, not all small molecules readily crystallize with a single orientation, so it becomes difficult to determine their crystal structures experimentally. The purpose of this study is to find a simple method to align small molecules that can be used to help resolve their crystal structures.

The alignment method on which this study focuses is drop casting on an inclined surface. Using an inclined surface causes alignment by creating a uniform evaporation front perpendicular to the incline direction [2]. With the right conditions, this evaporation front pins the crystallites as they nucleate, forcing them to grow in the incline direction [3].

Experimental Methods
The method was tested using 0.2, 0.5, 1.0, and 5.0 wt% solutions of 2,6-di(benzo[c][1,2,5]thiadiazol-4-yl)-4-hexyl-4H-dithieno[3,2-b:2',3'-d]pyrrole (BTD-DTP) in chlorobenzene. 150 μL of the solutions were drop casted on 0.5” x 1” glass substrates which were inclined at 1°56’ and 3°52’ angles using optical wedge prisms. They were allowed to evaporate at 65°C while being covered with a glass petri dish. Control samples were also made without the use of inclines. The glass substrates were cleaned by sonication in acetone, methanol, and isopropyl alcohol for 15 minutes each. Sample preparation was conducted inside a nitrogen-filled glove box [2].

All samples were characterized using optical and polarized optical microscopy. Alignment was measured by determining the standard deviation of angles of crystallites in optical microscope images taken from the largest uniform area of each sample and by calculating the largest region of crystallites of uniform extinction in polarized optical microscope images. ImageJ software was used for analyses.

Results and Discussion
Optical microscopy images of the samples, displayed in Figure 1, indicate that all samples show evidence of alignment.

![Image](Figure 1. Optical microscopy images of films of a) 0.2, b) 0.5, c) 1, and d) 5 wt% BTD-DTP prepared using a ~2° incline and e) 1 wt% with no incline at 500 magnification. The scale bar depicts 100 μm.)

It can be seen that more material is deposited with increasing solution concentrations, which is favorable. However, higher concentrations also cause increased growth of fibrous crystallites that branch off from the main aligned crystallites, which is detrimental to the overall alignment of the film.

The results of angular deviation and extinction region measurements are shown in Table 1.

<table>
<thead>
<tr>
<th>Concentration (wt%)</th>
<th>0.2</th>
<th>0.2</th>
<th>0.5</th>
<th>0.5</th>
<th>1.0</th>
<th>1.0</th>
<th>5.0</th>
<th>5.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Incline Angle (˚)</td>
<td>~2'</td>
<td>~4'</td>
<td>~2'</td>
<td>~4'</td>
<td>~2'</td>
<td>~4'</td>
<td>~2'</td>
<td>~4'</td>
</tr>
<tr>
<td>Angular Deviation (˚)</td>
<td>15.35</td>
<td>13.26</td>
<td>13.33</td>
<td>14.10</td>
<td>13.87</td>
<td>17.16</td>
<td>18.02</td>
<td>14.37</td>
</tr>
<tr>
<td>Extinction Region % Area</td>
<td>73.25</td>
<td>67.58</td>
<td>66.53</td>
<td>50.84</td>
<td>73.44</td>
<td>49.20</td>
<td>56.86</td>
<td>55.88</td>
</tr>
</tbody>
</table>

These results show that, while all samples showed some degree of alignment, those prepared with lower concentrations and drop casted on the ~2° incline exhibited the most alignment. However, the 0.2 wt% solution deposited too little material and the 1 wt% solution did not evaporate evenly, causing waves of crystallites to form when viewed with the naked eye. Thus, using a 0.5 wt% solution and a ~2° incline were found to be the best conditions for obtaining aligned thin films of BTD-DTP. These conditions also produced the most uniform films.

It is important to note that the data presented were taken from a ~2 mm² area of the whole substrate and are not necessarily representative of the entire film. However, the images were taken from the most uniform portions of the film and should provide a good approximation of the aligned regions.

Conclusions
BTD-DTP thin films were aligned by drop casting on an inclined surface and characterized using optical and polarized optical microscopy. The best alignment resulted from films prepared from a 0.5 wt% solution drop casted on a ~2° incline.

Future work includes preparing aligned samples on silicon substrates to be taken to a synchrotron source for grazing incidence wide angle x-ray scattering measurements. The results from this experiment will be used to investigate the crystal structure.

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References