

Organic Photovoltaics: Student Synthesis Of An Organic Photo Absorbing Polymer

Background

The industrialization of the past 2 centuries has been accomplished by the acquisition and use of energy based on hydrocarbons (petroleum/fossil fuels/coal). These relatively abundant hydrocarbons have been essential in fueling our modern economy and have given rise to our high standard of living. Hydrocarbons power our automobiles, jet aircraft, heat our home, and power most of our electrical grid. This system has served humanity well and use of this energy will only increase in the upcoming decades. Global energy use in 2010 was 17 TW and is expected to reach 27 TW in 2040 with much of this increase occurring in the developing world. But this system of energy has many shortcomings for its future use. Petroleum is a limited and nonrenewable resource and the fate of every 'burned' organic hydrocarbon is conversion to the greenhouse gas CO₂. Carbon dioxide emissions from burning fossil fuels is the leading cause of climate change as we have experienced since the late 1990s. Since then we have seen the warmest years on record as well as shifting weather patterns, rising sea levels, vanishing species and shrinking glaciers. Currently, atmospheric CO₂ levels are at 420 ppm as compared to 320 ppm in 1960. Preindustrial CO₂ levels averaged around 280 ppm.

Finding an alternative to our petroleum based system is imperative for the health of this planet. *Stability wedges* is a reference to the multiple solutions that when used together can substantially mitigate the global effects CO₂ emissions and bring them down to pre-industrial levels. Many of these 'wedges' are about replacing our current fossil fuels with 'clean' non CO₂ emitting and renewable fuel sources. Examples of replacement energy sources are geothermal, hydroelectric, tidal power, wind and solar energy.

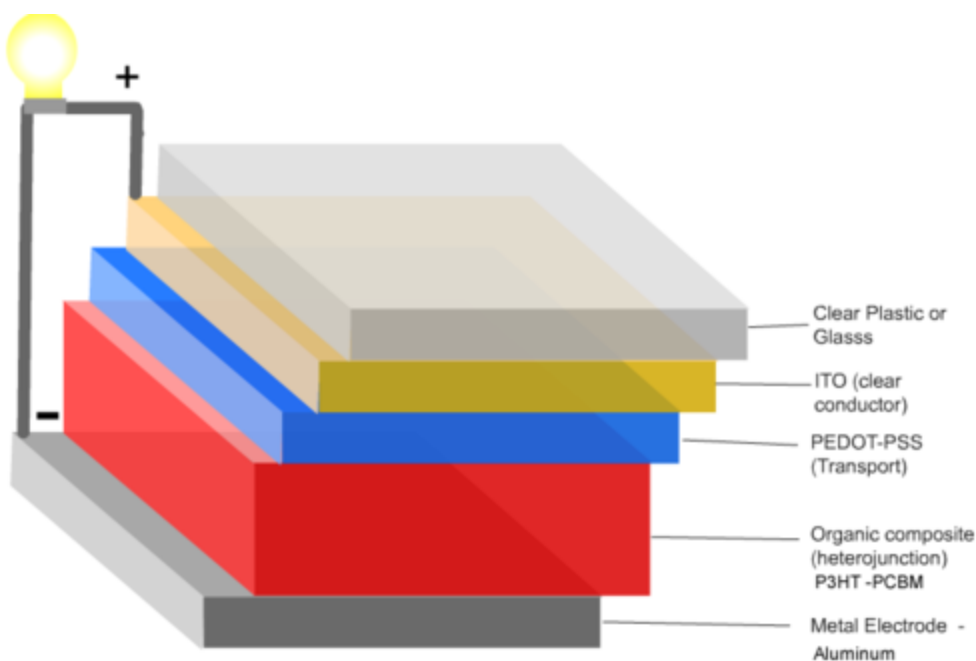
In this discussion we will focus on solar energy which has great promise when one considers that the energy from 90 minutes of sunlight can power the earth for a year. Solar energy technology is based on capturing sunlight and converting the energy of a photon into electricity. First generation silicon based solar cells, what we see on rooftops, currently supply only 1% of our global energy needs. There is enough space to dramatically expand our solar footprint as it is estimated that only 25000 square miles of solar panels would be needed to meet *all* of the United State energy needs (This is roughly the size of the state of West Virginia—or 0.6% the size of the US). Advantages of solar power are ever abundant sunlight that has an egalitarian quality of no borders or ownership. There is little maintenance and 20-30 year performance lifetimes. And most importantly, there are no CO₂ emissions associated with this technology. A major drawback to solar is the expense. Productions cost of silicon based cells are high involving energy intensive processes and high weight. The next generation photovoltaics are 'organic' photovoltaics that can potentially be produced at lower cost, are lighter weight and have more versatility of use. For this lab we will explore organic photovoltaics (For a more detailed discussion of Solar energy please see canvas course 1004266: *Energy big picture* and *Solar Energy* modules).

Organic Photovoltaics.

Organic photovoltaics incorporate organic **polymers** with extensive π conjugation. It is the π conjugated systems that enable these polymers to absorb the frequencies of light in the visible regions. When the conjugated system absorbs the photon an 'exciton' is formed, which is a species of an electron and an electron hole, which are bound together by the electrostatic coulomb force. The exciton can create current if it can separate into free positive (+) and negative (-) charges. This can be done if the exciton is

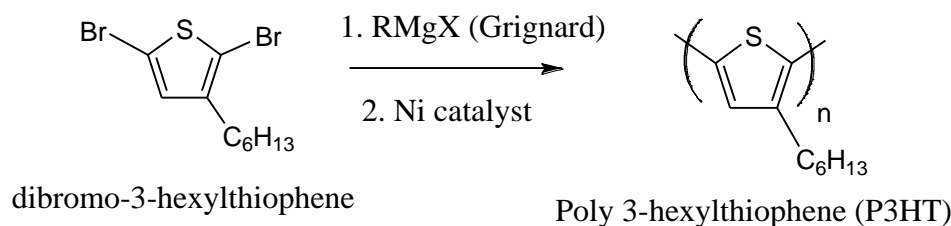
associated with a molecular system that contains an acceptor and donor molecules to facilitate the charge separation/dissociation. The dissociated exciton is the current that is manifested in the organic photo voltaic cell (for a more thorough explanation please see canvas course 1004266: *organic photovoltaics OPV*).

The organic photovoltaic cell we will study and construct will contains a light absorbing π conjugated system called poly(3-hexylthiophene) P3HT and an absorbing molecule phenyl C₆₀-butyric acid methyl ester (PCBM). This light absorbing organic composite will also be layered between an anode of tin doped indium oxide (ITO glass) and gallium-indium cathode. To aid in charge transport a composite of poly(ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS)is added to the ITO anode.



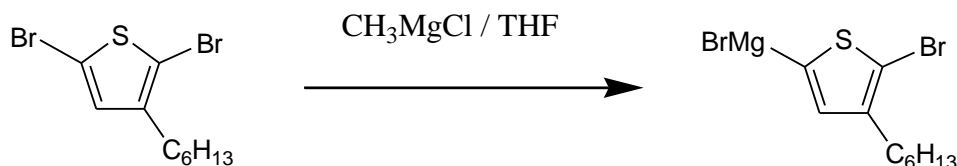
Another aspect of this is lab is that you will get to synthesize the key light absorbing molecule, P3HT using Grignard chemistry (see reaction scheme below). Once you synthesized this molecule you will blend it will PCBM to make the 'active layer' and then construct a solar cell by layering onto ITO glass PEDOT:PSS composite, P3HT:PCBM composite followed by an aluminum or Ga-In cathode.

Synthesis of Hexylthiophene polymer (P3HT)



Experimental: Synthesis of poly (3-hexylthiophene) P3HT

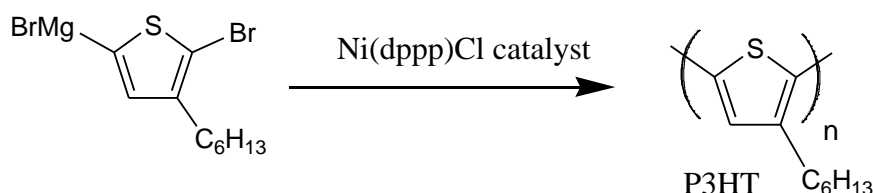
Step 1: Formation of the Grignard Monomer (2,5-dibromo-3-hexylthiophene + methyl magnesium bromide)



Note: Grignard reactions must be kept dry as water will quench the Grignard reagent

1. **Reflux apparatus set up.** Flame dry your 25 ml round bottom flask, Claisen head adapter and reflux condenser. Once the glassware has cooled down, assemble the reaction apparatus as shown on page 321 of PLKE. Fill the drying tube with Drierite. Place a rubber septa on top of the Claisen adapter.
2. **Adding the monomer.** Wear gloves for the next 3 steps. With a syringe uptake 0.24 mL of 2,5-dibromo-3-hexylthiophene. Add the dibromo-3-hexylethiophene through the septa into the 25 mL round bottom flask. With a syringe uptake 10 mL of dry THF and add through the septa into the 25 mL round bottom flask. Stir the solution at room temperature.
3. **Adding the Grignard reagent.** With a syringe uptake 1 mL of 1 M methyl magnesium chloride. Carefully add this solution through the septa to the THF/Thiophene solution—add dropwise making sure the Grignard adds directly to the THF solution and avoid having the Grignard solution drain down the side of the Claisen. Heat the reaction in a water bath at 80° C and reflux for 1 hour. Cool to room temp the last 5 minutes.

Step 2: Polymerization for formation of P3HT



4. **Adding the Nickel catalyst.** With a syringe, uptake 2 mL of the 2mg/mL of the Ni(dppp) Cl/THF solution (you are adding a total of 4 mg of catalyst). Add this solution through the septa making sure the reagent goes directly into the solution and not down the sides. Once added, heat the round bottom flask in a water bath at 80° C and reflux for 1 hour. The last 5 minutes cool down to room temp.
5. **GC/MS analysis of Grignard solution** (optional). While cooling down, remove the septa and with a pipet transfer 1 drop of the reaction mixture into GC-MS vial filled with

0.5 mL methanol. Then fill the GC-MS vial by adding 0.5 mL methylene chloride and cap. Label the reaction vial with your initials.

- 6. Precipitation of the polymer.** Quench the reaction with 1 mL of 6M HCL. Pour the reaction mixture into a 125 mL Erlenmyer flask containing 50 mL of methanol. A deep purple precipitate should now form. Allow the solution to sit overnight to form colloids that you will filter and collect during the next lab period.

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Step 3: Isolation and work-up of the H3PT polymer (done the next lab period)

1. Prepare a 'fluted' filter paper and place into a funnel which sits in an Erlenmeyer flask. Carefully pour off the clear liquid through the funnel and then finally scrap out the solid polymer into the filter paper (you can rinse with small portions of methanol to obtain the entire product). Let dry on the filter paper for 15 minutes then scrape the polymer onto a tared watch glass. Save this material for you solar cell construction next week.
2. (optional) Take an NMR and continue with soxhlet purification in this order: methanol, acetone, hexanes, chloroform.