

Engineering thin-layer organic solar cells using a novel tri-layer architecture

(2008-09)

Michael Crump
Materials Engineering
123 Ottawa Avenue N
Golden Valley MN 55422

Abstract

Thin-layer organic solar cells show promise as an alternative source of energy because they are less expensive to produce than currently used crystalline-silicon-based solar cells; however, they are only 1–5% efficient. My goal was to increase thin-layer organic solar cell efficiency by employing a tri-layer solar cell architecture.

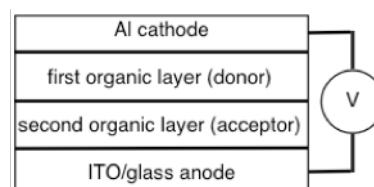
I used thermal evaporation to layer three organic compounds—buckminsterfullerene, copper phthalocyanine (CuPc), and naphthyl-diphenyl-diamine (NPD)—between an aluminum cathode and an indium-tin-oxide anode. I used NPD because it has been shown to increase open-circuit voltage (V_{OC}) in bi-layer cells. Results showed that efficiency was not increased because V_{OC} remained constant while short-circuit current (J_{SC}) decreased. In a second attempt, I replaced NPD with platinum octaethylporphyrin (PtOEP) because PtOEP, like NPD, has been shown to increase V_{OC} in bi-layer cells. Again, V_{OC} remained constant while J_{SC} decreased. The decrease in J_{SC} suggests that both tri-layer structures had high resistivity. To overcome this resistivity, an option is to dope NPD or PtOEP with more conductive materials. While the tri-layer architecture used in this project did not increase efficiency, the low cost of organic solar cells provides incentive to continue investigating these cells as an alternate source of electricity.

Introduction

Thin-layer organic solar cells show great promise as economical sources of solar energy. Once in production, these cells will cost much less to produce than even the most efficient crystalline-silicon-based solar cells because organic solar cells can be coated onto flexible substrates, using a roll-to-roll process similar to newspaper printing. However, organic solar cells that are currently available are only 1–5% efficient, whereas crystalline-silicon-based solar cells are 24% efficient (1). The purpose of my study was to increase the efficiency of organic solar cells to improve their viability as an alternative energy source. (Terms and abbreviations can be found in Appendix A.)

The simplest organic solar cells are bi-layer cells that consist of two different organic materials. These bi-layer cells were first engineered by C. W. Tang in 1986. In bi-layer cells, the first organic layer is an electron donor, whereas the second organic layer acts as an electron acceptor (Figure 1). Both of these layers are roughly 400 Å thick. These organic layers are sandwiched between an anode made of glass coated with indium-tin-oxide (ITO) and a cathode made from aluminum (2).

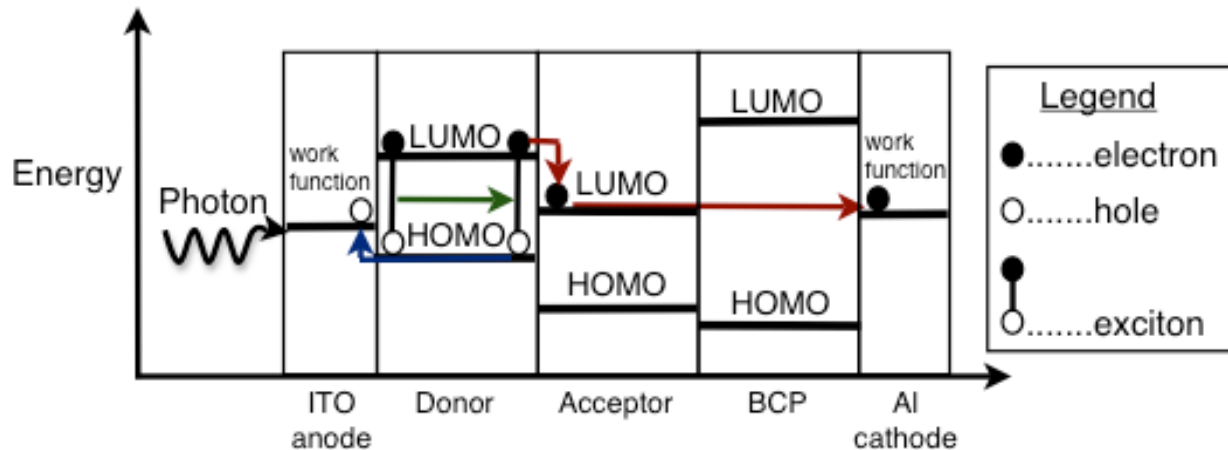
Figure 1: structure of a bi-layer organic cell (not drawn to scale)



To produce electrical current in bi-layer solar cells, photons pass through the ITO anode, exciting electrons from the highest occupied molecular orbital (HOMO) of the donor layer to the lowest unoccupied molecular orbital (LUMO) of the donor layer (Figure 2). This excitation results in formation of positively charged holes in the HOMO of the donor layer. The excited electrons in the LUMO, which are still bound to the positively charged holes in the HOMO, are called excitons. These excitons diffuse through the donor to the interface between the donor and acceptor layers. At this point, electrons dissociate from the positively charged holes due to the

lower energy of the LUMO of the acceptor layer. (Some energy is lost here in the form of heat.) The free electrons then diffuse through the acceptor layer to the work function of the aluminum cathode. At the same time, positively charged holes diffuse back through the donor layer to the work function of the ITO anode, completing the circuit. Because excitons can form in the acceptor layer, an exciton-blocking layer of bathocuproine (BCP) is used in modern organic solar cells to confine excitons to the donor/acceptor interface and to prevent damage to the aluminum cathode (3).

Figure 2. Energy diagram of a standard bi-layer OSC (all figures by author)



To improve organic solar cell efficiency (η_p), three factors must be considered: open-circuit voltage (V_{OC}), short-circuit current (J_{SC}), and fill factor (FF). Efficiency is directly related to these three factors (Equation 1).

Equation 1: Efficiency of thin-layer organic solar cell

$$\eta_p = V_{OC} \times J_{SC} \times FF$$

To determine efficiency, current is measured against voltage applied across an organic solar cell, as seen on the current density–voltage (J-V) curve in Figure 3. The J-V curve shows two factors: photocurrent and diode current. Photocurrent is generated by photons, which produce electrical power in an organic solar cell. Diode current is caused by voltage applied across an organic solar cell. V_{OC} is the point on the J-V curve where diode current and

photocurrent cancel each other, while J_{SC} is the point on the J-V curve where voltage is zero. The J-V curve also shows fill factor (FF). Fill factor is the shaded area under the J-V curve seen in the shaded box in the fourth quadrant divided by the product of V_{OC} and J_{SC} .

A study by Peumans et al. (2003) demonstrated that bi-layer organic solar cells generate a V_{OC} of only 0.5 V, while photons from solar radiation have a potential of 2.0 V (1). A major problem with organic solar cells is that any attempt to increase V_{OC} by decreasing diode current tends to decrease J_{SC} and fill factor as well. The goal of my project was to fabricate a thin-layer organic solar cell that employed a novel tri-layer architecture to increase V_{OC} without decreasing J_{SC} and fill factor.

In my study, I used a bi-layer solar cell structure as a control cell, which was the architecture used in the 2003 Peumans study (1). The control cell employed copper phthalocyanine (CuPc) as the donor layer and buckminsterfullerene (C_{60}) as the acceptor layer (Figure 4).

In my experimental organic solar cells, I utilized a novel tri-layer architecture (Figure 5). I fabricated the tri-layer cells, using the bi-layer configuration suggested in the Peumans study, while adding a third organic layer composed of naphthyl-diphenyl-diamine (NPD). I incorporated NPD because a study by Kushto et al. (2005) showed that replacing CuPc with NPD

Figure 3. J-V curve of a bi-layer organic solar cell

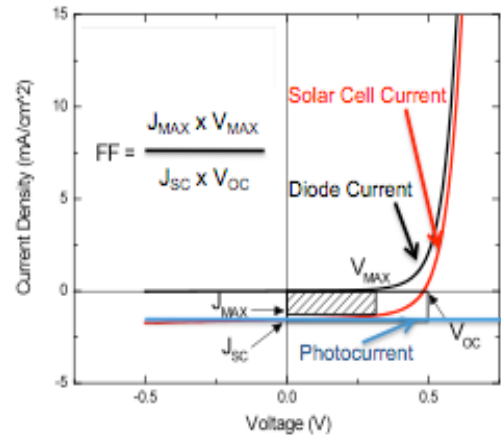


Figure 4. architecture of the control bi-layer organic solar cell

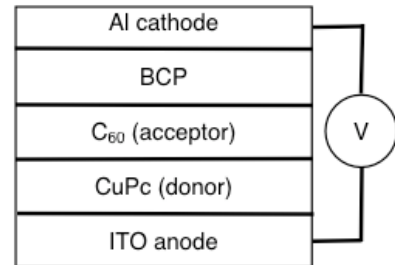
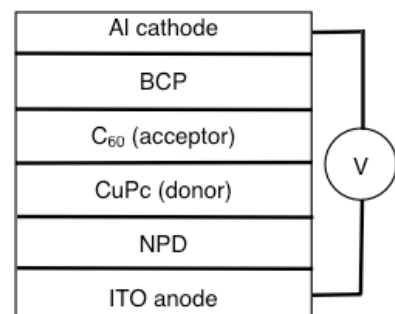
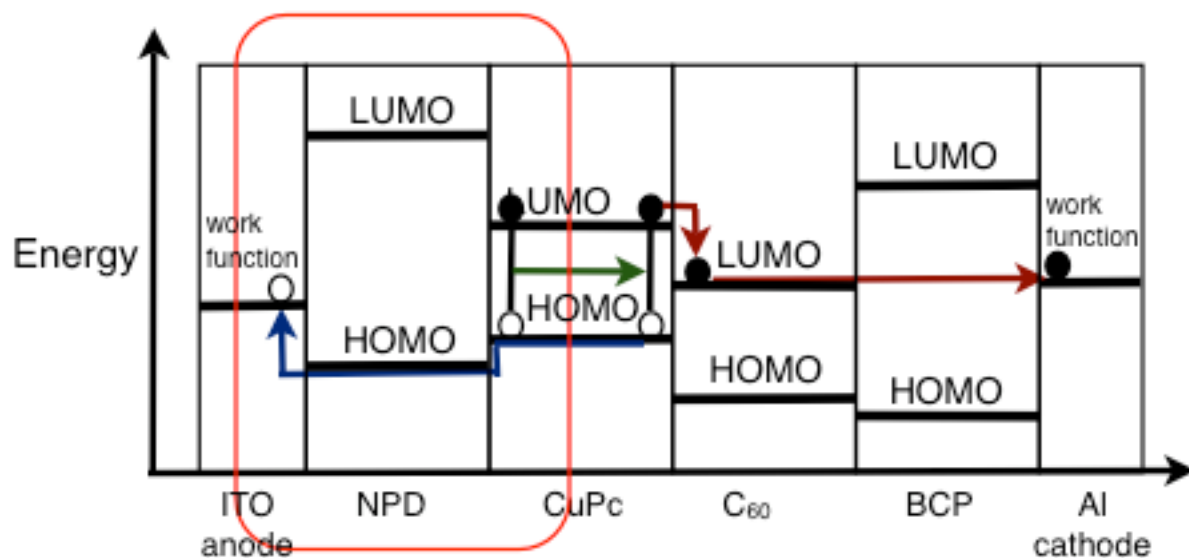


Figure 5. architecture of the first tri-layer organic solar cells



in a bi-layer organic solar cell increased V_{OC} ; however, efficiency in the Kushto study was not increased because J_{SC} decreased (4). So, I retained the CuPc layer because Peumans and Kushto showed that CuPc has a higher J_{SC} than NPD and absorbs a wider spectrum of light, therefore collecting more photons than NPD (1, 4). In addition, a study by Rand et al. (2005) showed a direct correlation between V_{OC} and the energy difference between the HOMO in CuPc and the LUMO in C_{60} in bi-layer organic solar cells; the Rand study implied that a lower HOMO, such as the HOMO of NPD, would induce a greater V_{OC} (5). Based on the Peumans, Kushto, and Rand studies, I hypothesized that adding NPD between the ITO anode and CuPc layer would increase V_{OC} without decreasing J_{SC} because NPD has a lower HOMO than the HOMO of CuPc, thus establishing a lower HOMO for holes to overcome (Figure 6).

Figure 6. Energy graph of a tri-layer organic solar cell employing NPD, where the red box indicates the low HOMO of NPD



In a second set of trials, I used a layer of platinum octaethylporphyrin (PtOEP) instead of NPD in the tri-layer architecture (Figure 7). Work by Holmes (2008) employed PtOEP instead of CuPc in a bi-layer organic solar cell, which increased V_{OC} from 0.5 to 0.75 V but decreased J_{SC} due to the resistivity of the PtOEP layer (6). I hypothesized that by using PtOEP instead of NPD

in the tri-layer architecture, V_{OC} would be increased with a lower reduction in J_{SC} because the resistivity of PtOEP would cause a higher V_{OC} while reducing losses in J_{SC} (Figure 8), thus increasing efficiency.

Figure 7: the architecture of the second tri-layer organic solar cell

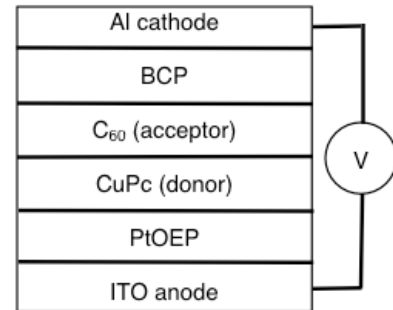
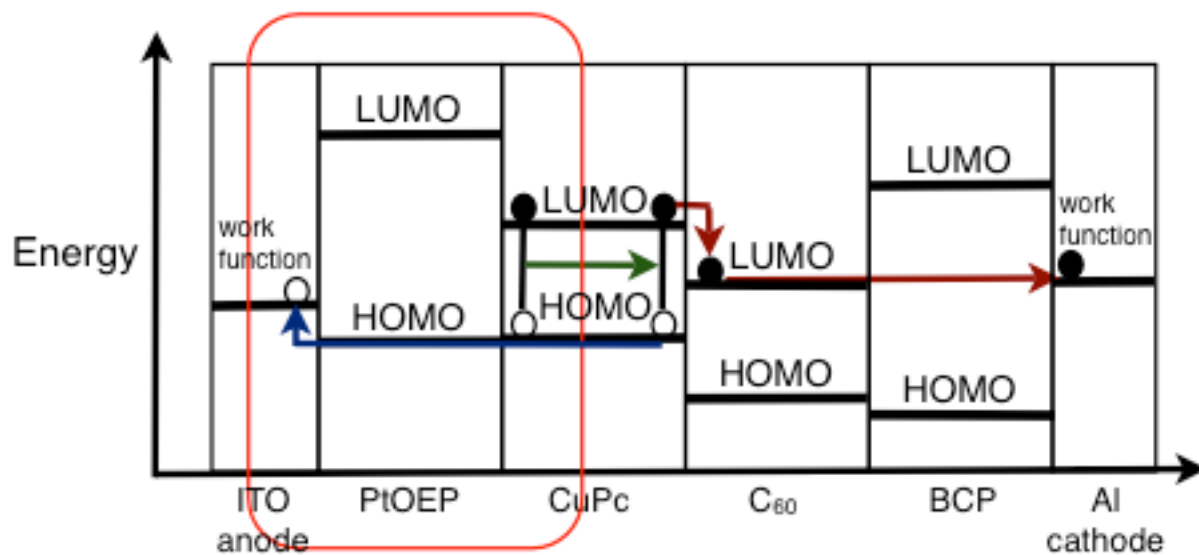


Figure 8. Energy graph of a tri-layer solar cell employing PtOEP, where the red box indicates the additional layer of PtOEP



Materials and Methods

Fabricating organic thin-layer photovoltaic cells

Organic solar cells were fabricated on pre-cleaned glass substrates (see Appendix B for cleaning protocol) that were pre-coated with 1500 Å of indium-tin-oxide. Before each fabrication, solid NPD, PtOEP, CuPc, C_{60} , BCP, and aluminum were prepared in a thermal evaporation chamber that was located inside a glove box. Combinations of organic materials were sublimed onto organic solar cells at 8.0×10^{-7} Torr (Table 1). Then, NPD, PtOEP, CuPc, and C_{60} were sublimed at 2.0 Å/s, and BCP was sublimed at 2.5 Å/s.

Table 1: Organic solar cell materials for both cell structures

Organic solar cell type	ITO anode thickness (Å)	NPD thickness (Å)	PtOEP thickness (Å)	CuPc thickness (Å)	C ₆₀ thickness (Å)	BCP thickness (Å)	Al cathode thickness (Å)
Cell 1	1500 Å	10–100 Å	N/A	200 Å	400 Å	100 Å	500 Å
Cell 2	1500 Å	N/A	10-100 Å	200 Å	400 Å	100 Å	500 Å

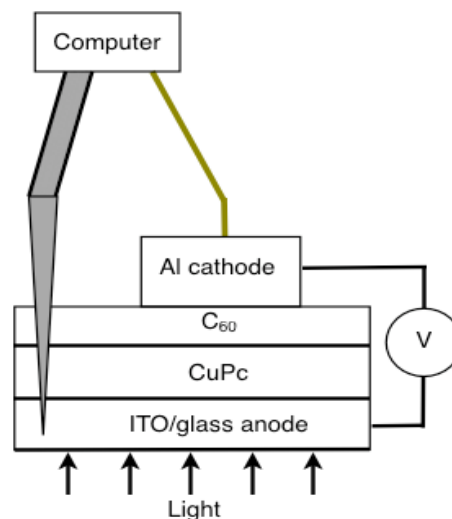
The resulting coated organic solar cells were removed from the evaporation chamber to the glove box where shadow mask templates, containing fifteen 1.015-mm holes (± 0.01 mm), were applied. The organic solar cells then were placed back into the evaporation chamber, and the chamber was pumped down to 8.0×10^{-7} Torr. An aluminum cathode was sublimed onto the cells at 3.0 \AA/s . The chamber was vented, and shadow mask templates were removed.

Testing the current density-voltage (J-V) parameters

A xenon lamp with an air-mass 1.5-global (AM1.5G) filter was warmed for thirty minutes, and illumination power was recorded with a multifunction optical meter. One of the fifteen aluminum cathode cells on each of the coated organic solar cells was aligned with a 1.5-mm hole in a testing plate. An anode probe was positioned in the ITO anode, and a cathode probe was positioned at one of the aluminum cathodes, defined by the shadow mask template (Figure 9). Voltage, ranging

from -0.5 V to 1.0 V, was applied across the organic solar cell in total darkness to measure diode current of the substrate as a function of voltage. Then, voltage in the same range was applied across each organic solar cell with lamp intensities, ranging from 7.0 mW/cm^2 to 1100 mW/cm^2 , to measure current as a function of voltage, in order to verify that results were consistent over the

Figure 9: positioning probes on an organic solar cell for testing



power intensity range. Figure 10 exemplifies plots of efficiency, V_{OC} , responsivity, fill factor, and reverse bias, showing that all parameters were consistent over the power density range. Finally, J-V tests were repeated at each of the fifteen aluminum cathodes, defined by the shadow mask template.

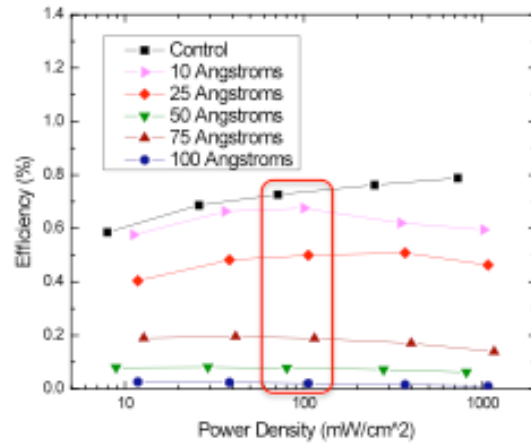
Results

Results are reported at a power density of 100 mW/cm^2 , which is one-sun intensity, because one sun is the condition found on Earth. (All results figures are found in Appendix C.)

NPD Results: Efficiency of the bi-layer control cell was 0.72%, whereas efficiency of the tri-layer cell with NPD decreased from 0.68% to 0.03% as thickness increased from 10 \AA to 100 \AA (Figure 11a). V_{OC} of the control was 0.44 V, whereas V_{OC} varied between 0.43 and 0.49 V as NPD thickness increased from 10 \AA to 100 \AA (Figure 11b). Responsivity of the control was 0.029 A/W, whereas responsivity of the tri-layer cell decreased from 0.028 A/W to 0.006 A/W as NPD thickness increased from 10 \AA to 100 \AA (Figure 11c). Fill factor of the control cell was 0.56, whereas fill factor of the tri-layer cell decreased from 0.55 to 0.09 as NPD thickness increased from 10 \AA to 100 \AA (Figure 11d). Reverse bias for the control was -0.012 mA/cm^2 , whereas reverse bias for the tri-layer cells varied between -0.001 and -0.002 mA/cm^2 as NPD thickness increased from 10 \AA to 100 \AA , with the exception of the tri-layer cell that had a reverse bias of -0.021 mA/cm^2 at a thickness of 25 \AA of NPD (Figure 11e).

PtOEP Results: Efficiency of the bi-layer control cell was 0.70%, whereas efficiency of the tri-layer cell decreased from 0.70% to 0.29% as PtOEP thickness increased from 10 \AA to

Figure 10: Example of parameters plotted against power density, where the red box indicates the results reported in this study



100 Å (Figure 12a). V_{OC} of the control cell was 0.50 V, whereas V_{OC} for the tri-layer cell decreased from 0.50 V to 0.44 V as PtOEP thickness increased from 10 Å to 100 Å (Figure 12b). Responsivity of the control cell was 0.023 A/W, whereas responsivity generally decreased in the tri-layer cell from 0.019 A/W to 0.014 A/W as PtOEP thickness increased from 10 Å to 50 Å. Also, as PtOEP thickness increased from 50 Å to 100 Å in the tri-layer cell, responsivity increased from 0.014 A/W to 0.022 A/W (Figure 12c). Fill factor for the control cell was 0.59, whereas fill factor for the tri-layer cell decreased from 0.53 to 0.31 as PtOEP thickness increased from 10 Å to 100 Å (Figure 12d). Reverse bias of the control cell was -0.027 mA/cm^2 , whereas reverse bias for the tri-layer cell varied within -0.001 and -0.002 mA/cm^2 as PtOEP thickness of the tri-layer cell increased from 10 Å to 100 Å (Figure 12e).

Discussion

Results did not support my hypothesis that using NPD in a tri-layer architecture would increase thin-layer organic solar cell efficiency. Employing NPD did not increase efficiency; in fact, efficiency decreased as NPD thickness increased. At every thickness, V_{OC} remained constant, while responsivity and fill factor decreased. Results suggest that the low HOMO and resistivity of NPD led to the loss in responsivity and fill factor, and increasing NPD thickness decreased responsivity and fill factor even further. Results also suggest that V_{OC} remained constant because any gains in V_{OC} due to a lower diode current resulting from the resistivity of NPD were offset by a reduction in responsivity (Figure 11). My hypothesis that adding NPD between the ITO anode and CuPc would increase V_{OC} without decreasing J_{SC} was not supported because, although NPD has a lower HOMO than the HOMO of CuPc for holes to overcome, the holes experienced more resistance due to the high resistivity of NPD.

Results also did not support my second hypothesis that using PtOEP in a tri-layer

architecture would increase thin-layer solar cell efficiency. Employing PtOEP did not increase efficiency (Figure 12). For the same reasons as in the NPD tri-layer architecture, efficiency decreased with added thickness of PtOEP up to 50 Å. Efficiency did increase with thicknesses >50 Å; however, efficiency was not greater than the control at any PtOEP thickness. This increase in efficiency at PtOEP thickness >50 Å suggests that responsivity increased as a result of additional exciton formation in the PtOEP layer, contributing to photovoltaic current. However, the static V_{OC} and the overall decrease in both responsivity and fill factor led to a lower organic solar cell efficiency of the tri-layer architecture compared to the control cell.

Conclusion

The goal of my study was to increase efficiency of organic solar cells by employing NPD and subsequently PtOEP in a novel tri-layer architecture. For all thicknesses of NPD or PtOEP, neither cell architecture increased efficiency due to reductions in responsivity and fill factor for both cell architectures.

Thin-layer organic solar cells have the potential to replace silicon-based solar cells, but there are still fundamental issues to overcome, such as low V_{OC} addressed in this study. One option for future research is to find an optimal balance between the high V_{OC} of NPD and PtOEP and the high J_{SC} of CuPc by blending the organic materials together in one layer. Another option is doping NPD or PtOEP with more conductive materials, as proposed in a study by Maennig (2004), to eliminate high resistivity of tri-layer organic solar cells, which could maintain a high V_{OC} without decreasing J_{SC} (7). Despite the current limitations of thin-layer organic solar cells, the low cost of organic solar cell production provides incentive to continue investigating thin-layer organic solar cells as a practical source of electricity.

Acknowledgements

Dr. Russell Holmes provided me with the opportunity to work in his lab, let me use his equipment, and helped me understand the theory behind my project. Also, I greatly appreciate the help from Wade Luhman, Richa Penda, and Grant Lodden, who are Dr. Holmes's graduate students. All three answered my questions and trained me to use the equipment. My Breck Advanced Science Research classmates and Lois Fruen, my Breck research teacher, gave me suggestions on my paper. Finally, Breck School and the University of Minnesota provided funding for my research.

Works Cited

- (1) Peumans, Peter et al. "Small molecular weight organic thin-film photodetectors and solar cells." *Journal of Applied Physics* 93 (2003): 3693-3723.
- (2) Mutolo, Kristin L. et al. "Enhanced Open-Circuit Voltage in Subphthalocyanine/C₆₀ Organic Photovoltaic Cells." *Journal of the American Chemical Society* 128 (2006): 8108-8109.
- (3) Streetman, Ben G, and Sanjay Banerjee. *Solid State Electronic Devices*. Upper Saddle River, NJ: Prentice Hall, 2000.
- (4) Kushto, Gary P. et al. "Flexible organic photovoltaics using conducting polymer electrodes." *Applied Physics Letters* 86 (2005): 1-3.
- (5) Rand, Barry P. et al. "Offset energies at organic semiconductor heterojunctions and their influence on the open-circuit voltage of thin-film solar cells." *Physical Review* 75 (2007): 1-11.
- (6) Holmes, Russell. Personal interview. 10 Jun. 2008.
- (7) Maennig, B. "Organic p-i-n solar cells." *Applied Physics A: Materials Science & Processing* 79 (2004): 1-14.

Additional References

Brabec, Christoph J. et al. "Production Aspects of Organic Photovoltaics and Their Impact on the Commercialization of Devices." *MRS Bulletin* 30 (2005): 50-52.

Callister, William D. *Materials Science and Engineering: An Introduction*. Hoboken, NJ: John Wiley & Sons, 2003.

Eisberg, Robert, and Robert Resnick. *Quantum Physics of Atoms, Molecules, Solids, Nuclei, and Particles*. New York: John Wiley & Sons, 1985.

Forrest, Stephen R. "The Limits to Organic Photovoltaic Cell Efficiency." *MRS Bulletin* 30 (2005): 28-32.

Forrest, Stephen R. "Ultrathin Organic Films Grown by Organic Molecular Beam Deposition and Related Techniques." *Chemistry Review* 97 (1997): 1793-1805, 1862-1896.

Forrest, Stephen R, and Peter Peumans. "Very-high-efficiency double-heterostructure copper phthalocyanines/C₆₀ photovoltaic cells." *Applied Physics Letters* 79 (2001): 126-128.

Gregg, Brian A. "The Photoconversion Mechanism of Excitonic Solar Cells." *MRS Bulletin* 30 (2005): 20-22.

Mutolo, Kristin L. et al. "Enhanced Open-Circuit Voltage in Subphthalocyanine/C₆₀ Organic Photovoltaic Cells." *Journal of the American Chemical Society* 128 (2006): 8108-8109.

Peumans, Peter et al. "Efficient photon harvesting at high optical intensities in ultrathin organic double-heterostructure photovoltaic diodes." *Applied Physics Letters* 76 (2000): 2650-2632.

Peumans, Peter et al. "Small molecular weight organic thin-film photodetectors and solar cells." *Journal of Applied Physics* 93 (2003): 3693-3723.

Rand, Barry P. et al. "Organic Double-Heterostructure Photovoltaic Cells Employing Thick Tris(acetylacetonato)ruthenium(III) Exciton-Blocking Layers." *Advanced Materials* (2005):

Rand, Barry P. et al. "Organic solar cells with sensitivity extending into the near infrared." *Applied Physics Letters* 87 (2005): 1-3.

Scharber, Markus C. et al. "Design Rules for Donors in Bulk-Heterojunction Solar Cells – Toward 10% Energy-Conversion Efficiency." *Advanced Materials* 18 (2006): 789-794.

Shrotriya, Vishal et al. "Accurate Measurement and Characterization of Organic Solar Cells." *Advanced Function Materials* 16 (2006): 2016-2023.

Streetman, Ben G, and Sanjay Banerjee. *Solid State Electronic Devices*. Upper Saddle River, NJ: Prentice Hall, 2000.

Tang, C. W. "Two-layer organic photovoltaic cell." *Applied Physics Letter* 48 (1986): 183-185.

Yang, Fan, et al. "Efficient Solar Cells Using All-Organic Nanocrystal Networks." *Advanced Materials* 19 (2007): 4166-4171.

Yang, Fan et al. "Simultaneous heterojunction organic solar cells with broad spectral sensitivity." *Applied Physics Letters* 92 (2008): 1-3.

Appendices

Appendix A: Glossary of terms

<i>Term</i>	<i>Abbreviation</i>	<i>Description</i>
Bathocuproine	BCP	BCP functions as a exciton-blocking layer
Buckminsterfullerene	C ₆₀	C ₆₀ disassociates excitons formed from incident photons
Copper phthalocyanine	CuPc	CuPc induces excitons to form from incident photons
Efficiency	η_p	Efficiency is the power output of a PV cell divided by the power input from a light source.
Fill factor	FF	FF is directly related to efficiency
Highest occupied molecular orbital	HOMO	HOMO is the highest electron energy level with electrons
Indium-tin-oxide anode	ITO anode	The ITO anode collects positively charged holes to complete the circuit
Lowest unoccupied molecular orbital	LUMO	LUMO is the lowest electron energy level without electrons
Naphthyl-diphenyl-diamine	NPD	NPD has a lower HOMO than CuPc to induce a greater V_{OC}
Open-circuit voltage	V_{OC}	V_{OC} is the voltage of a PV cell when current is zero
Platinum octaethylporphyrin	PtOEP	PtOEP has a lower HOMO than CuPc to induce a greater V_{OC}
Short-circuit current	J_{SC}	J_{SC} is the current of a PV cell when voltage is zero

Appendix B: Cleaning ITO substrates

Glass substrates, pre-coated with 1500 Å of indium tin oxide (ITO), were placed into 130 mL of tergitol, and ITO substrates were sonicated in dH₂O for five minutes. Sonication was repeated, using 130 mL of dH₂O once and acetone twice. Next, ITO substrates were cleaned in 130 mL of boiling isopropyl alcohol for five minutes, placed in fresh 130 mL of isopropyl alcohol, and cleaned again for five minutes. ITO substrates were dried with N₂ and placed into a temperature-controlled UV surface decontamination system for five minutes to remove residue

and carbon contaminants.

Appendix C. Figures 11 and 12

Figure 11: Performance of the control (0 Å) and the tri-layer architecture with NPD (10–100 Å) at one-sun intensity with AM1.5G

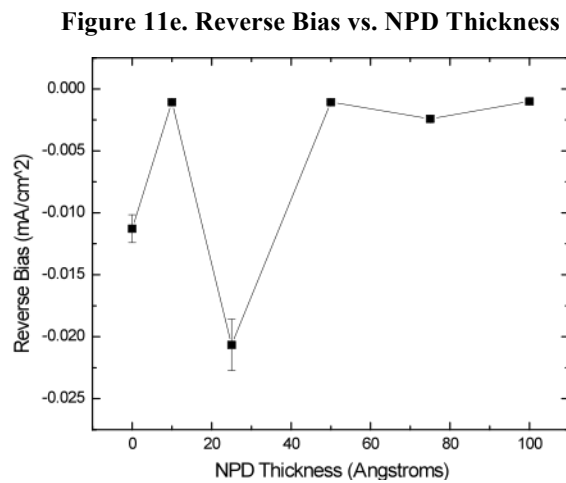
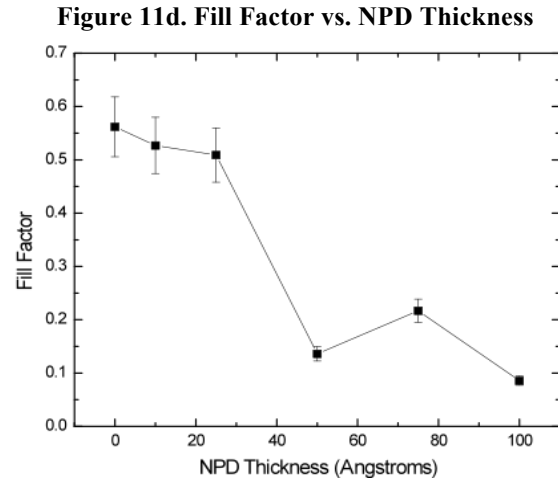
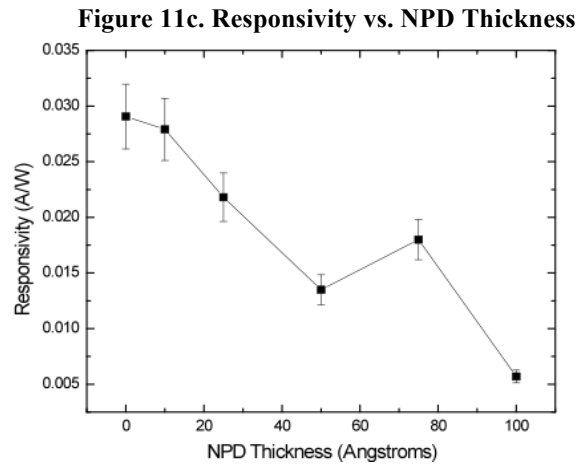
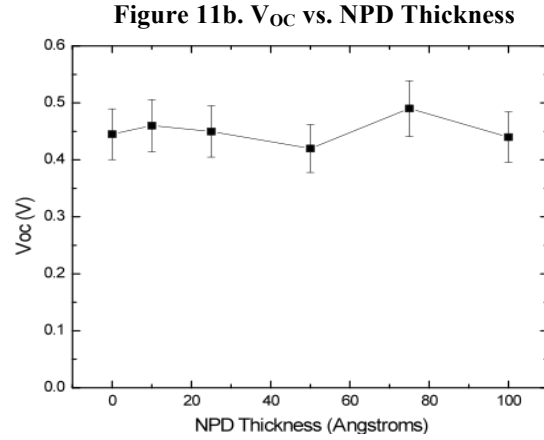
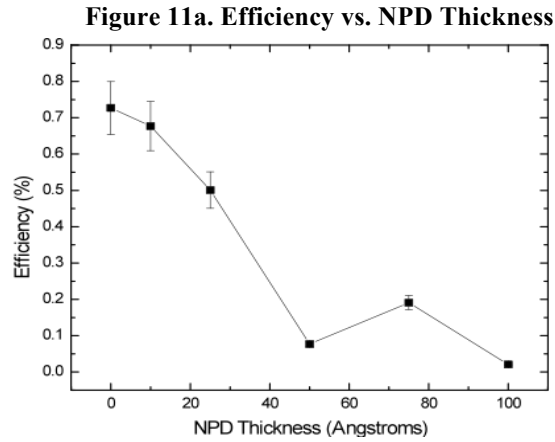


Figure 12. Performance of the control (0 Å) and the tri-layer architecture with PtOEP (10–100 Å) at one-sun intensity with AM1.5G

Figure 12a. Efficiency vs. PtOEP Thickness

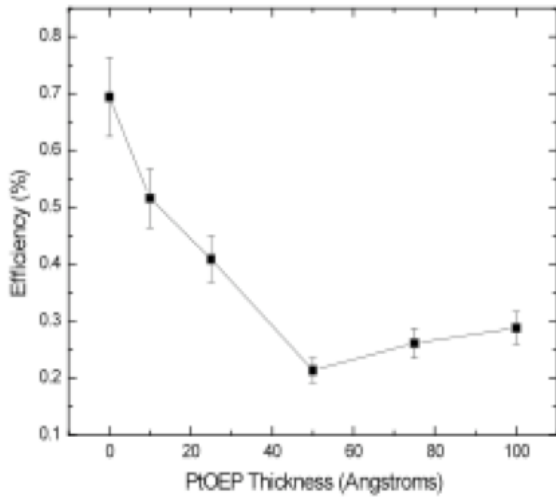


Figure 12b. Voc vs. PtOEP Thickness

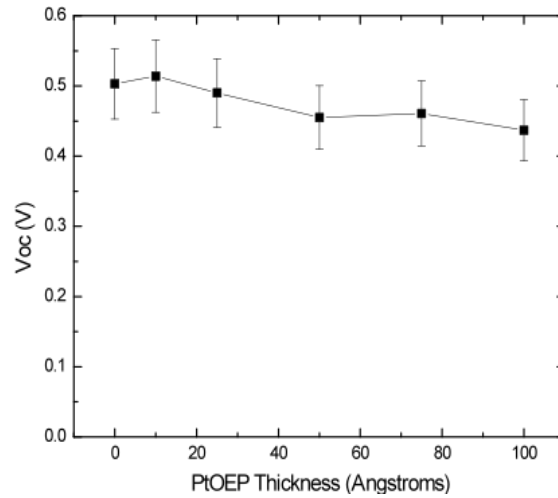


Figure 12c. Responsivity vs. PtOEP Thickness

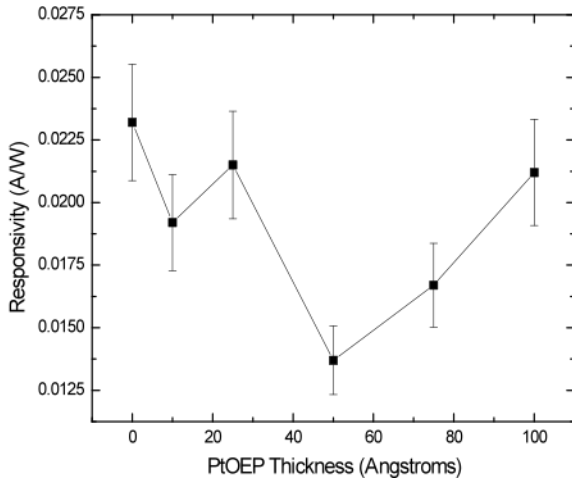


Figure 12d. Fill Factor vs. PtOEP Thickness

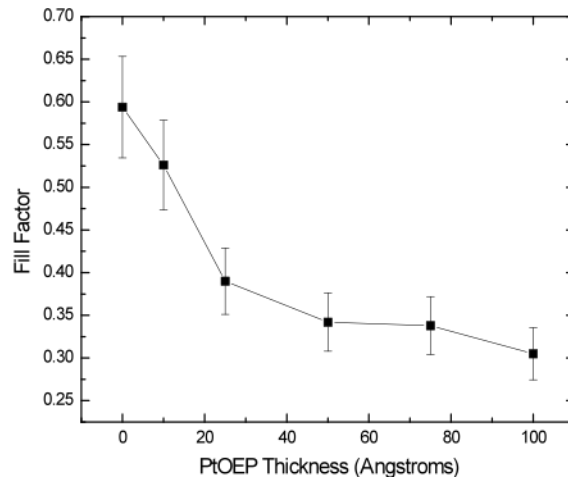


Figure 12e. Reverse Bias vs. PtOEP Thickness

