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Flipping the Switch: Keeping the Lights On Via a Transition to Organic Photovoltaics

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Flipping the Switch: Keeping the Lights On Via a Transition to Organic Photovoltaics

A thesis submitted to
Regis College
The Honors Program
In partial fulfillment of the requirements
For Graduation with Honors

Stephen Archuleta

May 2017

Thesis written by
Stephen Archuleta

Approved by

Thesis Advisor

Thesis Reader

Accepted by

Thesis advisor

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Preface and Acknowledgements

As a freshman starting out in the Honors Program at Regis University, I was informed that I would write an Honors Thesis during my senior year. Admittedly, I was intimidated by the size and scope of this project, and wondered many times what I had gotten myself into. As this project has come to its completion, this intimidation has been replaced by a sense of adventure and exploration. Through many long advisement meetings and long nights, I have become an explorer and a researcher, unafraid of stepping into new and unfamiliar territory. I realized that writing the best thesis possible involves putting a part of yourself into your work by expressing your passions, beliefs, and experiences through the words on the page.

When I decided to write this thesis about organic photovoltaics and climate change, I merged a few of my greatest interests into one project: technology, solar energy, and environmentalism. My goal has been to write a story about these things, bringing a wide range of different ideas into conversation in a way that will engage and excite my readers. In the following chapters, I propose one possible solution for the damage inflicted upon the earth's various natural systems. While my solution may not be the pathway we ultimately take to reverse climate change, I hope that this work will encourage others to think about and act upon these issues that I am passionate about. Every chain reaction has a beginning; hopefully, this thesis can be one of those beginnings.

I would like to thank my thesis reader, Dr. Lynetta Mier for being a huge part of the thesis process. Her guidance moved me from one draft to the next, and her knowledge proved invaluable each step of the way. Dr. Mier pushed me to explore on my own through literature research, and answered the many questions that piled up between thesis meetings. Her hands-

off approach allowed me to think independently, while knowing that I had a strong support system nearby.

Thank you to my thesis reader, Dr. Jim Seibert for all his help during the editing process. With just a few small comments, Dr. Seibert's feedback helped me to strengthen my writing style and my arguments by writing with conviction. Dr. Seibert provided a much-needed alternate point of view, which allowed us to have many insightful conversations.

Thank you to Dr. Tim Bowie, Dr. Thomas Howe, Dr. Catherine Kleier, and the rest of the Honors Program for their encouragement, support, patience, and guidance during this four-year journey. Through this program, we've grown as writers and critical thinkers, ultimately preparing us for the thesis challenges we faced ahead of us.

Thank you to my Honors Thesis Writing Circle, Kristy Nguyen, Brittany Truong, Sean Ankarlo, and KC Moore, for all their support in the past year. Seeing each other grow over four years and develop our proposals and ideas into a working thesis was both encouraging and inspiring. I would also like extend a special thanks to Kristy Nguyen, with whom I spent many hours working on thesis writing and research, which she so cleverly called "thesearch." Kristy's added encouragement and motivation was incredibly valuable to me in step of this process.

Thank you to my parents, who have always supported my education and encouraged me to give my best effort in everything I do. Their support has prepared me for all that I've accomplished, and inspires me to continue to reach for the stars. Thank you to my two sisters, my family, and my friends that have encouraged and believed in me from the start. Lastly, I would like to thank God for the strength to carry on through the challenges I faced, and the knowledge and wisdom that allowed me to achieve the goals I have set for myself.

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Introduction - The Writing on the Wall

In the mid-1990s, Coca-Cola used polar bears in their advertisements, which quickly became a staple of the brand. The corporation used the polar bears to extend their public outreach, appealing to the side of us that's naturally drawn to fuzzy and cute animals. Nowadays, these creatures hold a very different symbolic purpose as a common symbol for the progression of anthropogenic climate change. Polar bears, who are now walking on thin ice (literally and figuratively) in a warming Arctic environment, are just one of the many creatures who have already been affected by warmer temperatures in their local climate. These threatened species, which make up about 30-50% of the earth's total species, may be faced with extinction by mid-century. Extinction occurs at a natural background rate; however, we are currently observing extinction rates between 1,000 and 10,000 times as high as the normal background rate (Center for Biological Diversity). Since the start of the industrial revolution, the earth's dramatically increased extinction rate has been one of the most severe symptoms of anthropogenic climate change. As the viable number of ecosystems left for the world's species is shrinking, anthropogenic climate change poses a threat to the ecosystems still withstanding human influence. Human activity has a direct effect on the world's ecosystems, which unfortunately gives humans great destructive power over all the world's species. Deforestation, habitat destruction, and severe pollution displace large populations of species from their homes, or wipe them out altogether. With so many animal and plant species at risk, global food chains are also in danger of collapse, including the food chains that humans rely on for food. Many of today's societies fail to realize the interdependence of the earth's countless species, a mistake that will have disastrous repercussions on our way of life and theirs.

Many modern societies also fail to realize the severe impact that human activity has on the world's various climate systems. On the one hand, some people simply do not make the connection between human activity and climate change; on the other hand, others see the connection between human activity and climate change, but dismiss it as false. These deniers of climate change argue that the phenomena we have observed and attributed to anthropogenic climate change are simply due to natural variances; however, around $97 \pm 1\%$ of the general scientific community has come to a consensus that climate change is being propagated by human activities (Nuccitelli, Painting and Honeycutt). Numerous independent groups and laboratories around the globe argues for the existence of a global warming trend, providing consistent data and evidence that's simply impossible to ignore or refute. Data gathered by the National Aeronautics and Space Administration (NASA) and the National Oceanic and Atmospheric Administration (NOAA) have both collected data to support this hypothesis. Data collected by NASA and NOAA in 2016 shows that 2016 was the warmest year since modern record-keeping began in 1880. The two organizations also showed that 2014 and 2015 were the warmest years on record, thus making 2016 the third year in a row to claim the title of the warmest year on record (Potter, Cabbage and McCarthy). The Intergovernmental Panel on Climate Change (IPCC), a world-renowned group that gathers climate change statistics and data, also supports these claims. In its 2013 Summary for Policymakers, the IPCC argued that nearly the entire globe has seen warmer average surface temperatures, when considering climate prediction models that include data from 1880 to the present. These linear models tend to be the most accurate, due to the length of time that has been observed (i.e. the more data, the higher accuracy). Another critical component of the argument for the existence of global warming is the increasing concentration of carbon dioxide (CO₂), methane (CH₄), and nitrous

oxide (NO), with CO₂ being the most important and commonly emitted greenhouse gas. The IPCC argues that these greenhouse gases are at their highest levels in 800,000 years, and that the concentration of CO₂ has increased by 40% since the pre-industrial era (Intergovernmental Panel on Climate Change). **Figure 1** below shows the historical CO₂ concentration over the last 400,000 years, clearly illustrating how the CO₂ concentration has risen far above the highest historical levels. As of October 2016, the global average CO₂ concentration reached 404.93 ppm, an alarming increase of 7.06% from the 378.21 ppm level seen in January 2005 (National Aeronautics and Space Administration). In recent history, atmospheric CO₂ concentrations seem to be increasing somewhat linearly, but one of the greatest worries of climate scientists is that CO₂ concentrations will grow exponentially in the future, leading to a catastrophic runaway greenhouse effect.

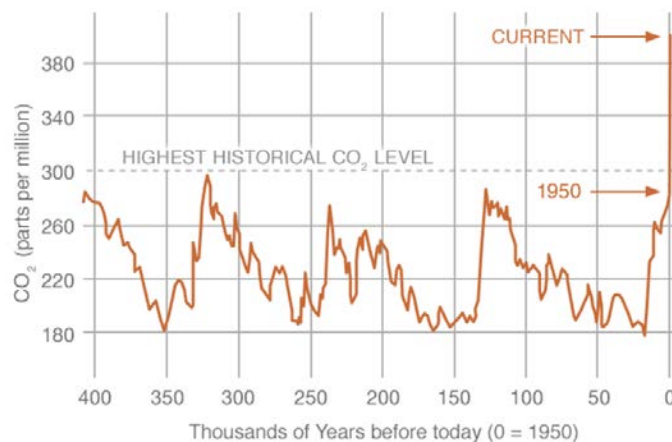


Figure 1 - Graph showing the historical concentration of CO₂ (in ppm) over the last 400,000 years (NASA and NOAA).

One reason behind this fear is the lifespan CO₂ in earth's atmosphere. Even if humans were able to completely eliminate emissions today, it would take many years for the atmospheric concentration of CO₂ to return to pre-industrial era levels. Some estimates argue that about 50% of the total anthropogenic emissions would be absorbed by natural CO₂ sinks

(vegetation and oceans) after 50 years, and about 80% over 300 years. Over time, the absorption by natural sinks decreases as the amount of excess (anthropogenic) CO₂ present decreases, which leads scientists to believe that the last 20% of the anthropogenic emissions will remain for tens, or possibly hundreds of thousands of years (Hausfather). Since we will not be able to immediately eliminate emissions and the emissions produced today will likely remain in the atmosphere for extended periods of time, the effects of climate change will persist far into the future. As emissions continue to increase, the timeline of human's destructive effect on the climate is stretched further into the future.

The most commonly discussed major effects of climate change include, but are not limited to the melting of the polar ice caps/rising sea levels, ocean acidification, and more frequent and intense severe weather events. Each of these effects works like a domino effect, causing other disastrous consequences for the organisms that experience them. Small changes in precipitation and average temperatures, can have devastating effects on the species within an ecosystem, sometimes even rendering the environment uninhabitable for certain species, thus contributing to extinction. As the effects of climate change take hold, local and global ecosystems, food chains, migration patterns, and seasonal weather patterns are severely disrupted, placing countless plant and animal species at risk. The collapse of food chains would certainly spell disaster for billions of people as well, leading to widespread famine and/or political and social unrest. Rising sea levels would threaten low-lying coastal areas, putting millions of people, homes, and businesses at risk. According to NASA, ocean levels are currently rising by about 3.4 ± 0.4 mm (0.134 ± 0.002 inches) per year, and have shown an overall rise of nearly 200 mm (7.87 inches) since 1870 (NASA). If warming trends continue to accelerate as

predicted, polar ice caps will melt and oceans will rise at an increasing rate, bringing disaster closer and closer to our present-day societies. Various independent sources have estimated the size of the populations that could be affected by rising sea levels, and although these estimates may vary widely based on the different criteria used to define the endangered populations, the numbers are nonetheless frightening. One such organization that studies climate impacts, Climate Central, provides some alarming estimates for the global population, as well as highlights nations with the highest risk. If current warming trends continue, Climate Central estimates that 147 to 216 million people around the world live in areas that may be below sea level or in regular flood levels by the end of the century. Some of the most at-risk nations include the Netherlands and Vietnam, having 47% (7.8 million) and 26% (23.4 million) of their total populations at risk for regular flooding in the future, respectively. The percentage of the Chinese population is much lower at 4%, but this percentage equates to nearly 50.5 million people at risk (Climate Central). Rising sea levels will influence where people can live, as well as the places they're able to work and the industries they work for. In the United States, the Environmental Protection Agency (EPA) estimates that 58% of the national gross domestic product (GDP) lies in coastal areas threatened by coastal flooding (Environmental Protection Agency). Tourism, recreation, offshore drilling, marine transportation, and fishing industries will be greatly affected by rising sea levels. Developed nations have other large contributors to their GDP to lessen the impact of losing these coastal industries; however, there are many developing nations and economies that will feel the full destructive force of rising sea levels. In the future, we will be able to move our homes and businesses further away from the shore to preserve our industries and way of life, but we will not be able to escape the far-reaching effects and enormous scope of climate change.

As our world struggles to maintain the balance of its many natural systems and processes, we as humans have proven that we can shift this balance. To lessen our impact on the future global climate, society must move towards more sustainable practices to fulfill our needs. At the root of our current dilemma is the debate over fossil fuels, which are by far our most popular energy source. Fossil fuels are consumed by various economic sectors, with some of the biggest contributors to CO₂ emissions being industry, transportation, and electricity and heat production (**Figure 2**). Together, these categories make up 21%, 15%, and 25% of our greenhouse gas emissions, respectively (Intergovernmental Panel on Climate Change). Replacing fossil fuels with renewable energy sources in these economic sectors would make a huge impact in the global effort to reduce emissions and slow the accelerating greenhouse effect our current models predict. As cliché as it sounds, renewable energy sources are the energy source of the future, simply because they are always available future generations. Many renewable energy sources are also appealing to developing nations, who may currently lack the infrastructure necessary to fully benefit from fossil fuels. Oil and coal, the largest sources of non-renewable energy, both require a large amount of infrastructure to obtain and refine them before they are ready for consumption and energy production. Rather than meeting energy demands with fossil fuel sources, developing nations have the benefit and ability to jump straight to renewable energy sources, a pathway which is much cheaper in the long run. For the nearly 1.2 billion people around the world (95% of which living in developing nations) who did not have access to electricity in 2016, finding an economically feasible renewable energy source would dramatically improve their quality of life and expedite their entry into the modernized world (International Energy Agency).

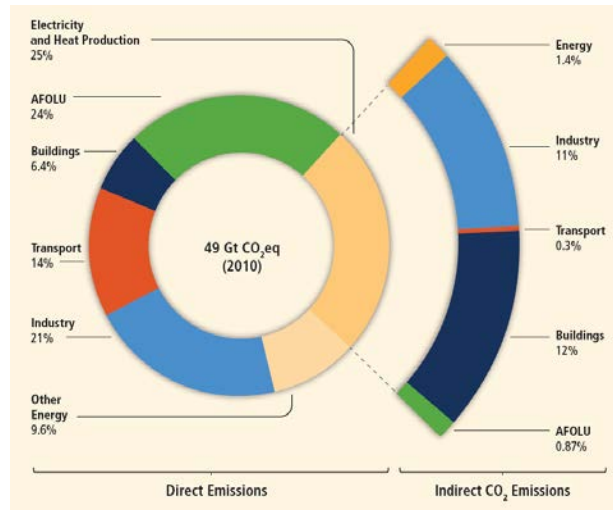


Figure 2 - Breakdown of greenhouse gas emissions in the U.S. by economic sector in 2010 (*Intergovernmental Panel on Climate Change*).

When analyzing the value behind different renewable energy sources, one must look at the abundance, potential electricity production, and environmental impact of utilizing the resource. Hydroelectric dams have the potential to generate power on a large scale, but they are poor performers in the other two categories. Hydroelectric dams typically create artificial lakes behind them, drastically changing the local landscape and ecosystem and leaving a large environmental footprint. Hydroelectric power is also restricted to where large rivers are present, severely limiting their abundance and availability. Wind turbines and wind farms have a very minimal environmental impact, although they are less efficient. Additionally, wind turbines are limited to regions where wind blows regularly, thus restricting their availability for large-scale power generation. Among the most popular forms of renewable energy, solar power is the only renewable energy source that meets the three criteria described before. Along with wind turbines, solar panels have a very minimal environmental impact, aside from the manufacturing process. However, solar panels hold the advantage over wind power in that they can be implemented in areas that already have an environmental impact, including on buildings,

rooftops, in dumps, etc. Secondly, solar energy isn't geographically restricted to the location of the energy source, due to the abundance of sunlight everywhere on earth. Lastly, solar energy is by far the renewable energy source with the highest potential energy output. In fact, solar energy is the only renewable energy source that can fully meet our energy demands. Abundance of solar energy is clearly not an issue, as supported by a few quick calculations. According to the International Energy Agency, the total world electricity production was approximately 29,903 TWh, or 2.72 TW in 2014 (International Energy Agency). We also know that the earth receives approximately 1 kilowatt per square meter (1 kW/m^2) of energy from the sun, after considering the absorption and reflection of sunlight by the atmosphere and clouds. Given the surface area of the state of Colorado ($2.70 \times 10^{11} \text{ m}^2$), we find that the total energy from the sun that hits the surface of Colorado at noon is about 270 TW. The most efficient solar cells currently marketed are silicon-based photovoltaic cells, which typically offer a maximum power conversion efficiency of around 34% (Schulze and Schmidt). Although this efficiency seems rather low, harnessing just 34% of the total light energy received by the earth (or even just on the surface of Colorado) at any given moment would still be far more than enough to satisfy global energy demands. If we were to cover the state of Colorado with solar panels with an efficiency of 34%, we would be able to harness about 91.7 TW of power at maximum production, which is 33.4 times greater than the global electricity production in 2014. Although we will never resort to covering the surface of an entire state with solar panels to meet our energy demands, this example demonstrates the immense potential electricity production that we can achieve through a widespread adoption of solar energy.

One of the greatest advantages to solar energy is that it is a rich and developing field, arguably unlike other renewable energy sources, including wind and hydroelectric. Although improvements can be made to any of the big three renewables, only solar energy possesses the potential for huge technological advances to increase efficiency and power output. Solar energy research is still progressing and finding new technologies to harness the sun's everlasting power, while wind and hydroelectric merely have the technology to harness what's currently available without much room for innovation. Silicon-based photovoltaics may be the pioneering technology of the solar energy world, but there are dozens of other technologies that are currently being researched or have been recently developed. One of the most promising of these developing solar energy technologies are organic photovoltaics (OPVs), which use organic molecules to carry out the conversion of light into electrical power (the photoelectric effect). Although organic solar cells currently have power conversion efficiencies much lower than that of silicon-based solar cells, they are cheaper and easier to manufacture. Additionally, OPVs are thin and flexible, allowing them to be used in many applications where silicon-based cells are not applicable. In the following three chapters, I will provide a thorough analysis of many different aspects of OPVs. Chapter 2 will describe how power conversion occurs in the active layer of an OPV, as well as explore how photonic upconversion (another emerging technology in the solar energy field) can increase power conversion efficiency. Chapter 3 will analyze the advantages and disadvantages to different types of molecules commonly used within the active layer of the solar cell, where the photoelectric effect takes place. Lastly, Chapter 4 will describe how the many layers of OPVs are oriented and the construction processes used to build a functioning solar cell.

Chapter 1 - How Do Organic Photovoltaics Work?

In organic photovoltaics (OPVs), the overall process of electricity generation occurs through four steps: exciton formation, exciton diffusion, electron transfer through charge separation, and charge recombination. In the first step of this process, a photon of light within a particular range of wavelengths is absorbed by the donor molecule. In the ground state of the molecule, all electrons are in the lowest possible energy levels; thus, a ground state electron occupies what is known as the highest-occupied molecular orbital (HOMO). Higher energy electronic orbitals of a ground state molecule are left unoccupied, including the lowest unoccupied molecular orbital (LUMO). When the molecule absorbs the energy of the photon, an electron from the ground state is promoted from the HOMO energy level to the LUMO energy level, which, thus creating an excited donor molecule with an increased energy. The excited molecule contains an electron (e^-) paired with a positive "hole" (h^+), which are defined as negative and positive charge carriers, respectively. In the second step, this pairing, known as an exciton, diffuses throughout the material in which it exists, always remaining as an excited electron and hole pair. The process of exciton diffusion is illustrated in **Figure 3** below.

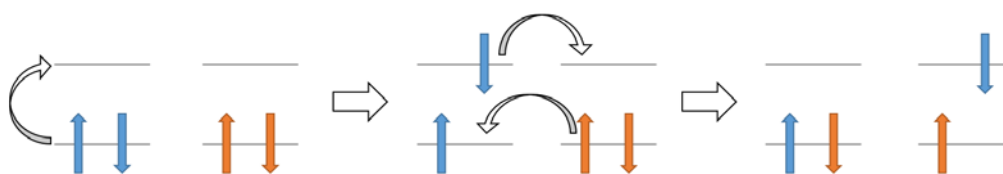


Figure 3 - Exciton formation (left) and exciton diffusion (center and right) between two donor molecules.

The third step in this process occurs at the heterojunction of the solar cell, which is the region where the donor and acceptor molecules meet to allow electron transfer. At this junction, the excited electron moves to the acceptor molecule, making it negatively charged, while the hole stays with the donor molecule, making it positively charged. The movement of

electrons in this step occurs through a process known as charge separation, which is governed by Marcus Theory and Marcus electron transfer (Marcus). The charged molecules formed in this process then create an electric field at the heterojunction that facilitates further charge separation, which drives current through the circuit. In the cell shown below in **Figure 4**, the electron blocking layer and the hole blocking layer also help to drive current through the circuit by ensuring that the electrons and holes flow in the correct direction.

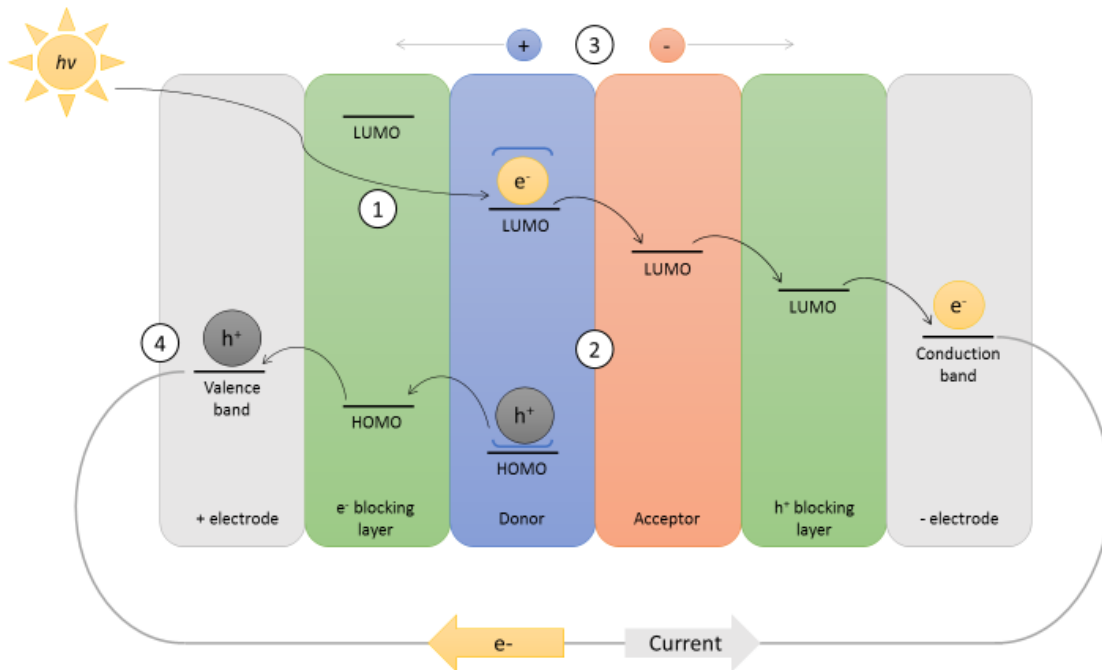


Figure 4 - Diagram illustrating the layers of an OPV and the four steps of electricity generation.

One of the challenges of OPVs is separating the charges of the exciton pair at the donor-acceptor heterojunction before the electron returns to the ground state (Kippelen and Brédas). In order to do so, the exciton must rapidly diffuse through the donor layer to get to the heterojunction. After the charges have been separated at the heterojunction of the cell, they move towards opposite electrodes. In addition to the electric field generated at the

heterojunction, the conservation of energy principle also helps to drive the current through the circuit. Electrons lose energy by moving “downhill” in the system, while the positive holes gain this lost energy by moving “uphill” in the system. These changes in energy cancel each other out to yield a net zero change in energy, in accordance with the conservation of energy principle. The electron then moves towards the negative electrode, through the external circuit, and towards the positive electrode, as shown in **Figure 4** above. Meanwhile, the holes move towards the positive electrode, where they recombine with electrons that travelled around the external circuit. In essence, the movement of electrons through the external circuit generates electricity, and the organic photovoltaics that make up the active layer provide the “push” that these electrons need to flow through the circuit. The orientation of the active layer molecules and the composition of the other layers in the cell greatly affect the ability for current to flow throughout the cell, and will be discussed in depth in Chapter 4.

The process of light absorption in the first step introduces a major design challenge for researchers and manufacturers of organic photovoltaics. In order to promote an electron to the excited state of the molecule, the incoming light must have a higher energy than the bandgap of the molecule. The bandgap is defined as the difference in energy between the molecule’s ground state and excited state. Incoming light that does not have enough energy to promote the electron to the excited state is also called sub-band gap light, and cannot be used in the production of electricity. Due to the structure, electronic properties, and bandgap of a molecule, the wavelengths of light that donor molecules will absorb are typically within a narrow range. As a result, the percentage of the total solar spectrum that can be absorbed and transmitted as electricity can be relatively limited, contributing to low power conversion efficiency. Power

conversion efficiency is defined as the ratio between the electricity generated by a device and the total energy going into the device. **Figure 5** shown below displays the solar irradiance spectrum both at sea level and above the atmosphere. The highest intensity output is in the visible light region, which corresponds to wavelengths between 400 and 700 nanometers. Most molecules used in organic photovoltaics absorb in the visible light region to take advantage of the high irradiance in this region of the solar spectrum. The wavelength of light λ is inversely related to the energy of the photon via the equation $E = \frac{hc}{\lambda}$, dictating that the energy of the photon increases as the wavelength decreases. Visible light has a shorter wavelength than infrared light (300-700 nm vs. 700-1,000,000 nm), which means that visible light photons are higher in energy than infrared light photons. The conservation of energy principle states that the change in energy of the molecule is equal to the energy of the photon; therefore, a higher energy photon will result in a higher energy absorber molecule. In **Figure 4** above, the electron is seen moving “downhill” in the system. If an electron starts out with a higher energy in the system, as if it absorbed a photon of visible light instead of infrared light, it will end with a higher energy as well. Electrons with higher energy can produce more electricity, therefore increasing the electricity production of the cell. Incorporating donor/absorber molecules that absorb high energy visible light and/or highly abundant infrared light is a major goal for OPV research, as it will greatly increase the power output of these cells.

As can be seen from **Figure 5** below, the observed solar spectrum at sea level is different than the observed solar spectrum without atmospheric absorption, i.e. in space. Due to varying atmospheric conditions and solar irradiance levels at different locations, measured efficiencies of solar cells produced and tested throughout the world were challenging to compare. To

remedy this, a set of standard conditions were created to normalize experimental results, thereby allowing fair and accurate comparisons among different solar cells. The standard light sources used were defined by national laboratories, in conjunction with the American Society for Testing and Materials (ASTM). The most recent standard solar spectra, titled ASTM G173-03, was developed using previous standard spectra in 2003 (National Renewable Energy Laboratory). One of the characteristics of this standard is the air mass coefficient, which describes the direct optical path length that the solar light takes through the atmosphere. Commonly abbreviated as AM, the air mass coefficient is equal to $\frac{1}{\cos\theta}$, where θ is equal to the zenith angle in degrees. The zenith angle is the angle between the sun and the normal, or perpendicular of the surface of the solar panel. For all terrestrial standard comparisons, the air mass coefficient is equal to 1.5 (θ is equal to 48°), commonly giving the name “AM 1.5” to the spectra associated with this standard. In addition to the air mass coefficient, the irradiance for standard testing conditions is set to 1000 W/m^2 , recreating the conditions of a solar panel pointed directly at the sun at noon near the spring and autumn equinoxes in the continental United States (Green Rhino Energy).

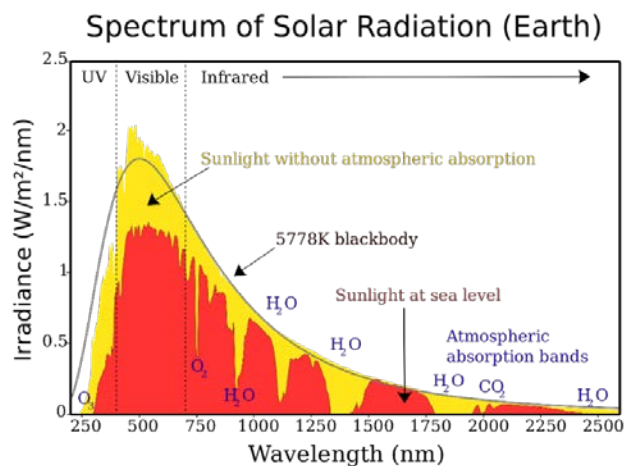


Figure 5 - Solar radiation spectrum plotting wavelength vs. irradiance (Wikimedia Commons) (Nick84).

When looking at the individual steps of the electricity generation process, it becomes apparent that there are many opportunities for future research and development in organic photovoltaic technology. In each of the steps discussed above, different physical and chemical processes are taking place, allowing for a broad range of possibilities to increase the efficiency of each step. In the first step dealing with light absorption, a common research goal is to find donor molecules with broad absorption spectra, thereby maximizing the amount of the solar spectrum harnessed by the cell. In addition to this, molecules that absorb visible light provide much more efficient electricity generation than those that only absorb in the infrared or ultraviolet regions of the solar spectrum. In the second step, finding molecules with the lowest possible resistance, or the highest possible electron mobility will encourage the greatest rate of exciton diffusion towards the donor-acceptor heterojunction. Maximizing the rate of diffusion serves to decrease the possibility of the electron returning to the ground state of the donor molecule before reaching the acceptor molecule at the interface. In the third step of charge separation, the difference between energy levels of the donor-acceptor pair plays a critical role. As the difference in energy levels decreases, the energy lost in the electron's downhill movement through the system will also decrease, therefore decreasing the energy density of the solar cell.

One of the most intriguing areas of research in organic photovoltaics, called photonic upconversion, aims to increase the power conversion efficiency of a cell by indirectly increasing the amount of the solar spectrum that is harnessed by the donor molecules in OPVs. Since most molecules used in OPVs absorb visible light, the lower energy infrared light, which makes up the largest portion of the solar spectrum, is unused. Photonic upconversion seeks to harness this

lost light through the addition of an upconverting layer in the solar cell. The upconverting layer is composed of sensitizer and emitter molecules that convert sub-bandgap light into light of higher energy, which can then be absorbed by the donor molecule and used to generate current.

It is necessary to first understand the ideas of absorption, fluorescence, intersystem crossing (ISC), and phosphorescence (each shown below in **Figure 6**) in order to fully explain and understand the upconversion process. After absorption, an electron (represented by the small black arrows in the diagram) in the S_1 state can fluoresce to return to the ground state (S_0). The electron may also undergo intersystem crossing to the lowest energy triplet state (T_1), where the electron may then phosphoresce back to the S_0 state. The most important idea to remember here is that fluorescence occurs from the excited S_1 state, while phosphorescence occurs from the excited T_1 state.

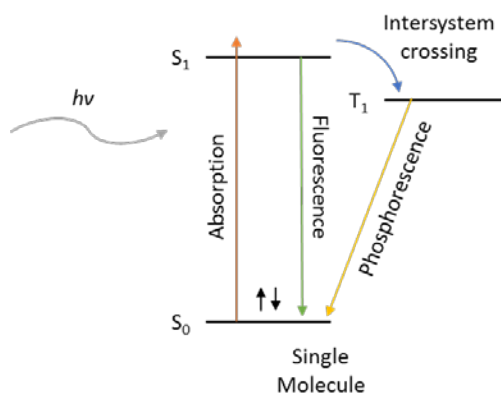


Figure 6 - Energy level diagram showing absorption, fluorescence, intersystem crossing, and phosphorescence.

Fluorescence and phosphorescence are both radiative processes; however, fluorescence occurs much quicker than phosphorescence. Fluorescence occurs on the order of 100 picoseconds to 10 nanoseconds (10^{-10} - 10^{-8} seconds), while phosphorescence occurs on the order

of 100 nanoseconds to 10 milliseconds (10^{-7} - 10^{-2} seconds). These timescales represent the lifetime of the electron in the respective excited states, or the length of time that the electron will remain in the excited state before decaying to the ground state. Therefore, an electron will remain in the T_1 state between 10 and 100 million times longer than it will remain in the longest lived S_1 states because phosphorescence is a slower process than fluorescence. The success of upconversion is highly dependent on the fact that excited triplet states have a longer lifetime than excited singlet states.

The first step of photonic upconversion begins when incident light is absorbed by the sensitizer molecule, promoting an electron to the excited S_1 state, as shown in **Figure 7** below. The light that is absorbed is sub-bandgap light, which is not absorbed by the donor molecule. The sensitizer molecule is chosen so that the excited electron preferentially moves to the T_1 state through intersystem crossing (ISC). In order for the upconversion process to continue, ISC must be faster than the competing process of fluorescence. The goal of this first step is to trap the excited sensitizer molecules in the T_1 state. To minimize the energy sacrificed through ISC (which inherently causes a loss of energy, being a “downhill” process), molecules are chosen so that the gap between the singlet and triplet state energy levels is also minimized.

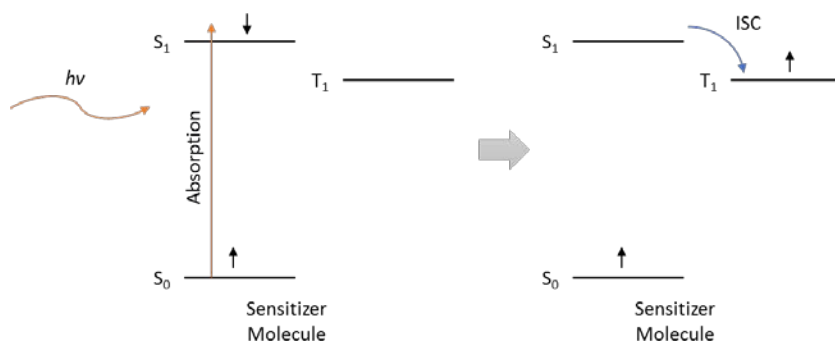


Figure 7 - First step of photonic upconversion, showing light absorption by the sensitizer molecule, then intersystem crossing.

Once in the T_1 state, the excited electron of the sensitizer molecule transfers its energy to the ground state electron of the emitter molecule through a process known as triplet energy transfer (TET). In order for the upconversion process to continue, TET must be faster than the competing process of phosphorescence. The second step of the upconversion process ends with the electrons of the sensitizer molecule returned to the S_0 state, and the electron of the emitter molecule excited to the T_1 state, as shown in **Figure 8** below.

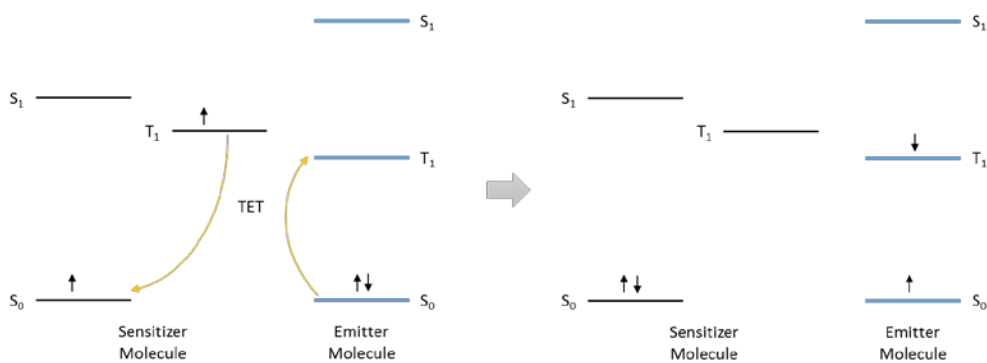


Figure 8 - Second step of photonic upconversion, showing triplet energy transfer (TET).

In the third step, triplet-triplet annihilation (TTA) occurs between two emitter molecules with electrons in the T_1 state, as shown below in **Figure 9**. In this process, the T_1 state electron from Emitter Molecule 2 is promoted to the S_1 state by gaining the energy of the T_1 state electron from Emitter Molecule 1. TTA requires that the energy level of the emitter molecule's S_1 state is just under double the energy level of its T_1 state. At the end of the third step, one emitter molecule is quenched to the S_0 state, while another is in the excited S_1 state.

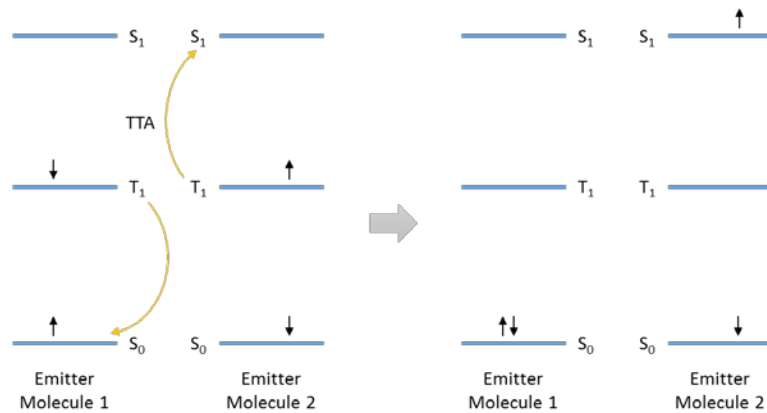


Figure 9 - Third step of photonic upconversion, showing triplet-triplet annihilation (TTA).

In the fourth step of the upconversion process, the excited emitter molecule emits a photon through fluorescence, as shown below in **Figure 10**. Although the wavelength of the emitted photon varies depending on which molecules are chosen, the emitted photon will have a higher energy than the bandgap of the donor molecule, thus allowing upconverted light to promote an electron from the ground state to the excited state. The net result of the three steps in the upconversion process is the “combination” of two lower energy photons absorbed by the sensitizer molecules into one higher energy photon given off by an emitter molecule. The unused portion of the solar spectrum can be upconverted and harnessed by the solar cell, therefore increasing the cell’s power conversion efficiency (PCE). Some estimates argue that upconversion may increase maximum PCE to around 43% for devices with a bandgap of 704 nm (1.76 eV, red end of visible spectrum), while crystalline silicon cells could see increases in efficiency from 34% to about 38% (Schulze and Schmidt). Since the bandgap for silicon is already in the infrared region of the spectrum (1,117 nm), the benefit of upconversion for silicon-based cells is somewhat limited.

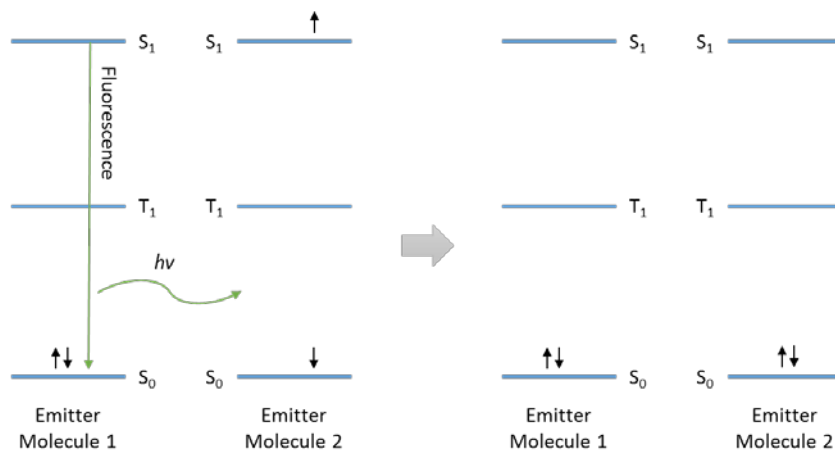


Figure 10 - Fourth step of photonic upconversion, showing fluorescence by the emitter molecule.

Chapter 2 - Molecules of the Active Layer

Chapter 2 described the process for electricity generation using organic photovoltaics through four main steps. Of these four steps, the first three take place in the active layer: exciton formation, exciton diffusion, and charge separation. The active layer molecules, typically designated as donor or acceptor molecules, therefore hold great influence over the power conversion efficiency of the cell. Their significance has sparked the interest of many researchers, who explore different combinations and types of molecules that can be used as donors or acceptors. In each of these target molecules, there are certain properties that make them suitable for use in the active layer; these properties will be discussed in depth in this chapter. A few examples of common donor and acceptor molecules will also be compared against the desired properties for each respective molecule.

One of the most intriguing features of organic photovoltaics comes from their thin, lightweight, and flexible structure. Due to these unique design characteristics, OPVs are theoretically able to be used in applications that current silicon-based solar cells are not suited for. The hope is that many different objects may be coated in OPVs, such as cars, cell phones, electronics, homes, office buildings, and skyscrapers. This technology allows for a more efficient use of space than much heavier and bulkier silicon-based solar cells, which require more space and supporting structure to be used on a large scale. In order to make these applications plausible, OPVs must be able to withstand the elements they are exposed to. Donor and acceptor molecules that exhibit thermal, air, and water stability will be necessary if OPVs are to be used in these promising new ways.

In addition to being stable in the presence of air, water, and heat, OPVs must also maintain structural integrity over time. In other words, the solar cell must be durable enough to withstand the elements without breaking, tearing, or leaking. There are two main reasons for this: efficiency and safety. Marketed solar cells are held to strict power conversion efficiency standards, including that their efficiency cannot degrade too quickly over time, otherwise the initial investment is never regained. National Renewable Energy Laboratory, a national leader in solar energy research, argues that a solar cell dropping below 80% efficiency of their original starting point (i.e. a cell starting out at 30% and dropping below 24%) after 25 years of operation constitutes a failure (Jordan and Kurtz). However, this is not a generally accepted guideline, since efficiency degradation rates vary so widely among different types of solar technology. For example, a highly efficient solar cell may degrade by a significant amount (50-60% of its original efficiency), but still maintain a higher efficiency than less efficient solar cells that haven't degraded as quickly. If the power conversion efficiency of OPVs degrades slower than that of silicon-based cells, OPVs might become more highly valued, despite their lower initial power conversion efficiency. On the other hand, safety of the environment and the public becomes a concern when dealing with the compounds used in OPVs. Using less toxic compounds in the cell necessary to minimize possible environmental impact, should the cell ever break apart.

Another way to maximize the power conversion efficiency of a solar cell is to find absorber/donor molecules with the broadest absorption spectrum. Molecules that exhibit broad absorption bands in the visible and infrared regions will be able to take advantage of the sun's highest intensity and largest output regions, respectively. Finding molecules that absorb in the visible region of light will also heavily contribute to increasing efficiency, for reasons discussed in

depth in the previous chapter. In some cases, a mixture of absorber molecules may be used to create a donor material with enhanced absorption properties. If the absorber/donor molecules in the mixture have non-overlapping spectra or very different maximum absorption wavelengths, the resultant combined absorption spectrum spans a much larger wavelength range than if a single absorber molecule is used. The biggest challenge in adopting this design strategy lies in matching the energy levels of both donor types to the acceptor molecule.

To ensure that the exciton can reach the heterojunction before the electron decays back to the ground state, the singlet state must be long-lived. Additionally, for the exciton to diffuse throughout the donor material to the heterojunction (second step of electricity generation), the excited donor material must have high electron mobility. Once the exciton reaches the heterojunction, charge separation occurs (third step of electricity generation). The electrons move from the donor molecules to the acceptor molecules, while the holes stay with the donor molecules. Charge separation occurs due to matching energy levels between the donor and acceptor molecules. The electron must move downhill through the system, while the hole moves “uphill.” Therefore, the excited singlet state of the acceptor molecule must be lower in energy than the excited singlet state of the donor molecule, as shown below in **Figure 11**. Since the donor molecule becomes positively charged after charge separation occurs, molecules that are hole-stabilizing, or stable as cations (positively charged species), must be used. If the donor molecule is poorly stabilized as a cation, it will prefer to remain in its much more stable neutral form, making charge separation improbable and power conversion less efficient.

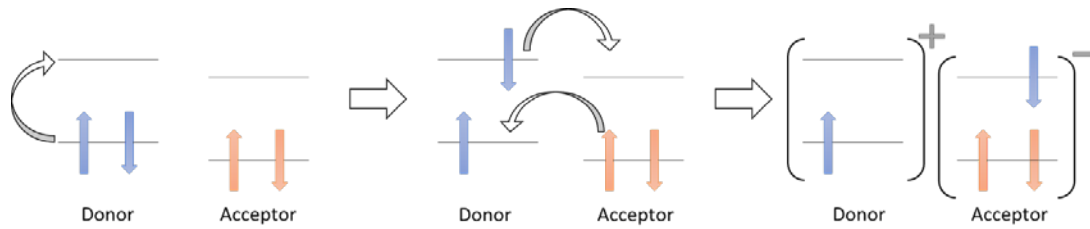


Figure 11 - Charge separation between a donor molecule (blue) and an acceptor molecule (green) in the active layer. Exciton formation is shown on the left, while charge separation is shown in the center and on the right.

One of the most effective donor species used in OPVs has typically been the conductive polymer, poly-3-hexylthiophene (P3HT); the structure of the monomer unit is illustrated alongside the molecule's absorption spectrum in **Figure 12** below. This figure shows that P3HT absorbs well in the visible region, showing band gaps of about 540 nm in solution and 636 nm in thin film (Cook, Furube and Katoh). The presence of the band gap at this wavelength allows for thin films of P3HT to absorb a large portion of the visible spectrum, thus helping to maximize power conversion efficiency. However, this band gap prevents the donor molecule from being able to harness the infrared portion of the solar spectrum, unlike silicon-based solar cells. Special attention should be given to the thin film absorption spectra, since P3HT is typically present as a thin film in the active layer of the cell.

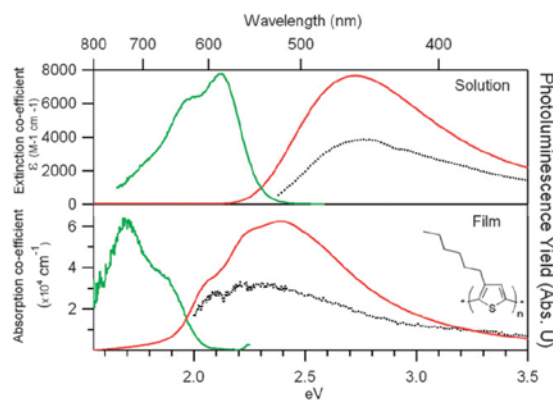


Figure 12 - Spectra for P3HT in solution (top) and thin film (bottom), displaying absorption extinction coefficient (red line), emission spectrum (green line), and excitation spectrum (black dotted line). (Cook, Furube and Katoh)

After instantaneous excitation, the excited singlet state of P3HT in solution exhibits a lifetime of around 600 picoseconds (6×10^{-10} seconds), with a quantum yield of 0.33 ± 0.07 (Cook, Furube and Katoh). The quantum yield describes the fraction of molecules that relax through fluorescence out of the total molecules excited (remember that fluorescence is just one of many relaxation pathways). As the quantum yield approaches 1.00, the fraction of molecules that relax through fluorescence increases, therefore decreasing the frequency of relaxation through alternate pathways. As a semi-conductive polymer, P3HT exhibits high electron mobility, promoting a high rate of exciton diffusion throughout the donor material. Once the exciton reaches the donor-acceptor interface, the excited electron is transferred to the acceptor molecule, a process taking about 100-120 femtoseconds (1×10^{-13} seconds) (Guo, Ohkita and Bente) (Ribas, Steer and Ruther). The back-electron transfer rate, which occurs when the excited electron given to the acceptor molecule recombines with the hole of the donor molecule, is around 800 picoseconds (8×10^{-10} seconds) for 70% of species, and has been estimated at 1 microsecond (1×10^{-6} seconds) for the remaining 30% of species (Guo, Ohkita and Bente).

When comparing the properties of the donor and acceptor molecules, one might notice numerous similarities. For example, acceptor molecules must also have high electron mobility to minimize electrical resistance. The acceptor molecule is negatively charged after charge separation occurs, and therefore must be able to efficiently transport electrons through the acceptor material and on to the external circuit. Efficient electron transport requires that the acceptor molecule must be stable as an anion, or a negatively charged species. If the anionic acceptor species isn't stabilized, undesired charge recombination will be more likely to occur at

the heterojunction because the charged state of the molecule would not be preferred. Charge recombination regenerates the neutral donor and acceptor molecules present before incident light was absorbed, therefore inhibiting the process of power conversion within the cell. A high rate of back electron transfer will decrease the power conversion efficiency of the cell; once again, minimizing this rate can be done by selecting molecules that are stable as charged species.

The most effective acceptor species used in OPVs have typically been fullerene derivatives (or “buckyballs”, as many people may recognize them), namely 6,6-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) and its PC₇₀BM counterpart, both of which are shown in **Figure 13** below. Fullerenes have shown great success as electron acceptors, exhibiting high electron affinity and mobility, isotropic charge transport (equal in magnitude regardless of direction of charge transport), and reversible electrochemical reduction (Lin and Zhan). In particular, PCBM molecules remain stable even after accepting up to four electrons (obtaining a -4 charge), due to the stabilization provided by the extensive conjugation within the buckyball portion of the molecule. Cells using a P3HT-PCBM donor-acceptor combination have demonstrated the highest power conversion efficiency (PCE) among bulk heterojunction OPVs, showing PCEs as high as 7% as of 2010 (Guo, Ohkita and Benten). In addition to possessing the electronic properties necessary as acceptor molecules, fullerenes are also able to form nanoscale morphological networks with donor molecules, allowing a bulk heterojunction active layer to be used. Despite these advantageous characteristics, PCBM molecules suffer from the same stability issues as P3HT molecules, exhibiting poor stability in water and air, posing huge design challenges for large-scale applications of cells with this type of active layer.

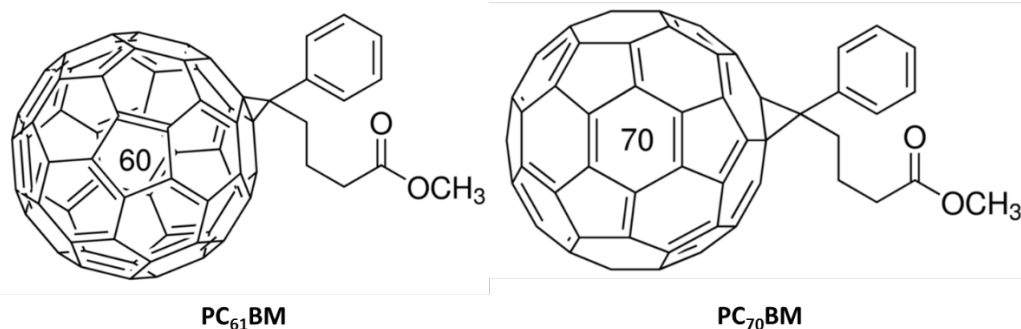


Figure 13 - Structure of 6,6-phenyl-C₆₁-butyric acid methyl ester and 6,6-phenyl-C₇₀-butyric acid methyl ester.

The absorption spectra for PCBM is weak in the visible region, but strong in the UV region. However, the weak visible absorption arguably doesn't hinder the device performance, since PCBM molecules serve as electron acceptors and are not required to exist in the excited state. Since the cell doesn't receive much UV light both in laboratory testing with the AM 1.5 standard spectrum and in real-world settings, PCBM isn't often present in the excited state. Therefore, its electrons remain in the ground state, and the molecule will readily accept the donor molecule's excited electron. Due to this spectral behavior, knowing the lifetime of the excited state of PCBM is much less important than for P3HT, because this excited state is seldom present and competing processes are not present.

Finding alternatives to fullerene acceptor molecules has quickly become a popular research topic in recent years. Most of this work has been focused around n-type (electron accepting and transporting) semiconducting polymers. The absorption spectra of these polymers often lie in the visible region, and their ease of chemical modification allows for manipulation of the absorption spectrum, unlike their PCBM competitors. The first all-polymer solar cells used cyanated poly(phenylenevinylene)s (CN-PPV, shown below in **Figure 14**) as polymer acceptor molecules, achieving a PCE of 2.0% (Lin and Zhan). Despite this early success, research shifted

away from the use of CN-PPV as acceptor molecules. Research now focuses on the use of other promising groups as acceptor molecules.

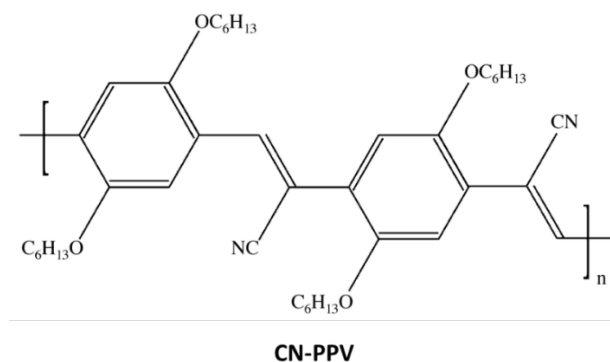


Figure 14 - Structure of a cyanated poly(phenylenevinylene) monomer unit.

Perylene diimides, a derivative of the parent molecule of perylene (structures shown below in **Figure 15**) and many other amide/imide-type molecules have sparked considerable interest as alternative acceptor or donor molecules. This interest is backed largely due to their generally great photostability and high receptivity to chemical modification at both the nitrogen atoms and the bay position carbons near the center of the atom, allowing easy modification of optical and electronic properties of the molecules. The ease of modification may allow PDI molecules to be manipulated in a way that will allow them to accept multiple charges. When a molecule can accept multiple charges, similarly to PCBM, the electron mobility going out (towards the electrode and external circuit) is allowed to be much lower because the molecule can remain stable as a multiply charged ion. Therefore, adding functional groups that allow for a highly-charged molecule may help to increase the electron mobility, as well as the solubility of the molecule. In many cases, PDI derivatives have low solubility/a strong tendency to aggregate, causing formation of large crystalline aggregate domains within the active layer. In the presence of larger aggregate domains, excitons may not be able to diffuse far enough to reach a

heterojunction outside of the domain, severely limiting the PCE of the device. Some research suggests that groups at the bay positions of the molecules will decrease the intermolecular attractions that cause aggregation by introducing steric, or spatial crowding effects (the bay positions are indicated by arrows on the PTCDA molecule in **Figure 15** below) (Huang, Barlow and Marder). Picking the right solvents is also crucial for ensuring that PDI molecules may be dissolved and processed into layers for the cell. Another tactic found to combat aggregation is the use of dimer PDI molecules. In one case, a dimer PDI material saw aggregate domain size reduced by 90%, and PCE increased from 0.13% to 4.03% (Zhang, Zhan and Hou).

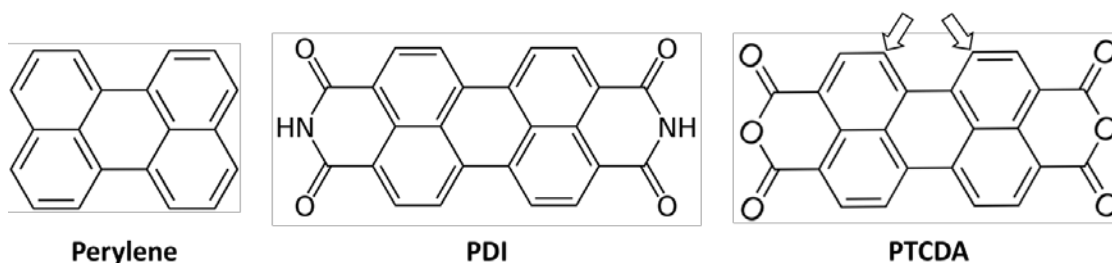


Figure 15 - Structures of perylene, perylene diimides (PDI), and perylenetetracarboxylic dianhydride (PTCDA), with the bay positions labeled by arrows on the PTCDA molecule. These positions are mirrored on the other side of the molecule, as well.

These PDI and perylene molecules exhibit strong absorption spectra in the visible region, in addition to high electron mobility and affinity, much like competing fullerene derivatives. The absorption spectra for a typical PDI molecule is shown below in **Figure 16**. Many of these all-polymer active layer blends have achieved power conversion efficiencies between 0.37% and 4.1% (Lin and Zhan). Although these PCEs are lower than that of P3HT:PCBM devices, all-polymer devices still hold great significance in research and application, due to their high stability in air, water, and heat.

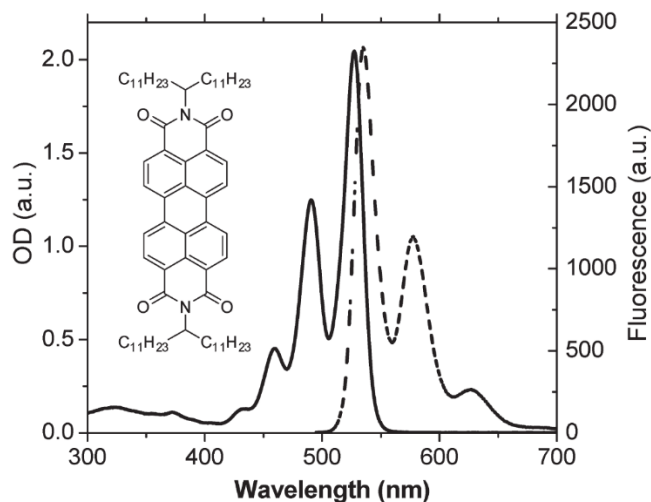


Figure 16 - Absorption (solid line) and emission (dotted line) spectra for a typical PDI molecule in toluene solution, with the structure shown in the spectra (Huang, Barlow and Marder).

In addition to having a favorable absorption spectrum as a donor molecule, perylene derivatives also possess a long-lived excited singlet state. For a perylene molecule, the excited singlet state lifetime has been measured at 3.78 nanoseconds (3.78×10^{-9} seconds), about 6 times longer than the measured singlet lifetime of P3HT acceptor molecules (6×10^{-10} seconds) (Ribas, Steer and Ruther). This longer lifetime may allow for a greater portion of excitons to diffuse to the heterojunction before they decay to the ground state, thus increasing the PCE. Additionally, the quantum yield of perylene has been measured at 0.89, over twice as high as that of the P3HT competitor (Ribas, Steer and Ruther). As the quantum yield increases, the proportion of molecules that relax through non-radiative pathways decreases, which may help to increase power conversion efficiency. Relaxation through fluorescence is far more common for perylene molecules than for P3HT molecules; in other words, competing relaxation processes, such as ISC and non-radiative relaxation occur less frequently than in P3HT molecules. Therefore, the perylene molecule is more likely to be found in the excited singlet state, also possibly contributing to a higher PCE.

The family of perylene-based molecules has not only been investigated for use as donor and acceptor molecules, but also for use as an upconverting molecule in the active layer (for a detailed description of upconversion, refer to Chapter 2). Past efforts to increase PCE through upconversion have been centered around the use of solid matrices doped with different upconverting lanthanide ions, such as Dy^{3+} , Er^{3+} , Gd^{3+} , Tm^{3+} , or Yb^{3+} (Schulze and Schmidt). Although they've provided the highest upconversion efficiencies for inorganic materials, the manufacturing of these upconverting layers in large quantities may prove to be both difficult and expensive, due to their presence as rare-earth metals. Perylene derivatives used as emitter and sensitizer molecules may serve as alternatives to inorganic upconverting systems, possessing the advantage of a cheaper and easier manufacturing process. The molecules selected for upconversion must be carefully selected, with great attention given to their absorption and emission spectra. To minimize self-absorption, the emission band of the emitter and the absorption bands of the emitter and sensitizer molecules must have as little overlap as possible. In other words, the goal is to make sure that the light emitted from the emitter molecule isn't absorbed by either the sensitizer or emitter molecules. Additionally, the molecules in the active layer must have high transmission in the absorption region of the sensitizer molecules, allowing the greatest amount of unused light to reach the upconverting layer (Schulze and Schmidt).

Chapter 3 – Building an Organic Photovoltaic Cell

In Chapter 2, a diagram illustrating the four steps in the process of electricity generation through an organic photovoltaic cell was introduced. This same diagram (**Figure 4** shown once again below) and the associated steps were briefly described to provide a fundamental understanding of these processes. However, discussions about the details of the layers, along with their construction, have been deferred until now. This chapter will discuss some of the overall construction processes that are used to assemble the different layers into a completed organic photovoltaic cell (OPV), as well as the design considerations associated with these processes. In Chapter 3, the molecules of the active layer were covered in depth, and will be briefly reviewed here. The molecules used in the other layers, namely the blocking layers and the electrodes, also be discussed. This chapter will also discuss the different heterojunction orientations used in the active layer. Lastly, this chapter will analyze each of these in comparison to the desired characteristics that are discussed.

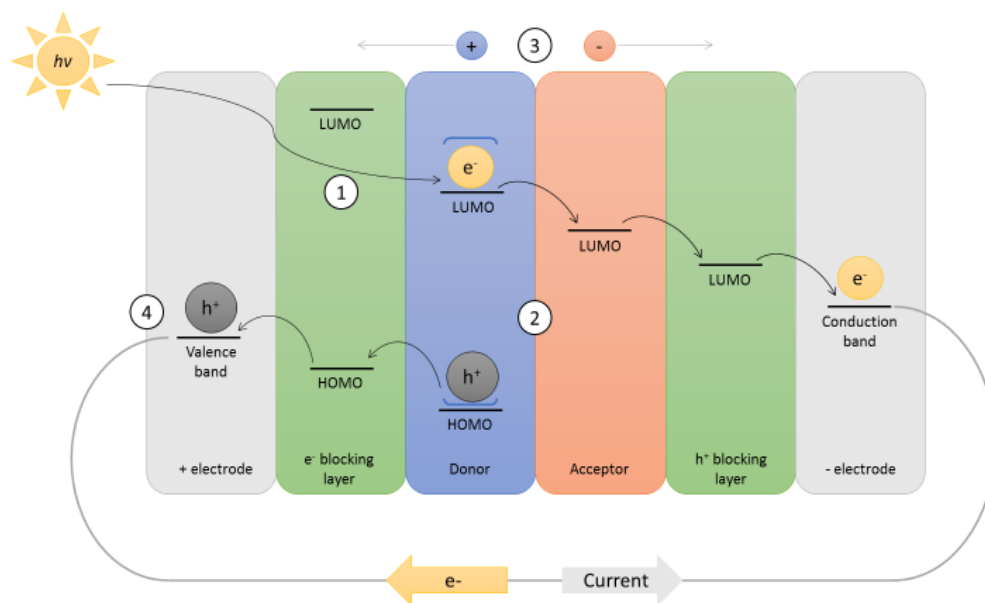


Figure 4 - Diagram illustrating the layers of an OPV and the four steps of electricity generation.

Before diving into the details of the different layers, it is important to discuss the manufacturing processes used to assemble the thin layers of materials into a functioning cell. The main deposition techniques that are utilized include spin coating, annealing, vapor deposition, masking/etching, and self-assembly. In the spin coating process, a small amount of coating material (donor, acceptor, etc.) is added to the center of the substrate (OPV). As the substrate is rotated at high speed, the coating material spreads over the substrate and off the edges. The volatile solvent used to dissolve the coating material evaporates during the spinning process, leaving the coating material behind. With variables of viscosity, coating material concentration, and the angular speed of the spinning substrate, it is easy to manipulate the thickness of the deposited film.

Another commonly used processing technique is vapor deposition. The coating material is vaporized, then directed into a vacuum chamber with the substrate. The coating material naturally condenses on the surface of the substrate, much like water vapor naturally condenses on the side of a glass of cold water on a hot day. Adjusting the temperature in the vacuum chamber, as well as the duration the substrate is in the vacuum chamber, allows the thickness of the deposited layer to be controlled. Successfully using vapor deposition requires the coating material to be vaporized without degrading, posing a challenge for picking molecules compatible with this processing technique.

The previous two techniques are commonly used in the construction of most OPVs; however, the microfabrication processes of masking and etching are limited to the construction of ordered heterojunction cells. In this process (see **Figure 17** below), a geometric pattern is transferred to the substrate by masking certain areas of the substrate with a light sensitive

chemical, called a photoresist. Light is shown through a photomask and onto the masked surface to create the desired pattern by breaking down the photoresist, leaving the coating material exposed. The exposed coating material is etched away and the remaining photoresist is removed, leaving the masked pattern behind in the substrate. These same masking and etching processes see widespread use throughout the electronics and computer industries as well, specifically in the manufacturing of computer chips and small circuitry.

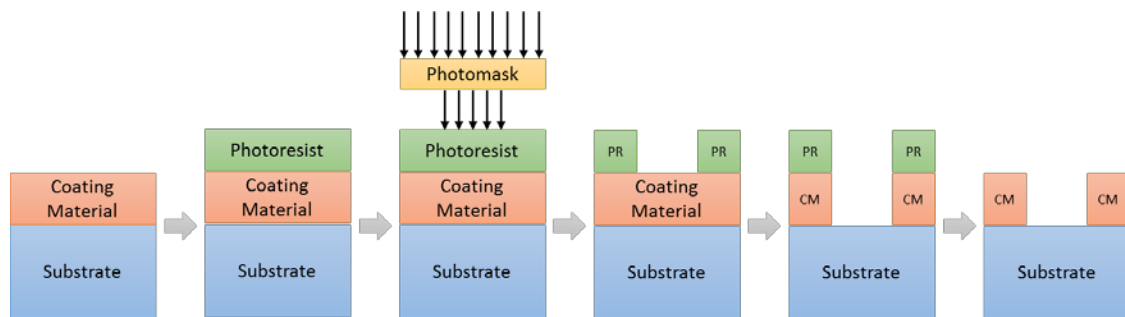


Figure 17 - Diagram of masking/etching processes used to apply coating materials in a geometric pattern.

The last deposition technique discussed here is molecular self-assembly. This technique is typically used in the active layer of the cell where the donor and acceptor molecules lie. With molecular self-assembly, the molecules of the active layer take on a defined arrangement without the help of outside influences or procedures. The molecules interact with each other through noncovalent interactions, or electrostatic interactions, two of which are illustrated below in **Figure 18**. Some of the intermolecular interactions present in self-aggregation include hydrogen bonding, coordination to metals, hydrophobic attraction, π -stacking, and/or Van der Waals forces. Hydrogen bonding occurs due to the polarization of N-H or O-H bonds, with the oxygen and nitrogen atoms obtaining a partial negative charge, and the hydrogen atoms obtaining a partial positive charge. The opposite charges attract each other, thereby forming a hydrogen bonding network. Metal coordination involves the binding of small groups, called

ligands, to a metal center. In this case, the ligands would be the donor or acceptor molecules. Hydrophobic attraction can be visualized when trying to mix a solution of non-polar and polar molecules, which are hydrophobic and hydrophilic compounds, respectively. In other words, this is essentially like mixing oil and water, where oil is hydrophobic and water is hydrophilic. Molecules of each type will self-aggregate (“like dissolves like”), due to their different electronic characteristics. In molecules capable of π -stacking, the π -bonds within the molecule formed by overlapping p or d orbitals creates an attractive force that holds the molecules together. Molecules with double bonds, including aromatics (present in many donor and acceptor molecules), are capable of aggregating in this way. The last of these intermolecular forces is Van der Waals forces, defined as the non-covalent, non-ionic, residual attractive or repulsive forces that occur between molecules and functional groups. These forces occur because of permanent or induced dipoles (instantaneously induced dipoles describe London dispersion forces) interacting with one another.

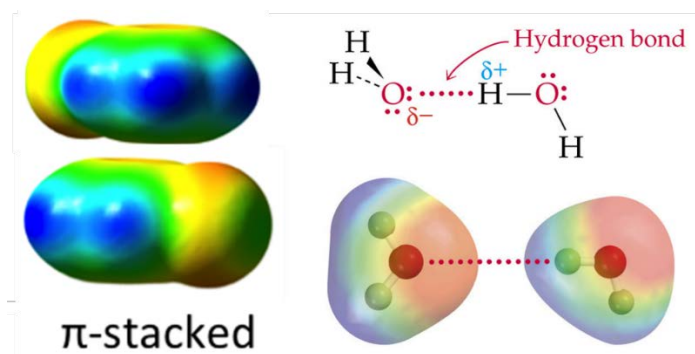


Figure 18 - Diagrams illustrating π -stacking (left), and hydrogen bonding between two water molecules (right), where red indicates areas of high electron density, and blue indicates low electron density.

In organic photovoltaics, the “active layer” serves as the home of the first three steps in the electricity generation process. In the second step of the process, the exciton diffuses through the donor material until it reaches the donor-acceptor interface. The maximum

distance that the exciton can diffuse before decaying back to the ground state referred to as the diffusion length; in most species, the diffusion length is often around 10 nm. In step 3 of the process, charge separation occurs at this heterojunction, and the electrons move from the donor to the acceptor molecules, while the holes stay with the donor molecules. Therefore, the distance that the exciton must travel to reach the interface, as well as the size and shape of the interface, are crucial design factors to consider when constructing the active layer in a way that maximizes the efficiency of the cell. To maximize the proportion of excitons that successfully reach the heterojunction, the surface area of this heterojunction must be as large as possible.

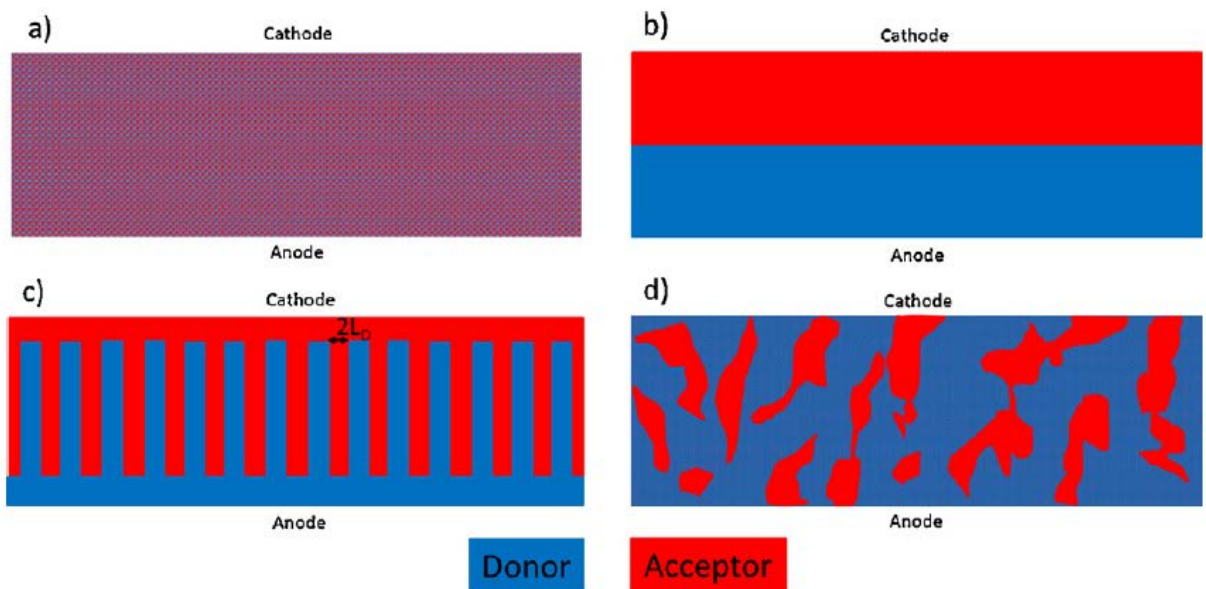


Figure 19 - Diagram illustrating four different heterojunction orientations: a) a fine mixture of donor and acceptor molecules, b) a bilayer heterojunction, c) an ordered heterojunction, and d) a bulk heterojunction arrangement (Scharber and Sariciftci).

There are four main orientations used to construct the interface of the active layer: nanoparticle arrangement, bilayer, bulk heterojunction, and ordered heterojunction (see **Figure 19** above). In a nanoparticle arrangement, the donor and acceptor molecules take the form of nanoparticles, which allows for an incredibly fine mixture, and thus a very high heterojunction

surface area. In a bilayer device, the donor and acceptor layers are distinct from one another, separated by the heterojunction in the middle. Using this design, the donor and acceptor layers are separately processed and assembled into the cell. The possibility of sequential processing may serve as an advantage for molecules that degrade at temperatures used in the processing of other layers. For example, if the acceptor layer is processed at 200°C, but the donor degrades at 150°C, the sequential processing will allow for the acceptor to be processed before the donor, preventing thermal damage to the donor. On the other hand, the orientation of the heterojunction in bilayer cells limits the efficiency of the cell, in comparison to the other designs. The bilayer interface must be within the diffusion length of the excitons for charge separation to occur. Therefore, the thickness of the donor and acceptor layers of bilayer cells must be thin to allow the maximum number of excitons to diffuse through the donor material and to the heterojunction.

A third type of interface, and arguably the most common, is the bulk heterojunction (BHJ) orientation. In cells of this type, the donor and acceptor layers are mixed together and processed simultaneously into the solar cell. In many cases, the BHJ orientation is achieved when attempting to create a nanoparticle arrangement, due to the self-aggregation of the donor and acceptor molecules into separate regions. When the donor and acceptor molecules are arranged in this fashion, the surface area of the interface is drastically increased, in comparison to the bilayer arrangement. The interpenetrating layers allow for a much higher probability that there will be an interface within the diffusion length of the exciton. As a result, the thickness of the active layer isn't limited by the exciton diffusion length of the molecules. As the area of the interface increases, the probability of charge separation increases as well, which

positively impacts the efficiency of the solar cell. Due to the mixed nature of the BHJ active layer, the donor and acceptor molecules must be able to be processed together, i.e. they both must be able to survive the processing conditions, unlike bilayer cells. An inherent design challenge for BHJ cells lies in the mixing of the donor and acceptor molecules in the active layer. The ideal BHJ active layer is free from large pockets of mainly donor/acceptor molecules, where charge separation may not occur at the expected rate, or the exciton may be trapped in the donor material (for example, when the distance to the interface is further than the exciton diffusion length). In essence, the highest efficiency BHJ cells are those where the donor and acceptor molecules are uniformly mixed throughout the cell, in a way that excitons may rapidly diffuse a short distance to a huge number of possible interfaces.

The last interface type commonly found in the active layer is the ordered heterojunction (OHJ) orientation. This design is best described as a more refined version of a BHJ cell, taking the idea of an interpenetrating network of donor and acceptor molecules and arranging them into an organized structure. As illustrated in **Figure 19** above, the “toothed” pattern serves to maximize interface surface area, while allowing for a distinct pattern to be constructed. In fact, the predictability of the interface structure and shape minimizes the occurrence of pockets of donor or acceptor molecules, a problem sometimes found in BHJ cells. The design and pattern of OHJ cells can be easily tailored to ensure that the distance to the interface is always shorter than the exciton diffusion length, thus increasing efficiency. However, the etching or masking processes described earlier in this chapter that are used to create the ordered heterojunction active layer add to the manufacturing costs of the cell, thus making it slightly less cost-competitive among other organic photovoltaic cells.

As mentioned in Chapter 3, one of the most common combinations of molecules forming a bulk heterojunction active layer of OPV cells is poly-3-hexyl thiophene (P3HT), 6,6-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM), or simply P3HT/PCBM (see **Figure 20** below). While this pairing has achieved the highest power conversion efficiency of any organic solar cell, it suffers from issues with water, air, and thermal stability. For OPVCs to be competitive with silicon-based solar cells, they must exhibit a high degree of stability over a long lifetime, and be able to withstand the elements and environmental conditions that they will be placed in. One alternative to a P3HT/PCBM active layer lies in perylenetetracarboxylic dianhydride (PTCDA, see **Figure 20**). Derivatives of PTCDA molecules can be easily made, allowing the photochemical and electronic characteristics of the molecule to be manipulated. These molecules also exhibit excellent air, water, thermal, and light stability, making them a very appealing alternative to current P3HT/PCBM systems.

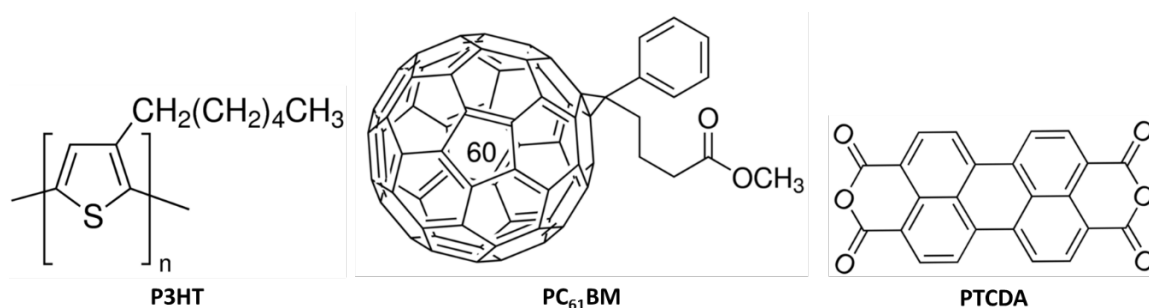


Figure 20 - Structures of poly-3-hexyl thiophene (P3HT), 6,6-phenyl-C₆₁-butyric acid methyl ester (PCBM), and perylenetetracarboxylic dianhydride (PTCDA).

After charge separation occurs at the heterojunction, the electrons move through the acceptor material towards the negative electrode, and the positive holes move through the donor material towards the positive electrode. This charge separation creates a positively charged donor and a negatively charged acceptor, and the resulting electric fields from these

charged species helps to facilitate further charge separation. These electric fields help to ensure that the charge flows in the correct direction (as previously illustrated in **Figure 4**), which is crucial to maximizing the efficiency of the solar cell. In addition to this, most organic photovoltaics now also have electron blocking and hole blocking layers surrounding the donor and acceptor layers, respectively. The energy levels of the blocking layers are carefully matched to the energy levels of the active layer to ensure that the current continues to flow in the correct direction. The key mechanism behind an electron blocking layer lies in the molecule's high bandgap, which is significantly higher than the bandgap of the adjacent donor molecules. Since electrons cannot move uphill in energy, the electron blocking layer prevents electrons in the excited state of the donor molecule from passing through. The presence of a dipole at the junction between the blocking layer and the active layer is also theorized to aid in directing current. For example, the negative end of a dipole resides in the NiO layer, while the positive end lies in the active layer, as shown in **Figure 21** below (Ratcliff, Meyer and Steirer). This dipole pushes positive holes through the electron blocking layer (which is also called a hole transport layer), and to the positive electrode. Many research teams have found that the efficiency of solar cells with these blocking layers is much higher than the efficiency of cells without them. These results are scattered throughout literature, arguing that it is necessary to include hole and electron blocking layers in OPVs to raise their efficiency, and ultimately make them more cost-competitive with silicon-based technologies.

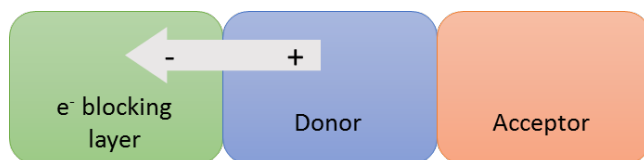


Figure 21 - Dipole (gray arrow) created at the interface between the electron blocking layer and the active layer.

One of the most popular choices for an electron blocking layer, or a hole transporting layer, is poly(3,4-ethylenedioxythiophene) polystyrene sulfonate, or PEDOT:PSS (see **Figure 22** below). This pairing of molecules exhibits excellent optical transparency and conductivity characteristics, making it a great choice for the blocking layer that sits between the active layer and the transparent electrode. Being an organic polymeric molecule, PEDOT:PSS is much less expensive to manufacture in large quantities, compared to other transparent conductors, such as indium tin oxide (ITO). Although it is used as an electron blocking layer in OPVs, PEDOT:PSS has also been investigated as a replacement for ITO in applications such as touchscreens and organic LEDs. However, this PEDOT:PSS combination is not without its drawbacks: in some cases, the aqueous PEDOT:PSS solutions have shown to be slightly acidic, which may cause corrosion to the adjacent positive electrode (Irwin, Bucholz and Hains). One alternative electron blocking layer that has been researched is nickel oxide (NiO), which exhibits an even higher band gap than PEDOT:PSS. Nickel oxide has also shown to form a stronger dipole at the blocking layer-active layer junction than the dipole formed when using PEDOT:PSS. Both characteristics could allow NiO to replace PEDOT:PSS as an electron blocking layer material with a strong positive contribution to power conversion efficiency of the solar cell. On the opposite side of the active layer, the hole blocking layer sits between the acceptor molecule and the negative electrode. Since the electron is flowing downhill in energy, the bandgap of the molecules in the hole blocking layer (also called the electron extracting layer) is lower than the bandgap of the adjacent acceptor molecules. Titanium oxide (TiO) has proven to be one of the most valuable hole blocking layers in use. In one study, a combination of a TiO hole blocking layer and an indium tin oxide electrode produced OPVs with more than double the PCE of their other OPVs without blocking layers (3.6% versus 1.6%, respectively) (Steim, Choulis and Schilinsky). This

data once again demonstrates that blocking layers are necessary for OPV construction, due to their positive contribution to electricity generation.

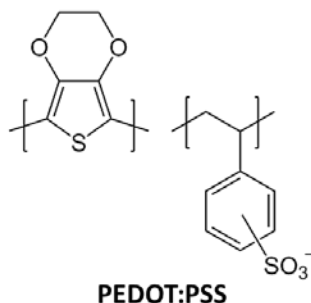


Figure 22 - Structure of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate, an electron blocking layer molecule.

After the electron passes through the hole blocking layer, it reaches the negative electrode, where it flows around the external circuit, then recombines with the holes that have moved through the electron blocking layer and to the positive electrode. These electrodes are made of conducting materials, and are often selected based on which molecules are used in the blocking layers. Since light must be able to reach the active layer of the cell, one of the electrodes, as well as the blocking layer below it, must be transparent. Additionally, this electrode must have a relatively high bandgap to avoid absorbing light in the solar spectra targeted by donor molecules. Among the most popular choices for transparent electrodes are transparent conducting oxides (TCOs). Indium tin oxide (ITO) has become the industry standard in TCOs, possessing both great transmittance and conductivity characteristics. With indium being both a rare-earth metal and the primary metal in ITO, large quantities of ITO films are quite expensive. Less costly TCOs, such as zinc aluminum oxide (AZO) and cadmium oxide (CdO), have been introduced, but see little use in organic photovoltaics due to their weaker performance than ITO. ITO has both a wider optical transmittance spectrum than AZO, due to its

higher bandgap energy (3.8 eV, 326.3 nm) than AZO (3.4 eV, or 364.7 nm) (Yun, Park and Baek). Zinc and aluminum are both common metals, making AZO a popular and much more cost friendly choice than ITO; however, AZO degrades upon exposure to moisture, whereas ITO remains unaffected. As for the other electrode, aluminum or magnesium are typically used. The electrodes are selected based on the material used in the adjacent blocking layer, in order to match the energy levels of the two species in a way that ensures current flows in the correct direction.

Towards the end of Chapter 2, I discussed the theory and motivation behind photonic upconversion research, namely that it holds promise for increasing the power conversion efficiency of not just OPVs, but of all solar energy cells. I also discussed the mechanism for upconversion and some of the basic requirements for molecules used for upconversion; most importantly, that their energy levels must match. When upconversion is used within a solar cell, the structure of the layers of the cell is slightly altered to accommodate the upconverting layer. This layer, which consists of both emitter and sensitizer molecules, is placed below the active layer of the cell to minimize competing absorption of the solar spectra harnessed by the donor molecules. Once the emitter molecules of the active layer emit the upconverted photon, this photon is absorbed by the donor molecules, thus increasing the overall portion of the solar spectrum harnessed by the cell. In addition to the upconverting layer, some construction techniques utilize a reflective layer below the upconverting layer to ensure that the maximum amount of incident light and upconverted light is directed towards the active layer for power conversion. The overall design challenges of including an upconverting layer and/or a reflective layer in the cell are limited to two main characteristics: compatibility of energy levels of the

molecules used, and the survivability of these layers during subsequent steps in the construction process of the cell. The energy levels of the upconverting molecules must be placed in a way that doesn't negatively interfere with the active layer molecules. Additionally, the upconverting layer must also share the same structural integrity and versatile stability as the active layer and electrodes to create a feasible solar cell.

Throughout this chapter, molecular properties and design considerations that govern the construction of all layers of OPV cells in the realm of small-scale research have been discussed. To bring OPVs into large-scale production and applications, people from many different disciplines must collaborate by following the same construction methods used in research, while considering the important design characteristics of the layers in the process. Synthetic chemists must find the most efficient and most environmentally friendly ways to synthesize the molecules to be used in the various layers of the cell.

Conclusion - The Decision Between Activism and Apathy

Over the course of human history, our societies have learned to adapt to problems in our quickly changing world through all forms of innovation. In the modern-day world, we recognize that we are faced with yet another quickly evolving issue: our climate systems are quickly changing, and the repercussions of 300 years of unregulated greenhouse gas emissions have quickly caught up to us. Climate change isn't something that we fear will happen in 10, 40, or even 100 years; climate change is happening right now. Decades of average surface temperature data show that the world is indeed warming, with many models predicting an accelerating warming rate in the coming years. In addition to quantitative data, we also see the qualitative effects of climate change: severe weather events have become more frequent and more intense, pointing to disruptions in the natural weather systems that drive these occurrences. Hotter summers, frequent droughts, and stronger storms seem like a big deal (and they are), but we seem to have adopted the mindset that we can adapt to the climate just as quickly as it is changing. However, I believe this is not the case. In the future, global warming will have much more disastrous consequences: ocean acidification, rising sea levels, shrinking coastlines, habitat destruction, agricultural devastation, and global food chain collapse, and the list goes on. The earth is warning us about the future of our planet through the changes that we experience today. The writing is on the wall, and it is up to us to recognize and act upon it.

In a modern world driven largely by fossil fuels, we release obscene amounts of greenhouse gases into the atmosphere and into the oceans (through absorption of atmospheric CO₂ by water). With CO₂ being the largest contributor to global warming and the most prevalent greenhouse gas, we must find ways to reduce CO₂ emissions throughout all of society. Reversing

the climbing atmospheric CO₂ concentration would require reducing emissions among all sectors of society; reduction in one sector, like transportation, will not be enough. With industry, transportation, and heat and energy production being the largest contributors of greenhouse gas emissions (totaling 61% of all emissions in the U.S.), these sectors offer a promising starting point for our campaign to reduce global CO₂ concentrations (Intergovernmental Panel on Climate Change). If we know *where* to begin reducing greenhouse gas emissions, the next logical step for us to take is to discover *how* we can accomplish this task. The answer to the question of *how* we will reduce emissions lies in finding a viable replacement for the fossil fuels that we so heavily depend on in today's world. Renewable energy sources are the best alternatives to fossil fuels for multiple reasons: renewables produce zero emissions, are infinitely abundant, and can be built with less infrastructure than fossil fuels. This last point serves as an added benefit for developing countries, where the high costs of fossil fuel infrastructure has kept the public from utilizing these resources. With advancements in research and manufacturing, renewable energy (and more specifically solar energy) may soon prove to be the pathway for developing nations to enter the modernized world, where developed nations shall work to reduce their ecological footprint.

Within the world of renewable energy, we have many different options to choose from, with wind, solar, and hydroelectric being the most popular. In deciding which technology to implement, one must consider many factors: abundance, potential energy production, and environmental impact. Some forms of renewable energy cannot be utilized in certain locations (i.e. hydroelectric power isn't an option away from rivers), and therefore have lower abundance. Potential energy production translates to the normal anticipated energy production, which

ideally meets the demands of the surrounding community. While renewable energy systems are meant to reduce our environmental impact through reducing greenhouse gas emissions, we also must consider the environmental impact of building these systems. As detailed in the Introduction, wind, solar, and hydroelectric each have their own set of advantages and disadvantages; however, I believe that solar energy holds the greatest advantages and promise for supporting the energy needs of the future. Solar energy is incredibly abundant, possesses great research and development potential, and boasts a relatively small environmental footprint. While silicon-based solar cells are the most widely used technology in photovoltaics, new technologies may one day dominate the solar energy market. Organic photovoltaics (OPVs) are one such developing solar technology, using thin layers of organic donor and acceptor molecules to generate electricity from sunlight. While OPVs are less efficient than silicon-based cells, they are more versatile in their applications. The thin profile, low weight, and flexibility of OPVs will allow for their use in consumer electronics, cars, siding of buildings, windows, and rooftops, often in cases where silicon-based solar cells simply cannot be utilized. It is also important to remember that OPVs are cheaper to produce than silicon-based cells, which serves as a huge advantage in the fight for the most cost-competitive technology on the market.

There are several major qualities that govern the success and feasibility of molecules for use in OPV power conversion. Researchers hope that various materials will be coated with OPVs, which requires that the materials used in them are stable in air, water, and heat. The molecular properties of the donor and acceptor layers must be carefully matched to maximize efficiency. Matching the energy levels of the donor and acceptor molecules is critical in determining what wavelengths of light the cell will utilize, as well as determining the power conversion efficiency

of the cell. The matching of energy levels and manipulation of electronic properties of molecules plays into one of the biggest goals of solar research: to construct solar cells that will utilize the highest energy and highest intensity portions of the solar spectrum. A secondary approach to this goal, photonic upconversion, is also in development for use in OPVs (and possibly all photovoltaic technologies). While silicon-based cells currently have higher power conversion efficiencies than OPVs, the advantages of OPVs provide motivation for further research and development. We know what properties and characteristics we are looking for in these organic molecules, and we are constantly searching for more efficient, more stable, and less toxic molecules to use in OPVs. We also have the skills and construction processes to incorporate these molecules into a functioning solar cell. We know how to build them and we are learning what to use in them, and we must always remember why we are investigating OPVs in the first place.

At this point in time, our societies are walking a fine line between activism and apathy, where the former involves working to restore balance to the earth's natural systems by reducing emissions, while the latter ends in global devastation by selfishly ignoring the signs of climate change. On the one hand, activism requires global cooperation among all areas of society, a seemingly impossible task for our heavily divided world. For activism to work, we must remember that the issue of climate change will affect all people, and it is our responsibility to care for one another. On the other hand, this apathy will inevitably lead to immense regret when we realize that the earth's climate is irreparably damaged. When looking back, we will wish that we acted sooner and/or decided to care about the rest of the species that live on this

planet that are also affected by our actions. The time is quickly approaching for our society to decide which path to follow, and we must be informed and decisive when the time comes.

If we choose activism, we must recognize that our fossil fuel addiction must be broken and replaced by renewable energy. Research into renewable energy is the key to living sustainably for both present and future generations. Renewable energy investments matter because it is our job to ensure that we leave the world a better place for our descendants. If we invest in the most promising renewable energy technologies now, future societies will thank us, and so will all the organisms of the earth. In the words of astronomer Carl Sagan, “A new consciousness is developing which sees the earth as a single organism, and recognizes that an organism at war with itself is doomed. We are one planet” (Malone). We must first change the way that our societies perceive the earth and its climate systems. We must recognize that we do not exist separately from the world, and we are not the rulers of the world and its resources and other living organisms. The repercussions of climate change have already affected us, and will undoubtedly continue to do so. We must then use our natural gifts of innovation and creativity to construct a society that actively works to preserve the world for those who will one day live in it. Activism also requires that we seek to change our societies not only for our benefit, but for the well-being of all life on earth. We are all deserving of a life on a healthy planet, and it is now up to mankind to make this ideal vision our reality.

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