

## A Supramolecular Polymer for Organic Photovoltaic Devices

Since 1750, atmospheric levels of carbon dioxide have increased from 275 ppm to 392 ppm in 2013, with continued annual increases of 2-3 ppm.<sup>1,2</sup> This steady increase has been partly attributed to anthropogenic causes, particularly the increased burning of fossil fuels, and the increase in carbon dioxide levels is believed to be a leading cause in global warming.<sup>3</sup> Future energy needs call for abundant, low-carbon technologies to reduce the environmental effects of fossil fuel consumption. Solar energy represents one of the most attractive options because the sun is the Earth's most abundant energy source.<sup>4</sup> The sun's light energy can be captured and converted into electricity with photovoltaic systems, commonly known as solar cells. While silicon solar cells are currently commercially available, they are too expensive to compete directly with fossil fuels in many parts of the world.<sup>4</sup>

Organic photovoltaics (OPVs) represent a potentially low-cost solution for harnessing solar energy. Unlike silicon solar cells, organic photovoltaics are solution-processable and have easily adjustable electronic properties.<sup>5</sup> The efficiency of OPVs is largely dependent on two processes: the creation of electron-hole pairs by light absorption and the transport of generated charges to electrodes. While a variety of chromophores are available to efficiently create charge pairs, controlling the morphology of the active layer is essential to generate strong charge transport and achieve high efficiencies.<sup>6</sup> In bulk heterojunction active layers, the organic semiconductor is mixed with an electron acceptor in solution and spin cast as a film. The resulting film typically has a large number of donor-acceptor domains, but the interfaces may not be properly aligned for charge transport.<sup>7</sup> Traditionally, polymer OPVs have demonstrated superior device architecture for efficient charge transport,<sup>8</sup> but polymer semiconductors suffer from polydispersity between batches and harder-to-control electronic properties.<sup>9</sup> These challenges may be addressed through the use of a chain-end functionalized supramolecular polymer, a chemical structure of repeating molecular units held together by intermolecular forces. Such a structure may demonstrate the superior morphology of a polymer with the consistency and tunability of a small molecule. My research will focus on synthesizing an end-to-end supramolecular polymer with strong absorption and fabricating solar devices to test the power conversion efficiency of the molecules.

The target molecule is shown in Figure 1. It contains a ureidopyrimidinone end-unit which provides strong self-recognition via quadruple hydrogen bonding. Self-recognition opens the possibility for molecular symmetry, which significantly expedites synthesis. In the ureidopyrimidinone unit, recognition occurs between the urea nitrogens (H-donors) and the carbonyl and pyridine groups (H-acceptors). This is illustrated in Figure 2. There is also a need to control for the effects of hydrogen-bonding assembly versus a random orientation of molecules in the active layer. Consequently, a second molecule will be synthesized with the urea amides methylated. This will eliminate the hydrogen-bonding ability of the molecule, which should prevent it from forming end-to-end assemblies in the active layer. The full synthesis scheme is shown in Scheme 1. The ureidopyrimidinone unit will be synthesized according to the procedure reported by Beijer et al.<sup>10</sup> The unit will then be brominated via radical bromination. The unit can then be coupled to the alkylated diketo-pyrrolo-pyrrole (DPP) core with a Horner-Wadsworth-Emmons olefination. DPP was chosen as the core chromophore because of its excellent absorption in the visible region. This molecule, as currently designed, may experience difficulties with solubility because the hydrogen bonding of the ureidopyrimidinone units and the  $\pi$ - $\pi$  stacking of DPP make it likely to form supramolecular assemblies in solution. To address

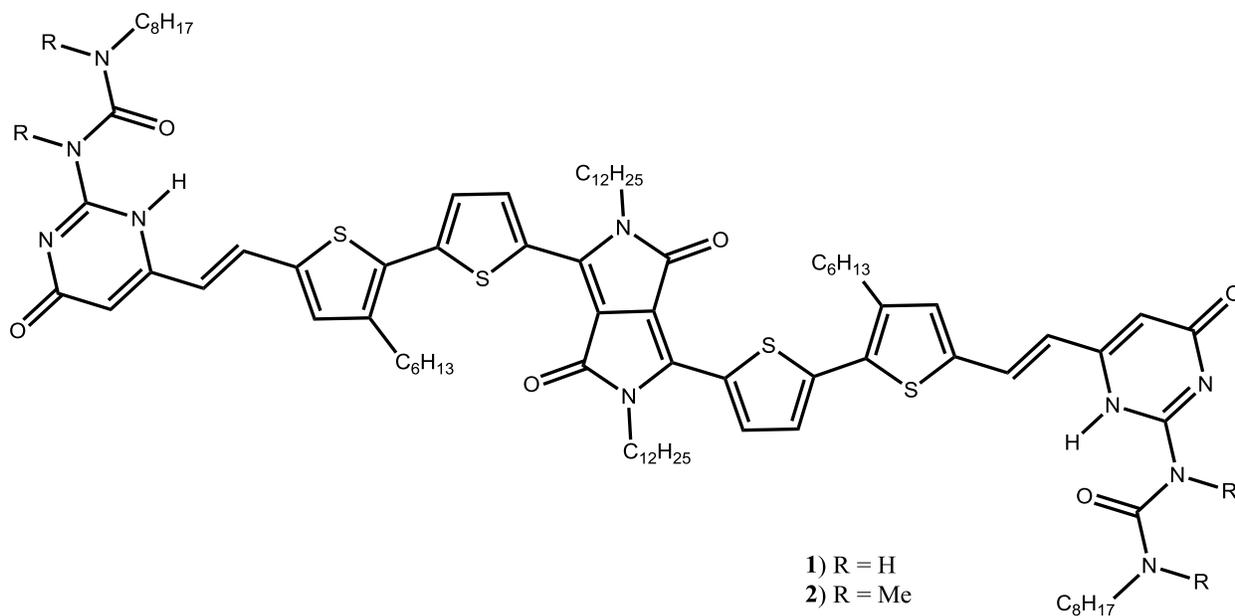
this problem, it may be necessary to add additional alkyl tails to the molecule or potentially to choose a different chromophore that does not stack as well as DPP.

The second phase of my research project will be the characterization of the synthesized supramolecular polymer. First, infrared spectroscopy can be used to confirm the presence of hydrogen bonding. Hydrogen bonding is indicated by a shift to lower wavenumbers of the N-H amide and carbonyl stretching frequencies in the infrared spectrum. Next, it will be important to determine the optical and electronic properties of the molecules. This will impact its ability to act as an effective electron donor in a photovoltaic device. Ultraviolet/visible spectroscopy will be used to determine the wavelengths of absorption and the bandgap of the molecule. Cyclic voltammetry will be used to determine the energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). Based on the characterization of similar molecules synthesized within the Stupp group, this molecule should show appropriate band gaps and energy levels for use in photovoltaic devices. The final step of characterization will be determining if the molecule forms supramolecular structures. While it can be difficult to predict the morphology of the active layer (where the synthesized electron donor is mixed with the electron donor PCBM-71), it has been shown that self-assembling materials can help increase the order of the donor-acceptor domains.<sup>11</sup> If the synthesized molecule shows evidence of a supramolecular assembly when analyzed by atomic force microscopy (AFM), then it is likely to show order donor domains in the solar device, which may lead to higher efficiencies.

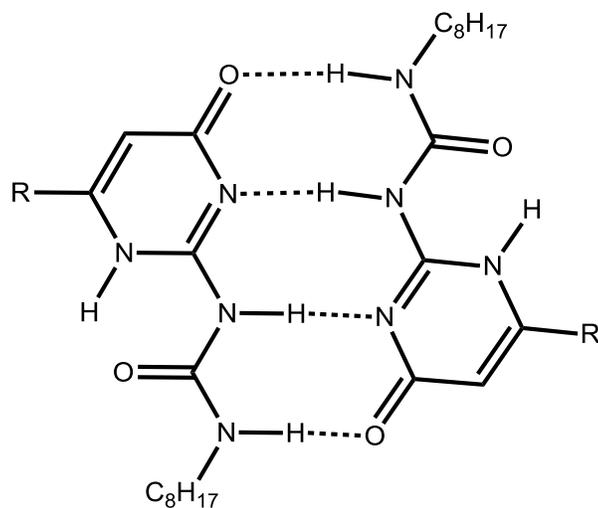
The final phase of this research project will be the fabrication of solar devices using the synthesized molecule. The devices begin with an indium-tin-oxide anode, followed by an electron blocking layer. The active layer, a mixture of the synthesized donor molecule and the PCBM-71 acceptor molecule, will then be spin cast onto the device as a thin film. The final layers are a hole blocking layer and an aluminum cathode. The active layer will be fabricated with different donor:acceptor ratios, different overall concentrations of material and different solvent additives in order to optimize the efficiency of the devices. The solar devices will be tested using a solar simulator to determine their efficiency. The power conversion efficiency of the solar cell is calculated by multiplying the peak current density ( $J_{SC}$ ), the open circuit voltage ( $V_{OC}$ ), and the fill factor and dividing by the input light power. The devices can be analyzed by AFM and x-ray scattering to learn more about the organization of molecules in the active layer.

My experiences at Northwestern have prepared me to take on this research project. During summer 2013, I completed 10 weeks of research as a Weinberg College summer research fellow, and I have continued to work in the Stupp group over the past two quarters. I have gained valuable experience in organic synthesis of electron donors, and I have been trained in all of the characterization methods discussed above. As a junior chemistry major, I will have completed both the organic chemistry and advanced laboratory sequences by the end of this year, which has taught me even more synthetic and analytical techniques that may be useful over the course of the summer.

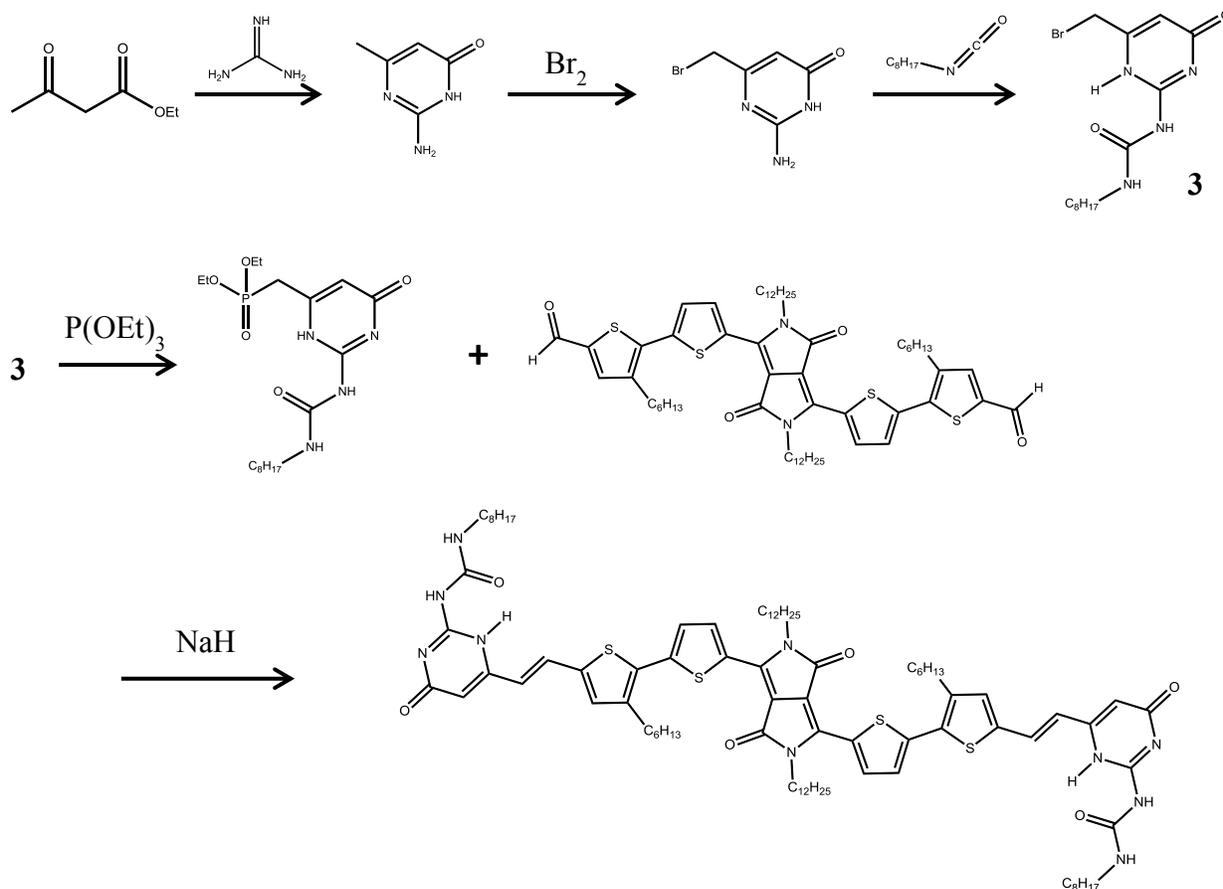
Summer research is an invaluable part of my education as a scientist. My schedule during the school year limits me to 10 to 15 hours of research time per week. Summer research provides the opportunity to commit to a project full-time, which will better prepare me for graduate work in chemistry and will give me a better opportunity to work towards publishable results. If the project proves successful during the summer, I will continue it into the fall, in the hopes of completing a senior thesis before my graduation in spring.



**Figure 1.** The electron donor molecule to be synthesized. The ureidopyrimidinone units will be synthesized with free amides to allow hydrogen bonding and with methylated amides to prevent hydrogen bonding.



**Figure 2.** Illustration of the hydrogen-bonding recognition between two ureidopyrimidinone units.



**Scheme 1.** Synthesis of a DPP-electron donor with a ureidopyrimidinone end unit.

## References

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