Organic photovoltaics (OPVs) represent a potentially low-cost solution for harnessing solar energy and addressing global energy needs. Organic photovoltaics can be broken down into two categories: polymer solar cells and small molecule solar cells. Polymer solar cells have so far achieved higher efficiencies because they typically exhibit superior device architecture compared to those of small molecules. However, small molecules remain interesting because they can be more easily functionalized to modify their electronic properties. An ideal electron donor would merge the improved morphology of polymers with the tunability of small-molecules. One possible solution to this end would be the use of a chain-end functionalized supramolecular polymer. My research this summer has focused on the development of a supramolecular polymer to be incorporated into OPV devices.

The initial synthetic scheme is shown in Figure 1. The target molecule utilized a ureidopyrimidinone end-unit to induce end-to-end interactions. The ureidopyrimidinone unit was chosen both because it demonstrates self-recognition and because its multiple hydrogen bonds should produce the desired directionality. This synthetic pathway ultimately proved to be infeasible, as the desired bromination at the methyl position of the pyrimidinone does not take place. The bromination was attempted with and without light and heat, using both molecular bromine and N-bromosuccinimide, but only bromination at the 5-position (alpha to the carbonyl) was observed to occur. Because the phosphite group cannot be added to the 5-position, it was impossible to proceed with the desired Horner-Wadsworth-Emmons olefination.

An alternative, but similar, ureatriazine end-unit was chosen for the second target molecule (5 in Figure 2). Like the ureidopyrimidinone moiety, the ureatriazine unit demonstrates multiple hydrogen bonds and self-recognition. The synthesis first converted 5-bromo-2-thiophenecarboxaldehyde to 5-bromo-2-thiophene carbonitrile. This molecule was reacted with dicyandiamide to form a 1,3,5-triazine with two free amines. By reacting this molecule with hexyl isocyanate, ureatriazine 4 was synthesized. This molecule was expected to be soluble in a variety of organic solvents, similar to the ureidopyrimidinone unit. Unfortunately, 4 was only observed to be soluble in DMSO or warm polar solvents. It was hoped that solubility could be achieved by attaching the end-units to a benzodithiophene (BDT) core with two ethyl-hexyl solubilizing tails. The ureatriazine end-units were attached to a stannylated BDT molecule via a Stille coupling. The solution turned from yellow to red overnight, suggesting an extension of the conjugation and a successful reaction. The collected product was observed to be slightly soluble in chloroform, but not soluble enough for characterization or for device fabrication. Mass spectrometry was attempted to confirm the formation of the product, but no signal was observed. Consequently, it became necessary to search for other possible solutions.

Returning to the ureidopyrimidinone end-unit, it was decided to synthesize a ureidopyrimidinone molecule with a thiophene, rather than a methyl, at the 6-position (6 in Figure 3). A similar molecule, with a phenyl ring in the 6-position, has been previously reported and is soluble in chloroform. First, 2-acetyltiophene was alkylated with diethyl carbonate. The resulting β-keto ester was condensed to the pyrimidinone. The free amine was reacted with
hexyl isocyanate to afford the 6-thiopheneureidopyrimidinone. Unlike 6-methyl pyrimidinone, this molecule was observed to be completely insoluble in dichloromethane and chloroform. The molecule showed limited solubility in DMSO, which allowed for the confirmation of the product by NMR, but the solubility issues complicated further reactions. Based on the similarly limited solubility of 4 and 6, it was concluded that the thiophene unit significantly reduces the solubility of the hydrogen bonding unit. The ureidopyrimidinone unit is known to strongly dimerize in solution, and thiophene units are known to be highly planar. It was, therefore, concluded that the addition of a thiophene to the hydrogen-bonding end-unit creates a large planar dimer in solution. This, evidently, prevents dissolution in most solvents.

Faced with these solubility issues, several pathways are currently being attempted towards the synthesis of a soluble supramolecular polymer. One potential solution is to add a spacer between the thiophene and the ureidopyrimidinone end-unit. Because it is known that that 5-position of the ureidopyrimidinone molecule can be brominated, it should be possible to attach a spacer via a cross-coupling reaction. The target molecule for this route is shown in Figure 4. Using a Sonogashira coupling, trimethylsilyl acetylene will be connected to the 5-bromo ureidopyrimidinone. After the deprotection of the TMS group, this molecule can be reacted with 2-bromothiophene using a second Sonogashira coupling. It is hoped that by adding the alkyne spacer between the thiophene and the end-unit, the overall solubility of the molecule will be increased, even though the spacer itself will also be rigid.

A second pathway currently being explored is to use an alternate pyrimidinone. It is possible to condense pyrimidinones from diethyl malonate instead of ethyl acetoacetate. Because diethyl malonate can be condensed with an aldehyde via a Knoevenagel condensation, it should be possible to follow a similar pathway to the one originally proposed. The new pathway is shown in Figure 5. Diethyl malonate can be condensed with 5-bromo-2-thiophenecarboxaldehyde. The condensation product can be reacted with guanidine to afford the alternative pyrimidinone. The urea unit can then be added by reacting the free amine with hexyl isocyanate. As discussed above, adding a spacer between the pyrimidinone and the thiophene should help improve solubility. Additionally, this pathway allows for flexibility when adding the end-unit. The ureidopyrimidinone can be constructed separately from the the core, and attached to the core via a Stille coupling. Alternatively, diethyl malonate can be condensed with a dialdehyde core, and the pyrimidinone can be built outwards from the core. This flexibility may help address any solubility problems that arise during synthesis.

Finally, it may be desirable to create a supramolecular polymer that uses halogen bonding rather than hydrogen bonding to direct assembly. Though not as strong as the multiple hydrogen-bonding end-units, halogen bonding is highly directional and can be stronger than individual hydrogen bonds. Additionally, halogen bonding units are much more soluble in organic solvents than hydrogen bonding moieties. A common halogen bonding system is pyridine with tetrafluoro-diiodobenzene. It may be possible to mimic this system using a difluoro-iodo-benzothiadiazole unit (Figure 6). The larger challenge will be incorporating the pyridine unit into the system. It will be necessary to use a ternary system (two electron donors and the electron acceptor), which have so far displayed low efficiencies, or an asymmetric electron molecule, which is much harder to synthesize. Despite these challenges, halogen bonding presents an interesting yet unused solution for driving assembly in OPV devices.
References

Figure 1. The initial synthetic scheme targeting an electron donor with a ureidopyrimidinone end-unit.
Figure 2. The second target molecule 5 utilized a ureatriazine unit to induce end-to-end interactions.

Figure 3. The third synthetic scheme attempted to synthesize a ureidopyrimidinone molecule with a thiophene at the 6-position.
Figure 4. The proposed synthetic scheme for a ureidopyrimidinone molecule with an alkyne spacer.

Figure 5. A proposed synthetic scheme for an alternative ureidopyrimidinone end-unit.

Figure 6. A potential halogen bonding system using difluoro-benzothiadiazole and pyridine.