DEVELOPMENT TOWARDS SIMPLE FABRICATION STEPS OF
A FLEXIBLE HEART RATE SENSING FILM

A Dissertation Presented

By

David Douglas Schmidt

to

The Department of Bioengineering

In partial fulfillment of the requirements for the degree of

Doctor of Philosophy

In the field of

Bioengineering

Northeastern University

Boston, Massachusetts

August, 2017
ABSTRACT

Heart rate provides information that can provide benefits for a number of different applications. Doctors use heart rate to monitor patient health, while psychologists can use it to monitor subject stress levels. This useful information has been the motivation for discovering effective and simple methods to make measurements, which has led to the development of non-invasive electrical and optical heart rate monitoring devices. Developments in robotics, health and mobile technology have created both a demand and a platform for heart rate monitoring outside of the laboratory or hospital. This type of mobile monitoring will require a device that patients and subjects can wear with ease, which means the device needs to be light-weight, simple to use, comfortable to wear, and have low power consumption, all while providing constant, useful information.

Recent developments in flexible circuits and optoelectronic materials may provide solutions to the design challenges presented by these requirements. The work proposed for this dissertation presents developments towards a thin film device that could make physiological measurements through natural contact, which can collect data with minimal work required by the wearer. The proposed device will implement Quantum Dots (QDs) and basic MEMS fabrication techniques to create a flexible thin-film optical heart rate sensor. Through using simplified methods for building large area devices, the work will explore how successfully low-cost, rapid fabrication steps outside of a cleanroom can be used for device development. The two main functions required for optical heart rate monitoring, light emission and detection, are evaluated. To study flexibility, the effects of cyclic bending on the device structure and performance are observed. Results show that low-cost rapid fabrication techniques are a valid means for flexible optoelectronic device fabrication, and that the device would benefit from both functional and structural improvements in the active layer. This work serves as proof that use of clean room facilities are not necessary to provide significant contributions towards optoelectronic research.
Acknowledgments

This work has been in part supported by National Science Foundation Award # 0954579 “CAREER: Bridging Cognitive Science and Sensor Technology: Non-intrusive and Multi-modality Sensing in Human-Machine Interactions”, #1333524 “Integrated Individualized Modeling towards Cognitive Control of Human-Machine Systems”, and # 1658450 “I-Corps: Thin Film Heart Rate Sensor” awarded to Dr. Yingzi Lin (PI). A special thanks goes out to Prof. Latika Menon in NEU’s Physics Department for use of the thermal evaporation machine in her lab, and Prof. Carol Livermore in the COE for use of the spin coating and storage facilities. Additional thanks go out to Dr. Yongmin Liu and Dr. Lin Li for provided light spectroscopy analysis machine, and the great engineering staff at Instron ® Applications Lab for providing the flexibility testing equipment. Thank you to my committee members, Prof. Kai-Tak Wan and Prof. Sagar Kamarthi for their guidance. Thank you to my advisor, Prof. Yingzi Lin, for her support, guidance and encouragement to pursue this work. A final thank you goes out to my family for always reminding me what is important in life, also for the food.
Table of Contents

List of Tables ................................................................................................................................. ix

List of Figures ................................................................................................................................. x

Abbreviations ................................................................................................................................. Error! Bookmark not defined.

Chapter 1: Introduction .................................................................................................................. 1

1.1. Motivation ................................................................................................................................. 1

1.1.1 Mobile Health Monitoring ................................................................................................... 1

1.1.2 Heart Rate and Cognitive State .......................................................................................... 2

1.1.3 Human-Robot Interaction and Perceived Safety ............................................................... 7

1.1.4 Optical Heart Rate Monitors ............................................................................................. 14

1.2 Research Objectives .................................................................................................................. 16

1.2.1 Specific Aim 1 Design: Near Infrared Light Emission, prove that QDs contribute .... 16

1.2.2 Specific Aim 2: Photovoltaic Effect ................................................................................. 17

1.2.3 Specific Aim 3: Flexibility Analysis ................................................................................. 17

1.3 Outlines ..................................................................................................................................... 18

Chapter 2: Background and Related Work ..................................................................................... 19

2.1 Introduction to luminescent conjugated polymer semiconductors ......................................... 19

2.2 Conjugated Polymers ............................................................................................................. 22
3.1.1 Materials and Solution Preparation ................................................................................. 49

3.1.2 EGaIn Device Assembly ................................................................................................. 49

3.2 EGaIn Device Testing ......................................................................................................... 51

3.3 Al OLED Device .................................................................................................................. 54

3.3.1 Device Structure ........................................................................................................... 54

3.3.2 Al OLED Cathode Application ....................................................................................... 55

3.4 Al Device Results ................................................................................................................. 55

3.5 Discussion of Results ......................................................................................................... 57

3.5.1 EGaIn Device Emission ................................................................................................. 57

3.5.2 Electrode Performance ................................................................................................... 59

3.5.3 Chapter Summary .......................................................................................................... 60

Chapter 4: Photovoltaic Effect ................................................................................................. 61

4.1 Introduction .......................................................................................................................... 61

4.2 Methodology ....................................................................................................................... 61

4.3 Results and Discussion ...................................................................................................... 62

4.3.1 Device Structures .......................................................................................................... 62

4.3.2 PPV Injection Barrier .................................................................................................... 63

4.3.3 Polymer Blending ......................................................................................................... 67

4.3.4 Extraction Barriers ....................................................................................................... 71
Chapter 5: Flexibility Analysis

5.1 Introduction

5.2 Materials Preparation

5.3 Cyclic Loading

5.4 Force and Deflection

5.5 Image Analysis

5.6 Flaw Features Identification

5.7 MEH-PPV Grouping

5.8 Al Cracking

5.9 Bending Forces

5.10 Device operation

5.11 PET Crystallization and Drying/Annealing Temperatures

5.12 Mechanical Analysis

5.13 Chapter Summary

Chapter 6: Optional Additional Fabrication Processes

6.1 ITO Patterning

6.2 QDs and Ligands

6.3 Chapter Summary
# Chapter 7: Conclusions and Recommendations

## 7.1 Conclusion

## 7.2 Recommendations

## Appendix

- Appendix 1 – ITO on PET Deflection Data
- Appendix 2 – Al OLED Deflection Data
- Appendix 3 – EGaIn OLED Deflection Data
- Appendix 4 – Al OLED Center Images before and after bending cycles

## References

## Related Publications & Academic Activities
List of Tables

Table 1 – MEH-PPV Properties reported by Azhar et al., 2015 ........................................... 34
Table 2 - EL Efficiencies reported by Kim et al., 1998 ....................................................... 41
Table 3 – Testing Sample Device Dimensions ................................................................. 78
Table 4 - Maximum forces from cyclic bending tests ...................................................... 83
Table 5 - Dimensions and Bending Inertias for layers in Al OLED Device ................. 95
Table 6 - Dimensions and Bending Inertias for layers in stock PET/ITO ................. 95
Table 7 - Estimated stresses from individual Al OLED layers as simple beams ......... 97
Table 8 - Estimated stresses from individual PET/ITO stock layers as simple beams ................................................................. 97
Table 9 - Estimated forces for deflection of individual Al OLED layers as simple beams .............................................................................................................................................. 98
Table 10 - Estimated forces for deflection of individual PET/ITO stock layers as simple beams .............................................................................................................................................. 98
List of Figures

Figure 1 – Two-Dimensional Emotional Space, Valence & Arousal presented by Colibazzi, 2010 .......................................................... 3

Figure 2 - Reciprocal & Coactive activity of the ANS, as defined by Bernston et al, 1991.......................................................... 4

Figure 3 - Physiological space, as defined by Bernston et. al., 1991 ....................... 5

Figure 4 - R-wave in Heart Rate Pattern......................................................... 7

Figure 5 - Experimental setup of LWRIII and HybridIII ..................................... 8

Figure 6 - Basic Framework of Human-Robot Interaction, provided by Rani et al., 2002 ................................................................. 10

Figure 7 - Setup of Robot Arm Anxiety Test by Kulic and Croft, 2004 ............... 11

Figure 8 - Fourier Transform of the Interbeat Interval by Rani et al., 2002 ......... 14

Figure 9 - Thought Technology BVP Sensor ..................................................... 15

Figure 10 - Light Spectrum Diagram............................................................... 20

Figure 11 - Energy level diagram (left) and emission spectrum (right) reported from Friend et. al (1999)......................................................... 21

Figure 12 – Polyenes, polymers with long, double bonded carbon chains presented by Hideki Shirakawa, 2001................................................. 23

Figure 13 - Conjugated polymer energy bands from Banerji et al., 2013 .......... 24
Figure 14 - Photoluminescence Principles form Banerji et al., 2013 ..................25

Figure 15 - Layered sandwich structure presented by Vasquez-Cordova et al., 2008..27

Figure 16 - Performance efficiencies reported by Nguyen et al., 2000 .................32

Figure 17 - Emission Spectra from MEH-PPV in different solutions by Cossiello et al., 2005.................................................................33

Figure 18 - Band gap of NEH-PPV from different concentrations reported by Azhar et al, 2015.................................................................................34

Figure 19 - Emission spectra of MEH-PPV spun at different speeds by Mustapha, 2010 ........................................................................................................35

Figure 20 - Emission spectra between annealed and un-annealed MEH-PPV samples from Cossiello et al., 2005 ..............................................................37

Figure 21 - Energy diagram reported by Brown et al., 1999 .........................40

Figure 22 - Energy diagram and voltage performances reported by Alam et al., 2002 ........................................................................................................42

Figure 23 - Fluorescent Nano Crystal Lumidots (TM)..................................................44

Figure 24 - Device Structure reported by Bakueva et al., 2004..........................46

Figure 25 - ITO coated PET with transparent tape mask (left), deposited layer of PEDOT:PSS (center), Layout for EGaIn and UV adhesive (right) ...............50

Figure 26 - EGaIn structure Diagram ...............................................................................51

Figure 27 - Finished devices using a MEH-PPV/QD blend (left) and MEH-PPV (right) as functional layers ........................................................................51
Figure 28 - CMOS PL images of MEH-PPV ................................................................. 52
Figure 29 - CMOS PL images of MEH-PPV/QD Blend .............................................. 52
Figure 30 - EL Spectra of MEH-PPV ................................................................. 53
Figure 31 - EL Spectra of MEH-PPV/QD Blend ...................................................... 53
Figure 32 - AL OLED device structure diagram .......................................................... 55
Figure 33 - Al OLED before (Left) and after (Center) Al evaporation, and after Mask Liftoff (Right) ........................................................................................................ 55
Figure 34 - Image of emission area from Al OLED ......................................................... 56
Figure 35 - Image of emission area from Al OLED, with Al electrode highlighted........ 57
Figure 36 - Photovoltaic characterization testing setup .................................................. 62
Figure 37 - Current response chart from McDonald Konstantatos et al., 2005 .......... 64
Figure 38 - Energy band diagram, and depiction of band tilting described by McDonald and Konstantatos, 2005 ........................................................................ 65
Figure 39 - Reverse bias hole injection and extraction paths for the device presented by McDonald and Konstantatos, 2005 ................................................................. 66
Figure 40 - Reverse bias electron injection and extraction paths for the device presented by McDonald and Konstantatos, 2005 ................................................................. 66
Figure 41 - Photovoltaic performance by Rauch et al., 2009 ........................................ 68
Figure 42 - Device structure provided by Rauch et al., 2009 ........................................ 69
Figure 43 - Reverse bias hole injection and extraction paths for the device presented by Rauch et al., 2009 ......................................................................................... 70
Figure 44 - Reverse bias electron paths for the device from Rauch et al., 2009 ........70

Figure 45 - Energy structure for the presented Al OLED device ..........................72

Figure 46 - Revised Energy diagram for the presented Al OLED device ..............73

Figure 47 - Hole injection and extraction paths for the Al OLED device structure ....74

Figure 48 - Electron injection and extraction paths for the Al OLED device structure ........................................................................................................74

Figure 49 - Cyclic bending setup provided by Instron Labs.................................79

Figure 50 - Al OLED and ITO on PET force and deflection data for 1k cycles ......80

Figure 51 - Al OLED and ITO on PET force and deflection data for first 100 of 1k cycles........................................................................................................81

Figure 52 - Al OLED and ITO on PET force and deflection data for last 100 of 1k cycles ........................................................................................................81

Figure 53 - EGAIn OLED force and deflection data for 1k cycles .......................82

Figure 54 - EGAIn OLED force and deflection data for first 100 of 1k cycles........82

Figure 55 - EGAIn OLED force and deflection data for last 100 of 1k cycles ........83

Figure 56 - PET/ITO no bending ............................................................................84

Figure 57 - PET/ITO center after bending .................................................................84

Figure 58 - EGAIn device image before bending .....................................................85

Figure 59 - EGAIn EGAIn device image after bending ........................................86

Figure 60 - Al OLED structure images, Al side up, before (top) and after (bottom) 1k bending cycles........................................................................................................87
Figure 61 - Al crater feature; Al view before bending (a), PET view before bending (b), Al view after bending (c), PET view after bending (d) ....................................................87

Figure 62 - Al smudge feature; Al view before bending (a), PET view before bending (b), Al view after bending (c), PET view after bending (d) .................................88

Figure 63 - Al Cracking feature; Al view before bending (a), PET view before bending (b), Al view after bending (c), PET view after bending (d) .........................89

Figure 64 - Temperature and Conduction relationship provided by Zhou et all, 201493

Figure 65 - 3-Point bending setup diagram .................................................................94

Figure 66 - Radius of curvature and neutral bending axis ............................................96

Figure 67 - Glass Photomask .......................................................................................101

Figure 68 - Patterned ITO on PET ...............................................................................102

Figure 69 - Lifetime performance provided by Rauch et al., 2009 .................................103

Figure 70 - ITO on PET force and deflection data for 1k cycles .........................108

Figure 71 - ITO on PET force and deflection data for 1st set of 100 cycles ........108

Figure 72 - ITO on PET force and deflection data for 2nd set of 100 cycles ..........109

Figure 73 - ITO on PET force and deflection data for 3rd set of 100 cycles ..........109

Figure 74 - ITO on PET force and deflection data for 4th set of 100 cycles ..........109

Figure 75 - ITO on PET force and deflection data for 5th set of 100 cycles ..........110

Figure 76 - ITO on PET force and deflection data for 6th set of 100 cycles ..........110

Figure 77 - ITO on PET force and deflection data for 7th set of 100 cycles ..........110
Figure 78 - ITO on PET force and deflection data for 8th set of 100 cycles .......... 111
Figure 79 - ITO on PET force and deflection data for 9th set of 100 cycles .......... 111
Figure 80 - ITO on PET force and deflection data for 10th set of 100 cycles .......... 111
Figure 81 - Al OLED force and deflection data for full set of 1k cycles .......... 112
Figure 82 - Al OLED force and deflection data for 1st set of 100 cycles .......... 112
Figure 83 - Al OLED force and deflection data for 2nd set of 100 cycles .......... 112
Figure 84 - Al OLED force and deflection data for 3rd set of 100 cycles .......... 113
Figure 85 - Al OLED force and deflection data for 4th set of 100 cycles .......... 113
Figure 86 - Al OLED force and deflection data for 5th set of 100 cycles .......... 113
Figure 87 - Al OLED force and deflection data for 6th set of 100 cycles .......... 114
Figure 88 - Al OLED force and deflection data for 7th set of 100 cycles .......... 114
Figure 89 - Al OLED force and deflection data for 8th set of 100 cycles .......... 114
Figure 90 - Al OLED force and deflection data for 9th set of 100 cycles .......... 115
Figure 91 - Al OLED force and deflection data for 10th set of 100 cycles .......... 115
Figure 92 - EGaIn force and deflection data for full set of 1k cycles .......... 116
Figure 93 - EGaIn OLED force and deflection data for 1st set of 100 cycles .......... 116
Figure 94 - EGaIn OLED force and deflection data for 2nd set of 100 cycles .......... 116
Figure 95 - EGaIn OLED force and deflection data for 3rd set of 100 cycles .......... 117
Figure 96 - EGaIn OLED force and deflection data for 4th set of 100 cycles .......... 117
Figure 97 - EGaIn OLED force and deflection data for 5th set of 100 cycles .......... 117
Figure 98 - EGaIn OLED force and deflection data for 6th set of 100 cycles ..........118
Figure 99 - EGaIn OLED force and deflection data for 7th set of 100 cycles ..........118
Figure 100 - EGaIn OLED force and deflection data for 8th set of 100 cycles ..........118
Figure 101 - EGaIn OLED force and deflection data for 9th set of 100 cycles ..........119
Figure 102 - EGaIn OLED force and deflection data for 10th set of 100 cycles ......119
Figure 103 - Al OLED structure image, Al side up, before bending cycles.............120
Figure 104 - Al OLED structure image, PET side up, before bending cycles...........120
Figure 105 - Al OLED structure image, Al side up, after 1k bending cycles............121
Figure 106 - Al OLED structure image, PET side up, after 1k bending cycles...........121
Chapter 1: Introduction

1.1. Motivation

1.1.1 Mobile Health Monitoring

Heart rate has long since been an essential metric for health monitoring in hospitals and research labs. The advantages of heart rate measurements outside of the hospital and lab environment are rapidly gaining popularity. Interviews with doctors, patients and technicians were carried out to learn more about what existing devices can achieve, and what is desired from new technology. Results from interviews provided a useful insight into the current state of mobile health monitoring, and serves as an appropriate background for the proposed technology.

Non-intrusive heart rate measurements can be made through either an electrical or optical approach. Electrocardiology monitors heart rate with three electrodes placed on the body. The setup typically consists of positive and negative electrodes, placed on opposite sides of the heart, typically around the left and right shoulders, and a third, ground electrode placed farther away from the heart, either down by the stomach, or on the back. Measurements capture the electrical activity of the heart, which can provide very detailed information to a cardiologist, who can use it for diagnosis. Optical sensors measure light reflected through skin tissue, typically at a fingertip, to monitor heart rate. This method, called photoplethysmography (PPG), provides much less detailed information, and less conclusions can be drawn from it compared to its electrical counterpart.

The Holter Monitor is an example of a wearable electrocardiogram used by doctors. It will be given to patients to wear typically 24 to 48 hours, and the information is
mainly used for diagnosis. The device costs two thousand dollars per patient per use. A wearable photoplethysmograph cannot provide data with the same quality, and cannot compete in useful data provided for diagnosis. Data from a photoplethysmograph can only provide information for heart rate, and heart rate variability. While not useful for diagnosis, these two factors are essential for continuous health tracking, which can be beneficial during patient recovery periods. Cardiac surgeons have identified the 30 days after hospital release as a critical period for patients recovering from heart valve surgery. This 30-day period holds the highest rate of mortality for patients, who are recovering from heart valve repair or replacement. Surgeons told us that if patients wore a heart rate monitor that could send them an alert in response to irregular heart activity, the hospital could react, and lives could be saved. To do this effectively, a monitoring device would need to be issued to every patient at risk of such an event. Devices like the Holter monitor are too expensive to issue to a large population of patients. Irregular heart activity can be identified by observing heart rate variability, which means the detailed information of an electrocardiogram is not needed. A low-cost, wearable photoplethysmograph could provide a solution to the problem presented.

1.1.2 Heart Rate and Cognitive State

Psychological studies use a two-dimensional space to determine human cognitive state (T. Colibazzi, 2010). The two dimensions explored are valence and arousal, depicted in fig. 1. The valence axis represents positive or negative emotion response, while the arousal axis represents the intensity of the response (G. Bernston J. C., 1994). Where a subject’s cognitive state lies on these two scales is determined in two different ways: subjectively, and experimentally. Subjective information is collected through questionnaires subjects are asked to fill out after work or a simulation.
Experimental information is collected by measuring a variety of physiological factors that reflect the state of the subject’s autonomic nervous system (ANS). The ANS is divided into two subsystems known as the sympathetic and parasympathetic nervous systems (SNS and PNS) (G. Bernston J. C., 1991). The activity of these two branches are known to depend directly on a subject’s cognitive state. This relationship between cognitive state and physiological responses makes these cues one of the most direct ways to physically measure cognitive state. Studies have found that the most reliable means of determining cognitive state is to collect both physiological and subjective data from subjects.

Psychophysiological studies have defined how physiological factors such as heart rate, respiration rate and skin conductance can determine how nervous or relaxed; or
how content or frustrated a human subject is. Psychophysiology studies report that the activity of physiological functions, such as respiration, heart rate and skin conductance, are dictated by a subject’s cognitive state. Because of this, these functions can be thought of as physiological signals, reflecting cognitive state. SNS activity promotes more energy going to skeletal muscle and sensory organs, activititating what is known as the “fight or flight” state. The PNS activates more internal organs, promoting bodily functions such as digestion, putting us in a state known as “rest and digest” (McCorry, 2007).

Figure 2 - Reciprocal & Coactive activity of the ANS, as defined by Bernston et al, 1991
Under normal conditions, both systems are working equally to achieve homeostasis, creating a balance. Under mental stress, the two systems become unbalanced, usually with the SNS becoming more active (P. Rani, 2002). Because of the opposing natures of the SNS and PNS, it would seem safe to assume that increased activity of one would suggest decreased activity of the other, known as Reciprocal Activation. If this were true, then physiological state could be defined as a single axis, rather than a two-dimensional plane. Bernston et al. presented that there are some instances where the activity of both branches increase, known as Coactive activity (G. Bernston J. C., 1991). The general idea of Reciprocal and Coactive ANS activity depicted by Bernston et al. are shown in fig. 2. Because both coactive and reciprocal activation have been identified, a two-dimensional space is required to accurately define all possibilities of physiological state, depicted in fig. 3.

Figure 3 - Physiological space, as defined by Bernston et. al., 1991
Physiological signals are known to be less dependent on culture, gender and age than other emotional responses, like facial expression or vocal feedback (P. Rani, 2002), meaning they are more reliable indicators for general studies. While this idea of ANS activity existing in a two-dimensional space is interesting, it is too complicated for the focus of this dissertation. To simplify the involvement of psychophysiology, only Reciprocal Activity of the ANS will be observed. The ANS influences smooth muscles to both dilate and contract blood vessels, as well as cardiac muscle to directly control Heart Rate (HR). It is known that Heart Rate Variability (HRV) can be used to measure affective state, and can thus be used to detect when a user is stressed (B. Friedman, 1998) (R. Dishman, 2000). It is known that Activation of the SNS increases HRV, while PNS activation decreases HRV. One of the easiest ways to measure HRV is to measure HR in the time domain (R. Rani, 2004). By looking at HR in real time, the systole, or the point of maximal contraction for each heartbeat, known as an R-wave, depicted in fig. 4, can be identified. The time between R-waves is known as the Interbeat Interval (IBI), and can be used to determine HRV in both the time or frequency domains (R. Rani, 2004).
Figure 4 - R-wave in Heart Rate Pattern

Observing HRV in the time domain has medical applications, as low HRV can be an indicator of Hypertension, Diabetes, and some pulmonary diseases. Frequency domain HRV observations have been used in research to monitor subject stress levels. To better understand how this can occur, the application of Human-Robot Interaction is introduced.

1.1.3 Human-Robot Interaction and Perceived Safety

Robots are developed to aid, work alongside, or instead of humans to create a safer, more productive world. Others are designed to restore or augment human functionality. These desired functions introduce a wide range of ways in which humans will be interacting with autonomous robots. Regardless of the type of interaction, human safety is a top priority for any robot working alongside or around humans. A need has been
recognized to define the metrics to be met for an autonomous robot to be deemed both safe and dependable (A. De Santis, 2008).

One main point of concern is collisions with machines autonomously navigating their environment. While completely avoiding human-robot collisions is ideal, even with proper planning, collisions can occur during human-robot cooperation (HRC). Minimizing the damage from an impact incident is a useful means to address this issue. This can be done during design by minimizing the weight and strength of a robot by identifying a maximum payload, and designing around that. Torque can be measured using a radial arrangement of simple strain gauges, which is small enough to fit inside a lightweight robotic arm (G. Hirzinger, 2001). Using this as a feedback can help monitor the load applied to robotic joints. This can be used to identify collisions, as well as ensure the robotic joint does not take on more load than it was designed for. Current controlled clutches have also been designed for robotic joints. Applying a current to a set of magnetic discs will decrease the amount of torque a joint can apply.

Figure 5 - Experimental setup of LWRIII and HybridIII

One main point of concern is collisions with machines autonomously navigating their environment. While completely avoiding human-robot collisions is ideal, even with proper planning, collisions can occur during human-robot cooperation (HRC). Minimizing the damage from an impact incident is a useful means to address this issue. This can be done during design by minimizing the weight and strength of a robot by identifying a maximum payload, and designing around that. Torque can be measured using a radial arrangement of simple strain gauges, which is small enough to fit inside a lightweight robotic arm (G. Hirzinger, 2001). Using this as a feedback can help monitor the load applied to robotic joints. This can be used to identify collisions, as well as ensure the robotic joint does not take on more load than it was designed for. Current controlled clutches have also been designed for robotic joints. Applying a current to a set of magnetic discs will decrease the amount of torque a joint can apply.
(T. Saito, 2007). Controlling this with a torque sensor is a good means for minimizing harm from collision incidents.

While greater control is helpful, it still cannot make collisions completely unavoidable. For that reason, human-machine collisions are being quantified to determine what types of injury would be sustained from collisions with robots (S. Haddadin A. A.-S., 2007). The robot used, the LWR III robotic arm, has the previously mentioned torque sensing joints, and a load-to-weight ratio similar to those of humans. In order to define the possible injuries sustained, the Abbreviated Injury Scale (AIS), a common and recognized scale in the automotive industry, was used. Collision tests were carried out according to the EuroNCAP, a European, manufacture-independent crash testing program. A Hybrid III dummy is used, which is equipped with sensors to detect the severity of head, neck and chest injuries. The robotic arm would collide with the head of the dummy at velocities ranging from 0.2 to 2 m/s, with 2 m/s being close to the impact speed that can cause damage to the robotic arm. Safety features were active on the robotic arm, so all testing was done with joint torque feedback stopping motion when specific joint torques are achieved. This reaction mechanism activated during high-velocity collisions resulting in collision times of 5-20 ms. Slower collisions did not activate the safety mechanism, resulting in low impact forces, but long, continuous impacts that pushed the head back farther. Because of this, the highest moments seen in the neck were caused at the fastest and slowest speeds. The fastest speed would cause a high force impact that would be cut off by the torque sensing joints, while the lowest speed was ignored by torque sensing, and would continuously apply force with sustained impact. This study proved that torque sensing alone is not enough to prevent damage from unexpected human-robot collisions. Results from this
study encouraged work into more robust algorithms to detect unexpected collisions for the safety of both humans and robots (S. Haddadin A. A.-S., 2008).

In order to cooperate effectively, the human needs to feel comfortable working alongside the robot. This will require the robot to have cognitive awareness. The idea of a robot reading a human’s mind is challenging, if not undesirable. Thankfully, this level of cognitive awareness is not necessary. More realistically, the target level of cognitive awareness should match that of two human co-workers. This “human” level of cognitive awareness is what is required in order to create a safe and productive working environment that utilizes HRC. This idea has been defined as “Implicit Communication,” where human affective state does not need to be told to the robot, but rather can be interpreted from collected data (Picard, 1997). A framework for this process has been presented by Rani et al., shown in fig. 6.

![Figure 6 - Basic Framework of Human-Robot Interaction, provided by Rani et al., 2002](image)

Human robot interaction studies measure different physiological factors to determine how comfortable or uncomfortable a person feels when operating or working alongside a machine.
The two most important metrics for reliable HRO are safety and dependability. The most productive working environment involving HRC can only be realized when the human both is, and feels safe (G. Hirzinger, 2001). A dependable, productive human-robot environment (HRE) can only be achieved when the human has a positive perception of the robot. Subjective studies can be used to determine how humans perceive the robots they interact with (C. Bartneck, 2009), with the most important perceived metric being safety. In order to analyze a subject’s perception of safety, studies have measured valence/arousal levels of subjects as robots move autonomously (D. Kulic E. C., 2005). The purpose of this study was to determine which robot motion would reduce anxiety during direct HRO. A robotic arm was used with four different motions defined by mixing two tasks with two movement plans. The tasks chosen were meant to cause direct contact with the user.

![Figure 7 - Setup of Robot Arm Anxiety Test by Kulic and Croft, 2004](image)

The first task was to pick up a ball from the table and place it in a subject’s hand. The second was to reach out, grab the ball from the user, then retract with the ball. The two paths were labeled Potential Field Planner and Safe Planner. The Potential Field Planner is a motion planning strategy that incorporates obstacle avoidance and goal attraction, based on a control scheme conceived in the 80’s (Khatib, 1986). The Potential Field Planner pre-plans the course movement objective beforehand, and plans
the details within these course objectives in real time in order to avoid obstacles. Maximum velocities are dictated by the distance between the center of mass of the arm joints and an obstacle or the goal. The safe planner is simply the Potential Field Planner with an extra strategy known as the Danger Criterion. The Danger Criterion is a feature that attempts to minimize the force of human-robot impact by dictating the inertia of the arm as a function of the distance between the center of mass of the arm joints and an obstacle (D. Kulic E. C., 2004). The two paths and two movement plans combine to make four Test Paths. Each Test Path was run at three different speeds; 10%, 50% and 100% of max joint velocity (3.14rad/s). This gives 12 different robot arm trajectories. Subjective and physiological data was collected. Subjective data included reporting levels of anxiety, calm, surprise, and arousal, while physiological responses were collected by measuring corrugator muscle activity, skin conductance, and heart rate. Subjective results showed that the Safe Planner induced slightly calmer reactions compared to the Potential Field planner, but slower movement speeds provided more significant reductions in anxiety levels. Physiological measurements determined that anxiety levels, determined from skin conductance and heart rate, were lower with slower movement speeds.

While the subject was safe during every test run, different movement types would elicit varying levels of arousal in subjects. This type of research can be used to determine what movement types humans are most comfortable with for an optimally safe and productive HRE. Heart rate can be a good indicator of anxiety levels, but is affected by many other factors, which create noise in the signal (D. Kulic R. C., 2007). Some studies look at heart rate variability in the frequency domain with good results (R. Rani, 2004), but others note that because of heart rate’s naturally low frequency,
this only works for post-processing, not processing in real time (D. Kulic R. C., 2007). Kulic et al. in 2006 attempted to measure heart rate in real time, and only 10 of 36 had a noticeable HR acceleration, which did not change between interactions. Rani et al. in 2002, decided to use post-processing frequency analysis (P. Rani, 2002). By taking the Fourier Transform of the interbeat interval, data known as the Power Spectral Density, essentially the standard deviation of the frequency spectrum of the interbeat interval, can be found. With this method, they were able to recognize the sympathetic and parasympathetic frequency bands. There are two general frequency bands, a Low Frequency and High Frequency band. The Low Frequency band is known to be around (0.04-0.15 Hz) and is associated with sympathetic activity, while the High Frequency band is known to be around (0.15-0.4 Hz), and is associated with parasympathetic activity (Electrophysiology, 1996). While these bands change from person-to-person, they remained constant within the same person, from day-to-day. Analyzing the magnitudes within these bands proved to be an effective method to recognize levels of sympathetic and parasympathetic activity (R. Rani, 2004).
1.1.4 Optical Heart Rate Monitors

Heart rate can be measured optically using a method called photoplethysmography. Skin has a known “tissue transparency window” in the light spectrum, which includes wavelengths in the Near Infrared Range (NIR) from 700nm to 1000nm. Light in this range can pass through skin up to 10cm before significant diffraction occurs. Oxygenated hemoglobin (HbO₂) in the blood has significant optical absorptive properties in this range. HbO₂ is carried in capillaries that run through skin tissue, which expand and contract in response to the systolic and diastolic pressures created by the beating heart. This creates a blood volume pulse (BVP) in skin tissue, which is directly related to heart rate (HR). The BVP can be measured by observing levels of HbO₂. This can be done optically with NIR light.

Figure 8 - Fourier Transform of the Interbeat Interval by Rani et al., 2002
Most optical HR sensing devices consist of a simple light source and photo-detector that both operate in the NIR range. Optical BVP sensors can be classified into one of three subjects: Clinical, Commercial, and Research. Clinical sensors need to be accurate and easy to use. Nellcor™’s SpO2 Sensor clips onto a finger easily, is reusable, and made to firmly grip the index finger for any patient. The sensor clip itself has OxiMax™ technology built in, which automatically calibrates the readings, eliminating noise from varying skin properties or movement. This almost eliminates the work required by the user to get accurate readings.

One example is a Heart Rate/BVP sensor by Thought Technology, which is designed to be strapped to the ventral face of a fingertip, shown in fig. 9. The device works well and proves that measuring reflected light from tissue by having the light source and detector adjacent to one another is an acceptable layout for a functioning optical BVP sensor. Homemade BVP sensors can be made using devices like the LEGO Mindstorms light sensor or the TCRT1010, which can both be wired to a custom circuit.
These are also reflective optical emitter/sensor devices, with an adjacent light source and detector. The TCRT1010 uses a NIR wavelength of 950nm. While technical specifications for the Thought Technologies and LEGO Mindstorms sensors are unavailable, it is safe to assume they also function in the NIR range. The most common way to use these devices is to strap them to the ventral face of a finger. While this is non-intrusive, it makes gripping anything with that hand difficult. Changing the amount of pressure applied from the finger will alter the overall signal magnitude. Because of this, psychophysiological studies that measure BVP often require test subjects to remain still during data collection (R. Picard, 2001). Some studies try to eliminate this by placing the sensor on a specific point on a device that the test subject must grip to use, collecting signals through natural contact (Lin, 2011). This will lower subject awareness of measurements, which is always desirable in HRO, but will increase the complexity of machine design. These advantages come with the trade-off of losing the guarantee of continuous measurement during a study by having the sensor at a single point on a device rather than secured to the subject. A sensor array on the object in use could improve chances of continuous measurement, as long as the subject remains in contact with the device.

1.2 Research Objectives

1.2.1 Specific Aim 1 Design: Near Infrared Light Emission, prove that QDs contribute

The goal of Specific Aim 1 is to prove that the methods can be put into practice, by using low-cost fabrication approaches to create a light emitting device from organic polymers on a flexible substrate. Once a light emitting structure is realized, Quantum Dots will be added to the polymer, and emission from devices with and without QDs
will be compared. A second device structure that complicates the fabrication process by adding the additional step of thermal evaporation is then developed, so that performance between the two structures can be compared. All structures will be treated as light-emitting devices, and emission spectra are collected as a performance metric.

1.2.2 Specific Aim 2: Photovoltaic Effect

The devices made in Specific Aim 1 will be treated as photovoltaic devices, with the goal to monitor response from a controlled source of light. The devices will be set in a circuit where current can be monitored while light from a source with industry-defined specifications is provided. A comparison of results with similar reported work is discussed.

1.2.3 Specific Aim 3: Flexibility Analysis

Many of the current methods use a glass substrate for LED and Photodiode fabrication. Flexible displays use PET as a substrate, and report flexibility functioning, to a limited degree. The devices fabricated in this work will be put through bending at a set radius of 1.5cm for a total of 1000 cycles. Results of flexibility will be determined by observing force and deflection relationships during bending, a visual analysis of layers before and after bending, and an electrical performance comparison of devices that have and have not gone through bending cycles. Results will be used to determine the effectiveness of the chosen fabrication methods in this work to create a flexible optoelectronic device.
1.3 Outlines

Chapter 1 of this dissertation is a contextual review to serve as background and motivation for the presented work. Chapter 2 presents a state of the arts for the science and technology applied in the presented work. Chapter 3 includes the proposed device structures, fabrication methods, and results from electroluminescence testing. Chapter 4 covers photovoltaic testing, as well as an in-depth analysis of the electronic structure to provide support for the presented results. Chapter 5 consists of flexibility analysis through cyclic bending, and results are compared to simple bending analysis for the various structure layers. Chapter 6 introduces additional fabrication processed that may be beneficial later in the product development process. The work is wrapped up in Chapter 7, which presents conclusions and direction for future work.
Chapter 2: Background and Related Work

The bulk of the work presented here focuses on the optoelectronic properties of both semiconducting conjugated polymers, and quantum dot nanocrystals. Both have a history of being used as either semiconductor light emitting or light sensitive elements, and are used as such in this work towards development of a flexible, thin film optoelectronic device operating in the near infrared (NIR) range. In order to describe the work performed, some fundamentals of electroluminescence, photovoltaics, and material semiconductor properties will be introduced.

2.1 Introduction to luminescent conjugated polymer semiconductors

There are distinct processes that can occur within a material for light emission to occur. The two known major processes are incandescence and luminescence (O'Hara, 2005). When an atom absorbs heat energy to enter an energetic state, and returns to ground by photons carrying the energy away, or light being emitted, the process is known as incandescent. Light emitted through a means of excitation other than heat is called luminescence, of which there are still more types. Triboluminescence is light emitted from mechanical forces, seen when specific crystalline structures are broken. Fluorescence, known as resonant emission, is when an atom enters an excited state by absorbing energy, from light or another source, and returns to the ground state by emitting the same amount of energy through photons. While this sounds very similar to the basic definition of light emission, the distinction is the specific amount of energy absorbed and emitted. This match in energy led to the process being defined as resonant emission. If resonant emission takes time to occur after excitation, not immediately
after the excited state is achieved, it is known as phosphorescence. If resonant emission does occur immediately after excitation, it is known as fluorescence. Resonant fluorescence is the focus of the present work, as this is what occurs in both organic conjugated polymers and inorganic quantum dot nanocrystals. Light color can be measured either by it’s wavelength, in nanometers, or photon energy, in electron volts. The relationship between the two is defined by the Planck-Einstein relation, stating that the energy of a photon is proportional to its wavelength, shown in eq 1.

\[ E = h \nu \]  

Where \( E \) is photon energy, \( h \) is Planck’s constant and \( \nu \) is the frequency of an electromagnetic wave, which is defined in eq. 2.

\[ \nu = c/\lambda \]  

Where \( c \) is the speed of light, and \( \lambda \) is the wavelength of light. Combining these two results in a standard form of planks relation, which provides a simplified conversion between the two units.

\[ E = \frac{1240}{\lambda} \]  

The spectrum of photon energy and wavelengths of visible light is shown in fig. 10.

Figure 10 - Light Spectrum Diagram
Observing the Fermi energy levels of a semiconducting organic conjugated polymer can provide an understanding what light the material can emit. All semiconductor energy levels have two key points; the Highest Occupied Molecular Orbital (HOMO), otherwise known as the upper edge of the valence band, and the Lowest Unoccupied Molecular Orbital (LUMO), known as the lower edge of the conduction band. Poly(p-phenylene vinylene) (PPV) is one of the first organic conjugated polymers synthesized to emit light, and will serve as an example to show the significance of these energy levels. The values help determine the compatibility of current flow at an interface between two materials, which is often portrayed in an energy diagram, like the one presented in fig. 11 for a device using Indium Tin Oxide (ITO), Poly (p-phenylene vinylene) (PPV) and Aluminum (Al), by Friend et. al (R.H. Friend, 1999). All values in an energy diagram are commonly expressed in electron volts (eV). Both ITO and Al are metal electrodes, and only have one significant energy level, known as their work function (WF). The work function of ITO is shown as $\Phi_{ITO}$ in fig. 11.

![Energy level diagram (left) and emission spectrum (right) reported from Friend et. al (1999)](image)

The WF for both electrodes are close to PPV’s HOMO and LUMO levels, which is partially what makes them acceptable electrodes in this device. The difference between
an electrode’s WF and a semiconductor HOMO and/or LUMO levels can create what is known as an energy barrier, and dictates the energy required for current to flow across the interface between the two materials. This is an important detail in optoelectronic device development, and will be touched on in more detail in Chapter 4. A semiconductor’s Energy Gap, the gap between HOMO and LUMO levels, is closely related to the photon energy that will emitted through fluorescence. PPV has HOMO and LUMO levels of 5.3 and 2.8 eV respectively, with an energy gap of 2.5 eV, and is reported to emit yellow-green light, around 550 nm. As a comparison, the 2.5 eV energy gap would suggest light emission around 500 nm, which does not match the measured 550 nm light emitted, which has a slightly lower photon energy of 2.25 eV. This mismatch shows that the entire bandgap is not responsible for emission, which matches what has been suggested, that photoexcitation leading to emission is produced in a band below the material’s bandgap (R.H. Friend, 1999). This concept is not a huge surprise, as no energy conversion process will have 100% efficiency, and will be subject to some form of energy loss. This example shows how a semiconductor’s energy gap is related to, and can be used to predict the light that will be emitted. In order to understand how light emission occurs in a semiconductor, properties of the polymer structure must be looked at in greater detail.

**2.2 Conjugated Polymers**

The path towards development of organic, conjugated polymer semiconductors began with the discovery of polyenes, which are polymers with long, double bonded carbon chains. The significance of this structure is that the energy gap size is directly related to the number of double bonds in a polymer. Even more specifically, this
structure allowed for a single (Pi) electron to be on each carbon atom, which is what allows conductivity. Eventually such polymers were developed that could be spin coated from solution onto substrates, which is a simple process for creating thin film layers over a large area for electronic device applications.

The path of development lead to two new features not seen before in organic polymers and polymer films. The ability to conduct electricity, and subsequently, the capacity for electrical excitation. The team that discovered this first feature won the Nobel Prize for Chemistry in 2000 (Shirakawa, 2001). Continued work on this idea lead to methods that can adjust the valence and conduction band. Further characterization discovered that an increasing number of double bonds in a polymer will decrease the energy gap. This became a way to custom tailor the energy gap of conjugated polymer films. Polymer tuning can make it easier for electrons to be excited from the valence band (V_b) to the conduction band (CB), as well as adjust the energy gap towards the visible light range. These two improvements, combined with the original discovery, leads to a conductive polymer with semiconductive, more specifically photoconductive, features (Rehahn, 2003). Such conductive polymers are known to have three main
applications – OLEDs, organic thin film transistors, and organic solar cells (Stephen R. Forrest, 2007).

Figure 13 - Conjugated polymer energy bands from Banerji et al., 2013

Light emission from a thin layer of a photoconductive organic polymer is possible if the layer is sandwiched between two electrode layers. The electrode work functions (WF) need to be compatible with the polymer HOMO and LUMO levels, and at least one electrode needs to be transparent, to allow emit light to escape the structure. A simple summary of OLED light emission is provided by Vazquez-Cordova et al., (Sergio Vasquez-Cordova, 2008); “Injection of holes and electrons from electrodes into the organic layer, where they recombine to form into excitons, then radiatively decay to produce light.” This process can be broken down into four key steps: Charge injection, charge transport, charge recombination, and exciton decay. Each of these steps are shown in fig. 14, and can be described in slightly more detail.
Step 1) Charge Injection: Electrons are injected into the conduction band (LUMO) of the polymer molecules from the cathode, while holes are injected into the polymer valence band (HOMO) from the anode. In order for this to happen efficiently, the respective Fermi levels of the anode and cathode need to match the polymer HOMO and LUMO levels. Additionally, sufficient injection requires very good electrical contact at these interfaces.

Step 2) Charge Transport: The two charges pass through the polymer layer in opposite directions – holes travel from the anode towards the cathode, electrons from the cathode towards the anode. Even passing through the thin layer of polymer requires energy. There are energy barriers between the polymer molecules. The act of holes and electrons overcoming this barrier to move between molecules is known as hopping. Not having the energy to overcome these barriers prevents molecule hopping, which will in turn prevent current from flowing through the polymer layer (Rehahn, 2003).
characterization of electron hopping was developed on ideas from Disorder Formalism (Sergio Vasquez-Cordova, 2008).

Step 3) Charge Recombination: An electron and hole that meet in a single molecule form an exciton. This act is called “recombination.” Of the recombinations that occur within conjugated polymers, 25% are singlet, 75% are triplet excitons (Klaus Mullen, 2006). These two types of exitons have a very short lifetime before they leave their energized state by releasing energy.

Step 4) Decay of Excitons: Exitons return to the ground state by releasing energy, which results in holes and electrons involved parting ways. Decay of triplet excitons occurs via release of heat energy. Decay of singlet excitons occurs via fluorescence, which is why conductive polymers can have a maximum EQE of 25%. Adjusting the Pi-conjugated system structure, the molecule bandgap can be controlled, which can be used to adjust the wavelength of light emitted.

Decades of work with PPV have led to two major polymers derived from it, 2-methoxy-5-2(2’-ethylhexy)-p-phenylene) (MEH-PPV) and a blend of PPV and poly(9,9dioctylfluorene) (F8), known as Superyellow. MEH PPV was the first soluble PPV derivative, which makes it less complex and costly to use in device fabrication compared to it’s predecessor, PPV (R.F. Cossiello, 2005).

The solubility of MEH-PPV makes it easier to work with than PPV, requiring less work to create a functional thin film from crystalline powder. MEH-PPV has proven to be popular for use in both electroluminescent and photovoltaic devices (Mustapha, 2011). The work presented uses MEH-PPV as the main electroluminescent element, and will be the emissive polymer discussed for the remainder of this work.
2.2.1 MEH-PPV Thin Films in OLEDs

MEH-PPV is a conjugated polymer derived from PPV, with HOMO and LUMO levels around 5.1 eV and 3 eV respectively, providing an energy gap of 2.1 eV, and emits light with a peak wavelength around 580 nm, with some variations due to differences in fabrication. For example, the optical energy gap has been calculated from measured absorption spectra of films spun from chlorobenzene solution at 2.47 eV (Mustapha, 2011), which matches previous reported LUMO and HOMO levels of 2.82 eV and 4.94 eV respectively (Sandeep Kumar, 2004).

Figure 15- Layered sandwich structure presented by Vasquez-Cordova et al., 2008

The most common MEH-PPV OLED structure involves a stack of layers, including two electrode layers, one anode and one cathode, an MEH-PPV functional layer, and optionally, a hole injection layer between the anode and MEH-PPV. This has been identified as the “typical sandwich structure” created by spin coating a polymer layer onto an electrode, and then evaporating another metal electrode on top (T. Q. Nguyen, 2000). The materials chosen for electrodes are important, as Fermi energy level compatibility dictates how well holes and electrons pass through the interface of two materials. The available layer deposition methods depend on the material chosen. The
most popular way to deposit MEH-PPV is to prepare it in solution, and then deposit the solution onto a substrate to create a continuous, thin film layer. Spin coating and doctor blading from solution are methods used for thin film deposition of polymers. Because of the simplicity of the process, spin coating is the predominant method used in research (Mustapha, 2011). Organic polymer layer thicknesses are typically in a sub-micron range, measured in the hundreds and tens of nanometers (Mustapha, 2011) (Chang, 2005).

2.2.2 Fabrication details and resulting physical properties and morphology

There are a number of different options to consider for solution preparation, including the solvent of choice, solution concentration, as well as mixing conditions and possible filtration. Deposition includes a set of variables including spin speed, spin time, drying time, and drying temperature. A number of different solvents have been reported for use, including chlorobenzene and toluene. The solutions take time to prepare, and are stirred overnight, or at an elevated temperature for less than a day. Once the solution is ready, it can be spun onto a substrate, but many report a filtration step before spin coating. Each of these details creates an opportunity for variation, and researchers are trying all combinations of methods. Azhar et al. prepare MEH-PPV in a toluene solution, stirring for 48 hours at room temp (Azhar, 2015). Mustapha et al. (2011) prepared MEH-PPV in a chlorobenzene solution, omit stirring time and conditions, but mentions that between stirring and spin coating, the solution was “filtered thoroughly” (Mustapha, 2011). While many papers mention a MEH-PPV solution filtration step, few provide details. Guo et al. mention in their methods that MEH-PPV solutions were filtered through a 0.45 um PTFO syringe filter (Guo, 2006).
These variations are far from insignificant to the resulting product. It is well documented that film morphology can be controlled by solution concentration, spin speed, and annealing (T. Q. Nguyen, 2000). When spin coating, film thicknesses can be controlled by polymer solution concentration, polymer molecular weight, spinning velocity, and the solvent evaporation weight (Chang, 2005) (Otilia Sanda Prelipceanu, 2007). The substrate surface energy also plays a role in how the solution will wet and spread during deposition. An understanding of how each of these details affects the functional layer’s physical form, morphology, electrical and optoelectronic performance has been and is still being aggressively pursued through research in the past two decades. To understand what has been discovered, a look at how measurements and characterizations are carried out is required.

2.2.3 Measuring Physical Properties

A variety of methods are available to characterize a polymer film’s physical form. Through both optical and mechanical methods, film thickness and surface properties can be evaluated. Surface profilometers use a small stylus to measure changes in surface profile, which is a mechanical method used to measure film thicknesses (Chang, 2005). Optical profilers, such as the Zygo NuView 6000, available in the KOSTAS clean room facilities at Northeastern, can provide information to characterize surface roughness and step heights for thin films of non-transparent materials, such as metals, through analysis of reflected light. Use of this machine requires no additional sample preparation, and can provide a height resolution of 1 nm. Spectrophotometers, such as the Nanospec Spectrophotometer at Northeastern, can use information from reflected monochromatic light to measure the thickness of translucent films, if the materials refractive index is known. Both of these optical devices require a mirror surface under
the films for measurements, most commonly by depositing the films onto a bare silicon wafer.

When measurements are not possible, film thicknesses can be estimated if the solution properties are known, using equation 1.

\[ h_f = k \times 1,0 \omega ^{-\beta} \]  

Where \( h_f \) is film thickness, \( k \) is a constant depending on solution viscosity, properties of the polymer and solvent. \( X \) is polymer weight fraction, \( W \) is spin speed, \( B \) is related to solvent evaporation rate, usually from 0.4 to 1.

### 2.2.4 Physical properties, morphology, and electrical and optical performance

The properties of a polymer film have a direct effect on the optical and electrical performance. The morphology of the polymer chains that make up the thin film can affect functional details such as conductivity and emission efficiency (T. Q. Nguyen, 2000). Architecture can also have effects on performance, such as how film thickness will change the distance charges need to pass between electrodes, which can dictate operational voltages (T. Q. Nguyen, 2000).

Methods other than observing the electrical properties of thin film organic polymers can be used to characterize functional films. The thickness, surface morphology, and UV/VIS spectra of a film can provide information on luminescence characteristics (Otilia Sanda Prelipceanu, 2007). UV/VIS spectroscopy measures the amount of light reflected by a sample, which can be used to determine the amount absorbed by the sample. For semiconducting polymers, the wavelength and intensity of light absorbed is closely related to what can be emitted. This method is used to characterize
luminescent properties without applying power, and can work in conjunction with those types of measurements as comparison for performance analysis. As an example, optical energy gaps have been calculated from measured absorption spectra of films spun from chlorobenzene solution at 2.47 eV (Mustapha, 2011), which matches previously reported LUMO and HOMO levels of 2.82 eV and 4.94 eV, respectively (Sandeep Kumar, 2004). This does vary slightly from other reports, likely due to differences in deposition methods used. For a better understanding of how methods can dictate performance, major work observing effects of each step are recognized.

2.2.5 Effect of solvent on polymer film

Polymers spun have been spun from solution using a wide range of organic solvents such as toluene, chloroform, and tetrahydrofuran. Work by Nguyen et al. (2000) (T. Q. Nguyen, 2000), focused on how the solvent used can affect the polymer chain aggregation and chain morphology, which in turn has an effect on conductivity and emission efficiency. These findings are based on the idea that increased interchain interactions in conjugated polymers promote carrier transport but reduce emission efficiency, and that these properties are carried over to films spun from solution, even after the solvent has evaporated. MEH-PPV in chlorobenzene promotes chain aggregation. Using tetrahydrofuran (THF) as a solvent results in comparably less chain aggregation, creating a higher turn-on voltage, but also higher External Luminescence Quantum Efficiency (ELQE).
Figure 16 - Performance efficiencies reported by Nguyen et al., 2000

To take advantage of both properties, the lab spun a tri-layer MEH-PPV structure from THF sandwiched between layers from CB to get both lower turn on voltage and higher ELQE performance (T. Q. Nguyen, 2000). Characterization by Cossiello et al. showcases how solvent types will affect polymer chain length, as well as the difference in performance from morphologies (R.F. Cossiello, 2005). THF & chloroform have a preference for MEH-PPV ramifications, which means more, shorter subdivisions of the polymer are created. Chlorobenzene, xylene, and toluene solvate the polymer backbone, forming longer chains. Use of solvents that promote longer polymer chains result in sharper emission peaks by comparison (R.F. Cossiello, 2005).
2.2.6 Effect of solution concentration on polymer film

MEH-PPV film characterization by Azhar et al. (2015) spun films from a single solvent, choosing toluene (Azhar, 2015). For the test, the solutions of concentrations ranging from 1-7 mg/ml were spun at 2000 rpm for 60 seconds, then annealed at 50°C for 60 seconds. Predictably, a solution with a higher concentration of MEH-PPV results in thicker films. X-ray spectrometry determined the film absorption spectra, which can...
be used to estimate the optical bandgaps. These bandgap results show how the emission spectrum can be adjusted, to a small degree, by simple changes in fabrication steps. Observing current-voltage relationships shows that films spun from 5 mg/ml concentrations have the best conductivity, but no electroluminescence was tested.

Table 1 – MEH-PPV Properties reported by Azhar et al., 2015

<table>
<thead>
<tr>
<th>Concentration (mg/ml)</th>
<th>Thickness (nm)</th>
<th>Energy Gap EG (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>27.8</td>
<td>2.00</td>
</tr>
<tr>
<td>3</td>
<td>59.7</td>
<td>2.00</td>
</tr>
<tr>
<td>5</td>
<td>85.8</td>
<td>2.06</td>
</tr>
<tr>
<td>7</td>
<td>104.8</td>
<td>2.08</td>
</tr>
</tbody>
</table>

Figure 18 - Band gap of NEH-PPV from different concentrations reported by Azhar et al., 2015
2.2.7  Effect of spin speed on polymer film

Characterization of differences in MEH-PPV films with a focus on spinner speed has been carried out (Mustapha, 2011). MEH-PPV was spun from a chlorobenzene solution of 0.1 mg/ml, at two different speeds, then dried at room temperature. Slower spinning speeds resulted in formation of thicker films. Film thickness has a significant effect on both absorption and electroluminescence amplitudes, but little effect on the wavelength. The results show that thicker films have greater absorbance, but less emission compared to films spun thinner.

![Figure 19 - Emission spectra of MEH-PPV spun at different speeds by Mustapha, 2010](image)

2.2.8  Effects of annealing

The significance of annealing seems to be overlooked by many labs, as there is a great deal of variance between procedures. After spin coating, films are left to dry, allowing any remaining solvent to evaporate. Different works have reported carrying
out this step at temperatures ranging from room temperature to as high as 215°C. Work that dries at 50°C or lower do not aim to anneal the material, but just to increase the solvent evaporation rate (T. Q. Nguyen, 2000).

Temperatures higher than 70°C are utilized for annealing purposes, but some conflict exists in reported details. MEH-PPV glass transition temperature is important to consider during this step, but two different temperatures have been reported. Nguyen et al. (2000) annealed at 210°C in a nitrogen dry box, and states that the film glass transition occurs around 216°C, with a measurement error of +/- 10°C (T. Q. Nguyen, 2000). Work annealing at a similar temperature, 200°C in atmosphere, reported that the annealing step has a significant improvement on luminescence performance (Otilia Sanda Prelipceanu, 2007). This work also discovered that controlling the heating rate can define surface roughness, which is worth considering when trying to interface with different conducting materials.

Other work on annealing claims MEH-PPV glass transition occurs at 70°C, and reports performance differences between films undergoing no annealing, and those annealed at 70°C. The work does show that annealing at 70°C results in sharper emission peaks, as well as a blue shift in overall emission. While these results are significant, they do nothing to prove glass transition in the MEH-PPV (R.F. Cossielo, 2005). Similar work dries films at 80°C, but only for the purpose of solvent evaporation, not to anneal or perform glass transition (Sergio Vasquez-Cordova, 2008). Annealing has proven to have interesting effects on MEH-PPV films, but the temperatures used will be limited by the substrate and electrode material chosen to work with.
Figure 20 - Emission spectra between annealed and un-annealed MEH-PPV samples from Cossiello et al., 2005

2.2.9 Patterning MEH-PPV films

Methods to pattern a layer of MEH-PPV are somewhat limited. Compared to metals, organic polymers have very low glass transition temperatures, which means the traditional patterning methods, such as chemical lithography, would destroy the film, or at the very least, significantly decrease performance. Because of this, well established patterning methods developed for Complimentary Metal-Oxide Semiconductor technologies are not an option.
Solution processed polymers are candidates for inkjet printing, a low-cost additive patterning method. This method often leads to pinholes forming in layers, which can cause shorts to form across the layer. This is a current topic for concern, but solutions found tend to work on an individual polymer basis (Jayesh Bharathan, 1998).

2.3 OLED Electrodes

2.3.1 Metal electrodes in OLEDs

Aluminum is a popular electrode used in a large variety of electronic devices, and has been long before OLED research began. It has a known work function of 4.2 eV, which is a close match to the LUMO level of MEH-PPV. The material is cheap, handled easily, and can be flexible when deposited in thin enough layers. Al can be deposited through thermal evaporation, which involves melting and boiling Al slugs, to form a thin layer on a sample positioned above. This method requires heating the Al source, but not the target sample it will be deposited onto, which makes it a favorable option for devices including organic polymers.

Magnesium (Mg) is another popular electrode material for OLED devices. Like Al, it has characteristically good conductivity, and can be deposited through thermal evaporation. It has an even lower work function, around 3.7 eV, and has distinct advantages, which will be explored in Chapter 4. Mg is reactive with oxygen, and will combust if exposed to the normal atmosphere. Work with Mg must be done in an inert environment, which complicates the required deposition process. Because of this limitation, another metal, typically Au, is deposited on top to protect Mg from atmosphere. This means Mg is only used in optoelectronic applications if the interface
with a semiconductor introduces a distinct advantage over other metals. Mg is not used in the current work, but will be brought up in discussions for performance comparison.

Indium Tin Oxide (ITO) is a clear, conductive metal popularly used in optoelectronic devices. Over two decades of study has resulted in a very significant optical electrode material. The electrode work function have been reported to be around 4.7-4.9 eV (Vazquez-Cordova et al. 2008). This value matches the HOMO level of MEH-PPV relatively well, making it a compatible anode for the polymer. In addition to the work function, the metal has low resistivity, is easy to pattern, and has close to complete transparency, around 90%. This collection of properties make ITO ideal for optoelectronic applications. The sandwich structure that OLEDs use causes MEH-PPV to be set between two electrodes, which would be useless if emitted light could not pass through one of the electrodes. ITO as an electrode allows the simple sandwich structure to be possible for OLEDs. Substrates already coated with ITO, such as glass slides coated with ITO, or ITO coated polyethylene terephthalate (PET), are commercially available, and serve as the foundational structure for the vast majority of OLED research. While ITO is used in many optoelectronic devices, there is research that explores performance improvements, either through additional layers, or an altogether replacement.

2.3.2 Organic electrodes in OLEDs

The development of conjugated polymer semiconductors is a result of research exploring the possibility of organic electrodes, which has occupied physicists and chemists for 50 years (Stephen R. Forrest, 2007). PEDOT:PSS is an organic polymer electrode that, while it can function on its own as an electrode, is often used in combination with ITO. PEDOT:PSS has been reported as “one of the most successful
polymers in the family of conductive polymers (Jian Zhou, 2014).” PEDOT:PSS, like MEH-PPV, can be spin coated from solution to form a thin film functional layer. Unlike MEH-PPV, there is little debate over what solution should be used. Most work reported uses PEDOT:PSS in water, in a solution that is 1.2% polymer by weight. OLED research using PET typically introduces it as a layer to enhance hole injection, spin coating it onto ITO before the functional MEH-PPV. Some work includes a filtration step prior to spin coating, but the advantages are not reported (Guo, 2006).

Figure 21 - Energy diagram reported by Brown et al., 1999

ITO and PEDOT:PSS both have similar work functions, with ITO around 4.9eV and PEDOT:PSS around 5.2eV. Despite this, work comparing an ITO electrode and an electrode using both ITO/PEDOT:PSS has shown that the hole injection barrier is significantly smaller at interfaces with the polymer. Most observed metal-organic interfaces have a 0.5-1.0 eV interface dipole barrier. Introducing PEDOT:PSS to these structures results in a smaller barrier ~0.3eV (N. Koch, 2003). This discovery was seen as an opportunity to lower the turn-on voltage of MEH-PPV OLEDs. PEDOT:PSS and
the original organic semiconductor, PPV, are identified as the dominant hole injection materials for OLEDs (Maksudul M. Alam, 2002). The reported 0.5V increase in built-in structure voltage that lowers turn on voltage from 30V to 15V also helps improve the functional lifetime of the polymer film (Brown et al., 1999). PEDOT:PSS acting as a hole injection layer provides significant advantages, but also ends up being problematic for other applications, which will be discussed in more depth in Chapter 4. Studies on the effect of cleaning treatments on ITO and PEDOT:PSS on OLED turn on voltages have found that treatments of ITO in combination with PEDOT:PSS had a great effect on turn on voltages (J. S. Kim, 1998).

Table 2 - EL Efficiencies reported by Kim et al., 1998

| ITO surface treatment | ITO/PDPV/Ca | | | ITO/PEDOT/PPV/Ca | | |
|-----------------------|-------------|-----------------|-----------------|-----------------|-----------------|
|                       | Turn-on V  | Efficiency      | Turn-on V  | Efficiency      |
|                       | (V)        | (Cd/A)          | (V)        | (Cd/A)          |
| Ultrasonic            | …          | 0.063           | 8.0        | 0.17            |
| Aquaregia (20’)       | 21.0       | 0.046           | 7.0        | 0.15            |
| O₂ plasma (10’)       | 31.5       | 0.1             | 6.5        | 0.26            |
| Aquaregia (20’)/O₂ plasma (10’) | 24.5 | 0.094 | 4.0 | 0.19 |
| O₂ plasma (10’)/aquaregia (20’) | … | … | … | … |

Chemical replacements for PEDOT:PSS as a hole injection layer are also being explored. A single molecule layer of quarterthiophene-2-phosphonate (4TP) will chemically bond to ITO simply by dipping an ITO coated glass slide into a 4TO-THF solution. 4TP has better current density than PEDOT:PSS, with operating voltages less than 1.5V (Guo, 2006). The monolayer is achieved by drying at 150°C, which is between the low drying temperature, and high annealing temperatures used in MEH-PPV OLEDs. This higher temperature will be the factors limiting when this type of layer can be applied.
An alternative approach to improving hole injection does so from the other side of the emissive polymer. The idea is that by placing an organic electrode between the emissive PPV and Al cathode as a hole blocking layer, electron injection is promoted. Most other work uses PEDOT:PSS to reduce the hole injection barrier by the anode to promote hole injection, this work places an organic electrode at the cathode to increase the hole injection barrier, to promote electron injection. The work shows that MEH-PPV with organic electrodes on both sides has the best luminescence intensity at a low turn-on voltage (Maksudul M. Alam, 2002).

Figure 22 - Energy diagram and voltage performances reported by Alam et al., 2002

2.4 Background: Quantum Dots

Quantum Dot Nanocrystals (QDs) have been created and studied since 1985 (A. Ekimov, 1985). These QDs were originally popular for their potoluminescent ability, absorbing and emitting specific wavelengths of light, through what is known as the
quantum confinement effect (Toshihide Takagahara, 1992). The specific wavelengths are directly related to crystal size, which can be controlled during the crystal growth process. This ability, called the quantum size effect or size tuning, broadens the possible applications, and QDs across the entire visible spectrum are commercially available at companies like Sigma Aldrich (Lumidots). Continued work with QDs has led to discovery of their optoelectronic properties. QDs are a semiconductor material with both photoluminescent and electroluminescent properties (V. Colvin, 1994). Using size tuning, applying power to the QDs will cause them to emit light. Alternately, absorption of light will cause the QDs to create a small voltage (S. McDonald G. K., 2005).
As the idea of size-tuning suggests, larger QDs function at larger wavelengths of light. Growing QDs for any wavelength in the visible spectrum is possible, but attempts to grow QDs large enough for the infrared range has introduced complications from effects such as ostwald ripening, which causes size distribution inconsistencies. One method discovered overcomes this issue by using a core-shell structure technique (N. Tessler, 2002) (M. Schlamp, 1997). This method uses two materials – a core material with properties that make it easier to grow, and a shell material with the desired optical properties. A specific solution was discovered for Lead Sulfide (PbS) quantum dots,
where varying temperatures and stabilizing ligand concentrations during QD growth have a direct effect on size distribution, along with an incubation process after growth that is found to cause effects opposite to ostwald ripening (M. Hines, 2003). Using these processes, PbS QDs with an absorption spectra ranging from 800 to 1800 nm can be grown. Creating core/shell QDs through an alloying process allows the quantum confinement effect to be tunable by crystal composition rather than size. This introduces a consistency not before seen in tuneable quantum dots, which allows for easier integration into optoelectronic devices (Xinhua Zhong, 2003).

Initial optoelectronic tests with QDs spun in a thin film show a low efficiency, of which ligands on the QD surface are suspected to effect. These ligands were introduced as stabilizing agents during the growth process, and are bonded to the NC surface after growth. Methods have been explored to exchange these ligands in an effort to increase QD efficiency as both an electroluminescent and photosensitive element (G. Konstantatos, 2006) (Sargent, 2005) (K. Bourdakos, 2008).

2.4.1 Quantum Dot LEDs

Light emitting diodes using quantum dots are explored in research, using structures almost identical to the previously defined “sandwich structure” used in OLED research, with spin coated layers of a mono-layer of QDs as the photoactive layer (L. Bakueva, 2004) (Daniel Ratchford, 2011).

An emissive layer consisting of a blend of QDs suspended in a conjugated polymer provided significant increases to efficiencies, proving that this is a better QD application method for OLEDs. Adding increasing amounts of QDs to a polymer film increases QD emission while decreasing polymer emission, while also increasing the
overall device turn-on voltage. This research suggests that an increasing presence of QDs in a polymer blend converts the polymer to a more transporting role than an emitting role (N. Tessler, 2002). Steps taken to reduce QD clumping and create a more even distribution of QDs in a polymer layer have proven to lower turn-on voltages, as well as increase emission efficiencies (B. Kwak, 2009).

![Device Structure reported by Bakueva et al., 2004](image)

**Figure 24** - Device Structure reported by Bakueva et al., 2004

### 2.4.2 Quantum Dot Photodetectors

Layers of spin coated quantum dots have also been used as photodetectors, with the motivation to reach the infrared light range that cannot be reached by traditional Si photodiodes. Initial work demonstrates a struggle in balancing responsivity while trying to keep dark currents low (G. Konstantatos, 2006). Continued work shows that QDs in a polymer blend also works in photovoltaics, and found that this, as well as introducing layers acting as injection barriers help reduce device dark currents (S. McDonald G. K., 2005). Work introducing an active matrix backplane provided evidence that QD polymer blend layers can successfully be used as the photosensitive element in an imaging array (Tobias Rauch, 2009). The most interesting result of this work is that the QD/polymer blend does not need to be patterned to act as separate pixels in an imaging
array. Incorporating the active matrix backplane into the known sandwich structure achieves local activation of the QD polymer blend, which is what allows a continuous, unpatterned QD polymer layer to be the photoactive element in a sensing array.

### 2.5 Sandwich Structure in OLEDs

Across the number of devices described above, including conjugated polymer OLEDs, Quantum Dot LEDs, Quantum Dot photodiodes, and QD/Polymer blend LEDs and Photodiodes, one common theme would present itself – the multilayered sandwich style structure. Because of the reported success as both light emitting and photosensitive structures, as well as the ability to be produced with low-cost methods, this sandwich style structure will be the structure of choice. The structure reduces necessary processes to spin coating and thermal evaporation. In the interest of further simplification, a second device architecture is addressed. A similar structure, with simpler methods has been introduced as a means to fabricate OLEDs outside of a cleanroom environment (Sergio Vasquez-Cordova, 2008).

### 2.6 Chapter Summary

The review presented covers the current state of conjugated organic polymers, quantum dot nanocrystals, and their use in optoelectronic devices. Award winning research lead to the discovery of conductive organic polymers, which paved the way for the material to be used as the active element in light emitting devices. Quantum Dot nanocrystals, initially developed and used for their photoluminescent properties, have been discovered to have both electroluminescent and photovoltaic properties. They have been used as functional elements in light emitting and photosensitive
elements. Devices using both materials use a similar architecture, and some devices include both materials in their architecture to improve performance. These observations provide the foundational logic for the presented device architecture, which is meant to serve as both a light emitting and photosensitive device.
Chapter 3: Quantum Dot/Polymer Organic Light Emitting Diode

3.1 Device Fabrication

3.1.1 Materials and Solution Preparation

Flexible sheets of ITO on PET, available from Sigma Aldrich (749745), are used for the substrate and electrodes. The sheets come with a protective cover over the ITO, so minimal cleaning/preparation is required. A solution of PEDOT:PSS in water (1.3% wt), available from Sigma Aldrich (483095), serves at the hole injection layer material. The organic polymer MEH-PPV (Sigma-Aldrich 753793-5ML) is prepared in toluene, 1 mg/ml, to create two identical solutions, stirred overnight at 50°C. One solution is then combined with a solution of alloyed CdSe/ZnS, 630 nm quantum dots in toluene, 1 mg/ml (Sigma-Aldrich 753793) to create a toluene solution blend with a weight ratio of 1:1 PPV:QDs, which is again stirred overnight at 50°C. Both solutions serve as the active layer solution material for devices with or without QDs. Gallium-Indium Eutectic (EGaIn) (Sigma-Aldrich 495425) and light curing adhesive (McMaster-Carr 74545A24) are additional materials used to secure the top electrode to the device.

3.1.2 EGaIn Device Assembly

Two different devices were made – both have the same device architectures, but one uses an MEH-PPV/QD blend solution as the active layer, and the other MEH-PPV solution. Starting with a 3x5 cm sheet of PET coated with ITO, a small piece of clear tape is set to cover an area about 2x3 cm at the end of the strip, as a mask. 4 drops of PEDOT:PSS solution are spin coated on at 2000rpm for 40 seconds, then dried on a hotplate at 80°C for 3 minutes, resulting in a ~1.5 cm diameter circle. A second layer
of PEDOT:PSS is then spun and dried using the same methods. Two layers of either the MEH-PPV/QD blend solution or just the MEH-PPV solution are then spin coated on, both at 2000 rpm for 40 seconds followed by drying at 80°C for 3 minutes. Before and after all drying steps, the clear tape mask was respectively removed and then replaced with a clean mask.

Figure 25 - ITO coated PET with transparent tape mask (left), deposited layer of PEDOT:PSS (center), Layout for EGaIn and UV adhesive (right)

After both polymer layers are deposited and dried, a UV curing adhesive is used to secure the top electrode. EGaIn is applied at the same time to provide a conductive contact between the electrode and polymer layer. A small droplet of Ga-In eutectic is applied to the center of the deposited polymer, forming an area around 0.25cm in diameter. UV cured adhesive is applied in a ~1.5cm ring, with the EGaIn at the center, shown in fig. 25. Because the ITO layer is unpatterned, the size and shape of the EGaIn anode is what defines the emissive layer’s active area. A second 3x5 cm sheet of ITO coated PET is then placed on top at an offset, to keep the 2x3 cm polymer-free area of ITO exposed, while completely covering the EGaIn and adhesive. The layout of this architecture can be seen in fig. 26.
3.2 EGaIn Device Testing

Measuring device resistance is a quick way to determine if it will function properly before connecting it to power. If the resistance is in the 1-5 kΩ range, there is a short in the device, meaning it will not function properly. If the resistance is orders of magnitude higher, typically in the MΩ range, it is worth applying power to see if light emission occurs.

Wires with flat ring connectors are secured to the ITO electrodes with alligator clips, connecting the device to a DC power source. Power is applied, starting at 1V and slowly increasing, to observe if light emission can be visible, which initially occurred at an applied power of 9V. To determine if the QDs contributed to emission, a light spectrum analysis was carried out with a Horiba iHR550 spectrometer for both devices with and without QDs, while connected to a power source supplying 14V. A CMOS
camera was used for alignment and to collect images of the emitting area device spectroscopy analysis.

Figure 28 - CMOS PL images of MEH-PPV

Figure 29 - CMOS PL images of MEH-PPV/QD Blend
CMOS camera images, shown in figs. 28 and 29, show that the entire area is not emitting light. Only small, discrete areas from both devices show signs of emission. Spectroscopy shows a noticeable difference in both the power and wavelengths of light.
emitted between the two samples, shown in figs. 30 and 31. The MEH-PPV device has two emission peaks around 590nm and 650nm, while emission from the MEH-PPV/QD blend has a single peak near 640nm. These results show that the methods do not result in consistent emission areas, but do allow both MEH-PPV and QDs to emit light.

3.3 Al OLED Device

The inconsistent emission areas, shown in figs. 28 and 29, served as a motivation to improve emission performance by introducing a more commonly used cathode to the device architecture. This new architecture is similar to those used in research exploring both conductive polymer and QD optoelectronic devices. Addition of the Al cathode requires the use of a thermal evaporator, which, depending on available resources, is neither a low-cost or large area fabrication method.

3.3.1 Device Structure

The device architecture used in this work is shown in fig. 32. This device, which will be called the Al OLED, is a standard multilayered OLED structure, consisting of an ITO anode on a PET substrate, a PEDOT:PSS hole injection layer, a MEH-PPV/QD hybrid emissive layer, and an Al cathode on top. The bottom four layers of the device, the substrate, anode, hole-injection layer, and emissive layer, are prepared identically to those in the EGaIn device. The only difference is the material and deposition method used for the Al cathode.
3.3.2 Al OLED Cathode Application

Aluminum is thermally evaporated onto the top of the structure, with strips of Kapton tape used as a mask. Because the ITO layer is unpatterned, the size and shape of the anode will be what defines the emissive layer’s active area. Al was deposited to form roughly 0.5x1 cm rectangular cathodes. The Al layers are 2 µm thick.

![Figure 32 - Al OLED device structure diagram]

3.4 Al Device Results

Al OLEDs tested have resistances ranging from 3 to 6 kΩ with turn-on voltages ranging from 3 to 6 V, but light emission fades too quickly for a light spectrum analysis to be made. Increasing voltage would cause emission to temporarily resume, which suggests that something in the functional layer is burning out quickly. Light emission
did occur over half of the active area, but there were small discrete areas that noticeably began emission sooner and stronger than other areas. The emitting area is shown in fig. 34, while the same area with an outline of the Al area, representing what should be the active area, in fig. 35.

Figure 34 - Image of emission area from Al OLED
3.5 Discussion of Results

3.5.1 EGaIn Device Emission

Results from camera images of the EGaIn devices show that the methods presented do not produce a continuous emitting area but rather discrete, inconsistent areas of light emission. In theory, any area of MEH-PPV in contact with the EGaIn should emit light. The presence of any light emission signifies that there is no electrical short within the device, but the inconsistencies must be a result of something preventing emission within the device structure, either in the active element, or in the conducting layers. From the areas that do emit light, spectroscopy results show two peaks from the MEH-PPV, at ~598 nm and ~641 nm, and a single peak from the MEH-PPV/QD blend at ~637 nm. This peak matches the wavelength of the QDs used, providing evidence that the QDs are contributing to light emission. Both the images and spectroscopy results show that the sample with QDs provided overall higher emission, but this was true across all
wavelengths, suggesting it was not a result of just the QDs. Both the emission power differences and discrete emission areas are likely due to inconsistencies created from the fabrication process.

Similar fabrication methods have previously been proven to work, with more consistent emission areas, on glass substrates. The authors recognize two possible reasons for the inconsistencies seen in this work— the sandwiching technique using eutectic and adhesive, or the MEH-PPV deposition methods. These are seen as the two main contributions to the shortcomings of the fabricated devices. Many of the reports that work with MEH-PPV mention a filtration step between solution preparation and layer deposition, but provide no details. Gao et al. report pushing the solution through a 0.45 um micropore syringe filter (Liang Gao, 2014). This was attempted in the current work, but the filter clogged up, preventing any solution from passing through.

External quantum efficiency (EQE) is one of the most important characteristics for evaluation of polymer light emitting diodes. Typically, measurements of the entire light spectrum from an integrating sphere are required to determine the EQE of a light emitting device. More recently, methods have been developed that provide an accurate estimate of EQE from measurements made from simpler, more affordable measurement systems (Manju Shukla, 2011), such as the Hiroba device used to observe the emission spectrum in this work. While these methods could provide an EQE estimate, a limited area was observed for measurements, and within that, only a limited area was actively emitting light. Because of these conditions, the data collected can be used to observe the emitted spectrum, but is not suitable for EQE characterization. Images of the devices show that the red-orange MEH-PPV areas are not distributed evenly, suggesting that
improvements to the polymer deposition process could result in more consistent emission areas.

The fabrication approach and substrate chosen for this work also present performance limitations that cannot be ignored. More prominent work performs deposition steps under vacuum (N. Koch, 2003) (S. McDonald G. K., 2005), which will help reduce structure imperfections from contamination when compared to deposition in atmosphere. As an example, spinning and baking a layer of PEDOT:PSS in atmosphere, as was done in this work, is reported to cause etching into the ITO layer, which can reduce overall device efficiencies (Guo, 2006). The inconsistent emission areas in this work may be a result of the level of control lost from the simplified fabrication steps used. Interestingly enough, similar work seems to rely on the observed clumping property of MEH-PPV, using it in a blend with another polymer to create small MEH-PPV pixels in the functional layer (Nisha A. Iyengar, 2003). This may suggest that other polymers, or a polymer blend could be explored for better results using simplified fabrication.

3.5.2 Electrode Performance

Both OELD structures use ITO as the anode, but have different cathodes, evaporated Al or a layer of EGaIn. Both polymer deposition steps were identical for the two OLED devices, and both anodes have similar work functions, around 4.2 eV. The difference in device resistances is most likely due to the different types of contact the two materials have with MEH-PPV, the extra material interface the Sandwich LED has between the EGaIn and ITO, as well as the significant difference in anode thicknesses. Deposition on a clear substrate prevents direct measurements, but based on deposition times, the Al layer is estimated to be ~2μm. The EGaIn is around the same thickness as
the adhesive, around 0.2mm. Thinner layers will experience less strain from bending, which suggests that the EGaIn OLED is far from ideal for flexible electronics. This will be explored in more depth in Chapter 5.

3.5.3 Chapter Summary

In this chapter, light emission devices are fabricated and tested, comparing results from emissive layers consisting of a polymer, and a polymer/quantum dot blend, using low-cost fabrication techniques that require only a bench-top spinner and a hotplate. Emission spectrum results show that quantum dots provide a significant change in device emission, proving that suspending the quantum dots in a polymer matrix is an effective way to achieve quantum dot electroluminescence, and that the simplified fabrication steps are an effective means to reach these results. A second device structure is then introduced that is more reliable, but requires a more complicated fabrication process. Results from both devices show that emission is limited to discrete areas, which is a result of polymer clumping. Adjustments made to functional layer deposition would provide significant improvements to both device structures.
Chapter 4: Photovoltaic Effect

4.1 Introduction

In this chapter, the devices created in Chapter 3 are no longer treated as emissive structures, but photosensitive structures. Using an external light source, the photoresponse of the devices are tested. Results are compared to previously reported work, and an in-depth review of functional structures are provided to support dissertation results.

4.2 Methodology

The same fabrication methods reported in Chapter 3 are used. Both EGaIn OLED and Al OLED structures are used for testing.

Flat ring connectors are secured to the fabricated device electrodes with alligator clips, which connect the device to a circuit with a variable power supply and a shunt resistor. Current measurements are made by monitoring voltage across a 480Ω shunt resistor with an NI 6069 DAQ, connected to a computer running LabView Signals Express. The setup was able to make measurements as accurate as 0.01 μA. A red LED (635 nm) was positioned 1 cm away from, and facing the device’s active area. The entire setup is contained in a box covered with a towel to prevent any outside light form influencing the system.

To begin testing, the power source is set to a constant voltage. Tests were carried out with the supply providing power in both a forward and reverse bias at values of 0, -2, -4, -6, and -9V. Data was collected for 9 seconds. The red LED was off for the first
and last three set of 3 seconds, and on for the second set. Data recorded is exported to Microsoft excel for analysis.

![Figure 36 - Photovoltaic characterization testing setup](image)

Current measurements show no photoresponse from each applied power. An increase in power did result in an increase in device current, but there was still no noticeable change in voltage for any device at any power when the LED was switched on or off.

4.3 Results and Discussion

4.3.1 Device Structures

An attempt to observe a photovoltaic effect from the fabricated devices was made, but there was no noticeable difference between measured dark and photocurrents. Photovoltaic devices with similar structures, including a hybrid organic/inorganic functional layer, have been reported (S. McDonald G. K., 2005) (Tobias Rauch, 2009). This suggests that a photovoltaic effect may be present in the devices fabricated in this
work, but cannot currently be observed. Two prominent works in this area are presented, which showcase the importance of both charge injection and extraction in optimizing the ratio of photo and dark currents. The structures of these works are compared to the one used in the present work, to provide insight into the material energy structures and how they dictate charge injection and extraction.

4.3.2 PPV Injection Barrier

Prominent work done by McDonald and Konstantatos use some similar materials as the presented work, but some differences that provide distinct advantages (S. McDonald G. K., 2005). Infrared PbS quantum dots are suspended in a MEH-PPV polymer, and PPV is used as a hole injection layer, which actually serves as an injection barrier. Al and Mg metals are used as electrodes.

The PPV was reported to lower PL efficiency, but help improve the photovoltaic effect by lowering the device’s overall dark current, which makes the photocurrent easier to measure. PPV lowers dark current by serving as an electron injection barrier between the electrode and functional layer. Additionally, the difference in work functions between the two metal electrodes are reported to create “band tilting,” which provides different barriers, depending on charge flow direction. This explains the reported current responses, where under the same light, the device with a reverse bias reacts with a stronger photocurrent than with a forward bias.
Figure 37 - Current response chart from McDonald Konstantatos et al., 2005.

With monochromatic illumination around 54 mW and a reverse bias of 5V, photo currents are reported to be 76 uA, with dark currents at 0 uA. The reported PPV layer requires annealing at 200°C, which is possible on a glass substrate, but is well beyond the glass transition temperature of a PET, making it incompatible with the flexible substrate. Regardless of these processes, the remarkably stable and low dark current makes exploring this structure worthwhile.
In order to more clearly understand the reported photoresponse, two essential processes must be observed: charge injection, and charge extraction. Charge injection refers to holes and electrons flowing through the device from the applied power source. The significant path for charge injection is from the electrodes to the QD, and the flow of these charges will characterize the device’s Dark Current. Charge extraction refers to photogenerated holes and electrons from the QD. The significant path for charge injection is from the QD to the electrodes. Figs. 39 and 40 show, under a reverse bias, the path for injected and extracted holes, and injected and extracted electrons, respectively, in the device reported by McDonald and Konstantatos (S. McDonald G. K., 2005).
Figure 39 - Reverse bias hole injection and extraction paths for the device presented by McDonald and Konstantatos, 2005

Figure 40 - Reverse bias electron injection and extraction paths for the device presented by McDonald and Konstantatos, 2005
As fig. 40 shows, injected electrons must travel from the ITO, through the PPV, and through the MEH-PPV to reach the PbS QDs, while extracted electrons must travel from the QDs, through the MEH-PPV, to the Mg electrode. The difference between the ITO work function and PPV LUMO level serves as a significant barrier for injected electrons, while the difference between the QDs and MEH-PPV’s LUMO levels serves as a slight barrier for electron extraction. Looking at fig. 39, the difference between Mg’s work function and MEH-PPV’s HOMO level acts as a hole injection barrier, while there is no significant hole extraction barrier created. If a forward bias is applied, the ITO/PPV interface would provide a smaller hole injection barrier than it does for electrons in the reverse bias. In a forward bias, the Mg/MEH-PPV interface would provide a smaller electron injection barrier than it does for holes in the reverse bias. While operating with a reverse bias, the device structure provides significant hole and electron injection barriers, as well as a small electron extraction barrier. McDonald and Konstantatos acknowledge this, and state that hole extraction is the main contributor to photocurrent. They also suggest that the advantages that the PPV injection barriers provide far outweigh the disadvantage created by the MEH-PPV electron extraction barrier, which is reinforced by their results, reporting a photoresponse greater than 100 nA, which is above the typical range of similar work.

### 4.3.3 Polymer Blending

PPV can create a significant barrier that improves dark/photo current ratios, but is not necessary for an observable photovoltaic effect from Quantum Dots in a polymer matrix. QDs in a polymer matrix have been reported as effective photodetectors using the same electrodes reported in the current work, PEDOT:PSS and Al. With monochromatic illumination of 31.2 uW and a -6V applied bias, photocurrents
measured in the nanoamp range have been reported by Rauch et al. (Tobias Rauch, 2009). This response is lower than those reported by McDonald and Konstantatos, and looking deeper into the device structures can provide an explanation.

Figure 41 - Photovoltaic performance by Rauch et al., 2009
Instead of focusing on overall device structure, Rauch’s work emphasizes the importance of band alignment within the functional layer. The device uses a blend of two polymers and PbS QDs, and reports that the band alignments help with both hole and electron conduction from the QDs. The two polymers are reported to have a “staggered alignment,” which means they both interact with the QDs differently. PCBM’s 4.3eV LUMO level allows for easy electron transport to and from the QDs, while P3HT’s 4.9eV HOMO level allows for easy hole transport. To test this effectiveness, the blend was compared to functional layer blends of QDs and just one polymer. PCBM has a much higher reported efficiency (2.3%) than the P3HT layer (0.2%), suggesting the LUMO alignment with the QD is more important, but the efficiency from a blend of both shows a significant improvement (15%), suggesting charge transport to both electrodes is more important for performance efficiency.
Figure 43 - Reverse bias hole injection and extraction paths for the device presented by Rauch et al., 2009

Figure 44 - Reverse bias electron paths for the device from Rauch et al., 2009
Rauch’s structure creates almost negligible extraction barriers, but also provides smaller injection barriers compared to McDonald & Konstantatos. Comparing McDonald’s dark current in fig. 37 to Rauch’s dark current in fig. 41 serves to show the importance of both injection barriers and an extraction path. Rauch’s device has very good extraction paths and small injection barriers. The effective extraction paths cause photocurrents reported by Rauch to rise and level out at very low voltages. The smaller injection barriers allow the dark current to slowly catch up to the photocurrent as applied voltage increases. Because of these properties, Rauch’s structure works best at a low reverse bias, between 1 and 3 volts. McDonald’s structure has less effective extraction paths than Rauch, but higher injection barriers. McDonald’s less effective extraction paths cause photo currents to rise more slowly, requiring higher biases to be applied. The high injection barriers make this requirement acceptable, keeping the dark current near zero at higher applied voltages. Because of these properties, McDonald’s device operates best at a negative bias between 3 and 5 volts. These two works highlight the importance of the relationship between charge injection and extraction paths. An ideal photovoltaic response is created by a device structure with no barriers for photogenerated charges for high photocurrents, and high charge injection barriers for low dark currents. While Rauch’s work has a faster photocurrent response at lower voltages, McDonald’s report shows both lower dark currents, and overall higher photocurrents. The difference in results between the two suggest that while both features are important, effective injection barriers provide more overall advantages than photogenerated charge extraction paths.

4.3.4 Extraction Barriers
Equipped with a better understanding of the relationship between quantum dots and conjugated polymers, as well as the role their Fermi Energy Levels play in interaction, a more in-depth analysis can be made on the structure created in the current work. Energy levels for the device are shown in figure 45. The QDs used in the current work have two different energy levels. One for the CdSe core, and another for the alloyed ZnS shell. This traditional energy diagram does show levels for all materials in the device, but it does not effectively represent the flow of injected or extracted charges.

Figure 45 - Energy structure for the presented Al OLED device
Figure 46 - Revised Energy diagram for the presented Al OLED device

Charge injection under a reverse bias for the current device structure requires electrons to travel from the PEDOT:PSS into and through the polymer matrix, into the ZnS shell, and finally into the CdSe core. Holes are injected from the Al cathode, through the MEH-PPV and ZnS into the CdSe core. A better representation for these paths is shown in fig. 46, where the hole and electron path can be followed easily.

The path for charge extraction is very similar, just in opposite directions. Holes and electrons are generated inside the CdSe core, and must be transported through the ZnS shell, to the polymer matrix, where holes will go to the PEDOT:PSS anode, and electrons to the Al cathode. Hole and electron charge and extraction paths can be seen in figs. 47 and 48.
Figure 47 - Hole injection and extraction paths for the Al OLED device structure

Figure 48 - Electron injection and extraction paths for the Al OLED device structure
Figure 47 shows that a significant hole injection barrier is provided between Al and MEH-PPV, as well as between the MEH-PPV and ZnS. A hole extraction barrier also exists between the ZnS and CdSe. Fig. 48 tells a similar story for electrons, with an injection barrier between PEDOT:PSS and MEH-PPV, and an extraction barrier between CdSe and ZnS. Unlike the works by Rauch and McDonald, two significant extraction barriers are present in the current work, both within the QD. The ZnS shell causes a barrier for any charges trying to leave the CdSe core. Advertised for use in optoelectronic devices, this barrier does present advantages for electroluminescence. As described in Chapter 2, light emission from conjugated polymers relies on exciton formation. Exciton formation occurs when a hole and electron are present and excited in the same molecule, so increasing the chances of these charges meeting in a molecule will help increase luminescence. The barrier between the ZnS shell and CdSe core traps charges in the QD core, which helps improve the chances of exciton formation increasing OLED performance. These barriers that help OLED performance actually hinder photovoltaic performance. The ZnS/CdSe interface is only a barrier for charge extraction – it does not serve as an injection barrier, which is counterproductive to the lessons presented by Rauch and McDonald. This barrier reduces photocurrents, does nothing to hinder dark current, and is most likely the reason why a photovoltaic response could not be observed in the current device.

4.4 Summary

In Chapter 4, the photovoltaic properties of the devices created in the previous chapter are tested. No photovoltaic response could be observed from the device. The results are compared to two main pieces of work that use similar device structures. The comparison leads to an in-
depth review of device architectures, which pinpoints the Fermi energy levels of the quantum dots as a key area for concern. The materials that make up the alloyed core/shell structure of the quantum dots used in this work create a charge extraction barrier. The extraction barriers cause low photocurrents, resulting in almost no separation between dark and photo currents. This is concluded to be the main reason why a photovoltaic effect cannot be observed in the presented device.
Chapter 5: Flexibility Analysis

5.1 Introduction

Achieving flexibility while avoiding significant degradation of optical and electrical performance metrics is a key goal in the presented work. To explore flexibility, the two device structures fabricated in Chapter 3 of this work are put through a cyclic bending test at a set radius of curvature. To provide a comparison, a stock piece of ITO coated PET that is used as the substrate layer for both devices is also put through testing. Response forces from bending are observed, and device structure properties are observed before and after bending. Results point towards two layers as potential issues for flexible devices. These issues are discussed in more detail, and possible solutions are presented.

5.2 Materials Preparation

The two types of structures introduced in the previous two aims are used in this analysis. Both a double substrate EGaIn OLED, and a single substrate Al OLED, as well as a strip of ITO coated PET, are put through flexibility testing. Fabrication methods are identical to those used in Chapter 3. Only devices with an MEH-PPV/QD blend layer were used for testing. Device dimensions are provided in table 3. The samples were bent using an Instron 3300 Single Column Machine, which is set to apply a fixed deflection at a set rate, and adjust applied forces accordingly.
Table 3 – Testing Sample Device Dimensions

<table>
<thead>
<tr>
<th>Device</th>
<th>Length (mm)</th>
<th>Width (mm)</th>
<th>Thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO/PET</td>
<td>70</td>
<td>17</td>
<td>0.127</td>
</tr>
<tr>
<td>EGaIn OLED</td>
<td>45</td>
<td>26</td>
<td>0.34</td>
</tr>
<tr>
<td>Al OLED</td>
<td>60</td>
<td>16</td>
<td>0.14</td>
</tr>
</tbody>
</table>

5.3 Cyclic Loading

Work on flexible electronics has explored flexibility at bend radiiuses as small as 1 cm (Gerwin H. Gelinck, 2004). The three samples were bent at a 1.8 cm radius for 1000 cycles via 3-point bending using an Instron 3300 Single Column Machine, which is set to apply deflection at a fixed rate of 30 cycles per minute, while recording responding forces. The radius resulted in a bending strain of 0.35%, which is within the range of similar work (H.K. Lin, 2013).

The samples did not experience any additional processing steps. Samples were placed on two supporting points set 1.4 cm apart, and were deflected by a third point directly between the two supports. One full bending cycle involved pressing down for 1.4 mm of deflection, followed by releasing back to 0 mm deflection. All samples were tested with the PET side facing up, meaning deposited structures experienced tension from bending. Active areas of the OLEDs were set to stay at the centermost point during bending, as similar work with PET and ITO has reported that this is where the maximum bending stresses occur (Khalid Alzoubi, 2011). The Instron machine recorded force and deflection data throughout the duration of testing.
5.4 Force and Deflection

Due to the test set up, all layers on the PET substrate experienced tension during bending. A proper bending stress/strain analysis for the functional layers would require an accurate measurement of distance from the neutral bending axis from each layer, and variations in the MEH-PPV/QD layer would cause strain estimations to be unreliable. In order to avoid this inconsistency, bending analysis is kept in simple terms of force and deflection. Figs. 50-55 show sets of force and deflection charts for the three samples. The first set shows data for the full 1k cycles, while the second and third show the first and last set of 100 cycles, for comparison. The full set of 1000 bending cycles for all three samples are available in Appendices 1, 2, and 3. The stock sample shows the least change in force over the 1k cycles, while the two OLED samples both show a
significant change. The changes in response force for the Al OLED occur almost entirely during the first 100 cycles, after which the sample exhibits behavior very similar to the stock sample, aside from a small baseline shift. The EGaIn OLED shows a decrease in response force roughly over the first 300 cycles, after which all cycles look almost identical to cycle set 10. Cracking sounds were audible during the EGaIn OLED first 300 cycles, which is the sound of the adhesive breaking apart from the device. Table 4 shows a list of maximum forces, all of which were seen at the maximum point of deflection. The maximum force for the full set is presented alongside the maximum force seen at the last 100 cycles, to show the decrease in reaction forces throughout the test. Both OLED structures underwent a significant decrease in reaction forces, while the stock sample reaction remained relatively unchanged.

Figure 50 - Al OLED and ITO on PET force and deflection data for 1k cycles
Figure 51 - Al OLED and ITO on PET force and deflection data for first 100 of 1k cycles

Figure 52 - Al OLED and ITO on PET force and deflection data for last 100 of 1k cycles
Figure 53 - EGaIn OLED force and deflection data for 1k cycles

Figure 54 - EGaIn OLED force and deflection data for first 100 of 1k cycles
Table 4 - Maximum forces from cyclic bending tests

<table>
<thead>
<tr>
<th>Sample</th>
<th>Maximum Force (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Full Test</td>
</tr>
<tr>
<td>AI OLED</td>
<td>1.0</td>
</tr>
<tr>
<td>Stock Sample</td>
<td>0.7</td>
</tr>
<tr>
<td>2PET OLED</td>
<td>10.6</td>
</tr>
</tbody>
</table>

5.5 Image Analysis

Surface images of the samples were taken at 10x with an Optiphot 200 Fluorescence Microscope. Images of two separate areas on the stock sample, one that has and one that has not undergone bending, were captured, shown in figs. 56 and 57. Both images show defects on the surface, with the cycled area showing more, and larger cracking. Cracking is observed to form roughly 30 from the bending axis, which contradicts
previous work, which reported that cracks form parallel to the bending axis (Khalid Alzoubi, 2011).

![Figure 56 - PET/ITO no bending](image)

![Figure 57 - PET/ITO center after bending](image)

For the EGaIn OLED, an area showing EGaIn and MEH-PPV is imaged before and after cycling. The images were taken with the MEH-PPV on top, so the EGaIn can be seen underneath the MEH-PPV, in figs. 58 and 59. The images show that some holes
in the MEH-PPV bundles appear larger after bending, which may be where EGaIn began to move through the MEH-PPV, creating device shorts. There is also a noticeable change in the EGaIn edge contours. Both observations show that the EGaIn’s form is susceptible to change from bending.

Figure 58 - EGaIn device image before bending
Two areas were captured for the Al OLED; one at the corner, and one in the center of the Al. No changes before and after bending were noticeable in the center, images are provided in Appendix 4. The corner image showcases three different flaw features that can result from errors in the fabrication process: cracking, craters, and smudging. Shown in figs. 61-63, these areas are observed from both sides, the Al side and the PET side, to observe both the Al surface as well as the two polymer layers underneath. From the PET side, the presence of MEH-PPV and PEDOT:PSS appear as red and blue, respectively.
Figure 60 - Al OLED structure images, Al side up, before (top) and after (bottom) 1k bending cycles

Figure 61 - Al crater feature; Al view before bending (a), PET view before bending (b), Al view after bending (c), PET view after bending (d)
Figure 62 - Al smudge feature; Al view before bending (a), PET view before bending (b), Al view after bending (c), PET view after bending (d)
5.6 Flaw Features Identification

Al cracking, shown in fig. 63, occurs at the edge of the AL feature, and is likely a result of the crude method of using Kapton tape as a mask, occurring when the mask is lifted off by hand after deposition. Al craters are a result of inconsistent deposition of the polymer layers. The same crater shape can be seen from both sides of the sample. From the PET side, the color and increased reflectivity suggests that both polymers are absent, meaning the Al is directly deposited onto the ITO in this area. The crater outline seen from the Al side is an edge, as the Al in the crater is at a lower height with no
polymer layers underneath it. Coloration on both sides suggest that the smudge feature
is missing both polymer layers. This is likely a result of a handling or storage mishap.
Light emission is proof that neither the crater nor the smudge created device shorts.
After cyclic loading, no major change is observed in both the crater and smudge
features, but a significant increase in cracking appears. New cracking appears to
develop from or between existing cracks, but no new areas of cracking are observed.
Images from the center area show no significant changes after bending.

5.7 MEH-PPV Grouping

MEH-PPV clusters are visible from the PET side images, showing inconsistencies
in that layer. These areas create somewhat observable shadows from the AL side,
suggesting that MEH-PPV clumping causes a significant change in thickness.
Additionally, when a voltage is applied, light is emitted from the edges of these clusters,
which suggests two conditions. The first is that there is no short from the PEDOT:PSS
to the Al that would allow current flow to skip the MEH-PPV. This leads to the second
point, that there is MEH-PPV in the visibly blue areas as well, which would be
necessary to prevent shorts, but that there is significantly more at the red areas. The
significant differences in thicknesses created by this clumping could cause imperfections
when thinner cathodes are deposited on top, which may results in faster cathode
structure breakdown form bending. This is an issue that would need to be improved
before a thinner cathode layer could be applied.
5.8 Al Cracking

Initial cracking shown at the AL edges most likely occurred when Kapton tape, used as a mask, is removed after deposition. Al was present on top of the Kapton mask, but the tape was thick enough to prevent a connection between Al on and off of the mask. This was checked by measuring continuity between the two sections of Al. This means the cracks were not a result of Al pulling or tearing apart during mask liftoff, but more likely a result of shear forces between the deposited Al and Kapton mask. These cracks are the only area where structural degradation is visible after cyclic bending. While thermal deposition may not be a cost-effective method, the low cost and work function of Al make it desirable as a cathode. Patterning through use of a shadow mask that does not directly contact the device during evaporation may allow Al to be suitable as an electrode for low-cost flexible optoelectronics.

5.9 Bending Forces

The noticeable decrease in reaction force from both OLEDs shows that bending causes structural break down. The relatively constant reaction force from the stock piece suggests that the structural breakdown seen in both OLEDs does not occur in the PET substrate, but most likely in the layers deposited. Images before and after cycling do not show any apparent degradation in the polymer layers. For the Sandwich OLED, the noticeable change in the EGaIn shape and adhesive cracking are proof that the bending causes too much motion between the two PET substrates for the cured, solidified adhesive to keep together. Imaging of the Al OLED provides visual proof of Al cracking, but no noticeable structural change in the other flaw features. Differences
in reaction forces between the Al OLED and stock piece show that the deposited functional layers are experiencing bending.

5.10 Device operation

Al OLEDs that tested before bending, had device resistances ranging from 3 to 6 k\(\Omega\) with turn on voltages from 6 to 9 V. In order to observe performance after bending, no power was applied to the Al OLED that underwent cyclic bending until after the full 1k cycles. This was done to avoid the rapid device burnout reported in Chapter 3. After bending, the device was measured to have a resistance around 5kOms, and a 6V turn-on voltage, but light emission was short lived. Both the resistance and the light emission performance are similar to that reported from unbent samples.

5.11 PET Crystallization and Drying/Annealing Temperatures

Most work on OLED materials use glass substrates, which allows drying and annealing of deposited layers to occur at high temperatures. Using PET as a substitute for glass enables flexibility, but also limits the temperatures that can be applied during layer deposition. Glass transition temperature (\(T_G\)) for amorphous PET, which appears clear, is 67°C, while crystalline PET, which has an opaque appearance, has a \(T_G\) around 81°C (Demirel et al., 2011). Thermal crystallization can occur at temperatures above the glass transition temperature, which is observed to increase material opaqueness. Crystallization can occur more rapidly if stress is induced while above \(T_G\). Crystallization changes the device mechanical structure, including an increase in stiffness. To avoid crystallization, polymer layers were dried at 80°C while resting on a flat surface. While this is above amorphous PET \(T_G\), no visible increase in opacity
suggests that minimal crystallization occurred during the deposition process. Similar work on glass substrates using PEDOT:PSS reports drying the deposited layer at 200°C (Rauch et al., 2009). Reports have shown that heating and cooling cycles, shown in fig. 64, can manipulate PEDOT:PSS conductivity. The results indicate that heating PEDOT:PSS at higher temperatures does significantly increase hole transport at room temperature (Zhou et al., 2014). This treatment improves conductivity, but drying at room temperature also provides conductive layers of PEDOT:PSS, proving that heating is beneficial, but not necessary.

![Figure 64 - Temperature and Conduction relationship provided by Zhou et all, 2014](image)

Treated as an elastic material, heating also increases the storage modulus of PEDOT:PSS, which would increase the stress experienced from the applied bending strain. The glass transition temperature of MEH-PPV has been reported to be around 70°C, and heating at this temperature provides a sharper emission peak (Cossiello et al., 2005). Drying at temperatures around 70-80°C appears to provide a balance
between treating MEH-PPV and PEDOT:PSS for optical and electrical performance, while maintaining device flexibility.

5.12 Mechanical Analysis

Two simple bending analyses have been carried out on the two tested OLED structures to observe stresses in the device layers, as a comparison to the measured testing results. For this analysis, the substrate and all other layers from both devices are treated as individual simple beams. Bending inertias and stresses that would result from the moment created from the 3 point bending test are estimated for each layer individually. Afterward, the force that would be required to cause the tested deflection is estimated for each layer individually to provide insight into the different measured forces. An illustration of the 3-point bending setup tested is provided in fig. 65.

![3-Point bending setup diagram](image)

**Figure 65 - 3-Point bending setup diagram**

Bending moments are estimated using Timoshenko beam fundamentals, shown in equation 5, because the substrate is flexible, and the rotation occurring between the cross section and bending line are not negligible.
\[ EI = \frac{Eh^2b}{12(1 - \nu^2)} \quad eq. 5 \]

Where \( b \) is the layer width, \( h \) is thickness, and \( \nu \) is the Poisson’s ratio. Bending inertias calculated and the dimensions used for each layer are shown in table 5. To simplify estimations, the widths of all layers in each device are estimated to be uniform. ITO and PET layer thicknesses are provided by the manufacturer. Deposited layer thicknesses could not be measured, and are estimated based on deposition conditions, in comparison with similar reported work.

<table>
<thead>
<tr>
<th>Material</th>
<th>( b ) (cm)</th>
<th>( h ) (µm)</th>
<th>( I ) (m(^4))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>1.6</td>
<td>127</td>
<td>3.11\times10^{-15}</td>
</tr>
<tr>
<td>ITO</td>
<td>1.6</td>
<td>0.2</td>
<td>1.20\times10^{-23}</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>1.6</td>
<td>0.16</td>
<td>6.22\times10^{-24}</td>
</tr>
<tr>
<td>MEH-PPV</td>
<td>1.6</td>
<td>0.15</td>
<td>5.12\times10^{-24}</td>
</tr>
<tr>
<td>Al</td>
<td>1.6</td>
<td>2</td>
<td>1.21\times10^{-20}</td>
</tr>
<tr>
<td>Kapton Tape</td>
<td>1.6</td>
<td>25.4</td>
<td>2.47\times10^{-17}</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Material</th>
<th>( b ) (cm)</th>
<th>( h ) (µm)</th>
<th>( I ) (m(^4))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>1.7</td>
<td>127</td>
<td>3.31\times10^{-15}</td>
</tr>
<tr>
<td>ITO</td>
<td>1.7</td>
<td>0.2</td>
<td>1.28\times10^{-23}</td>
</tr>
</tbody>
</table>

From simple beam definitions relating the applied moment to the resulting radius of curvature, shown in eq. 5, and Hooke’s Law, eq. 6, stresses in each material can be estimated from the applied moment, shown in eq. 7.
Where ρ is the radius of curvature, M is the applied moment, E is the material modulus of elasticity, σ is stress, ε is strain, and c is distance from the bending neutral axis. Visualizations of ρ and c are shown in fig. 66. Maximum stress will occur farthest from the bending neutral axis. To simplify estimations, the deposited film thicknesses are assumed to be negligible, and c for all instances is set as half of the PET thickness, 63.5 μm.

![Figure 66 - Radius of curvature and neutral bending axis](image)

The maximum moment, which occurs directly between the two supports, where the load is applied, at L/2, as shown in fig. 65, is shown in eq. 9.

\[
M = \frac{PL}{4} 
\]  

\text{eq. 9}
Where $P$ is force applied, and $L$ is the distance between the two supports. The max forces reported for both devices, shown in table 4, is used for $P$, and $L$ is the span between the supports, 1.4cm. Combining eq. 8 and eq. 9 with data from table 4, stress can be estimated with eq. 10. Estimated stresses for both devices are shown in tables 7 and 8.

$$
\sigma = \frac{PLc}{4I}
$$  \hspace{1cm} eq. 10

Table 7 - Estimated stresses from individual Al OLED layers as simple beams

<table>
<thead>
<tr>
<th>Material</th>
<th>Stress (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>0.035</td>
</tr>
<tr>
<td>ITO</td>
<td>$9.2 \times 10^6$</td>
</tr>
<tr>
<td>PEDOT:PPS</td>
<td>$17.8 \times 10^6$</td>
</tr>
<tr>
<td>MEH-PPV</td>
<td>$21.6 \times 10^6$</td>
</tr>
<tr>
<td>Al</td>
<td>9141.76</td>
</tr>
<tr>
<td>Kapton Tape</td>
<td>4.498</td>
</tr>
</tbody>
</table>

Table 8 - Estimated stresses from individual PET/ITO stock layers as simple beams

<table>
<thead>
<tr>
<th>Material</th>
<th>Stress (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>0.0235</td>
</tr>
<tr>
<td>ITO</td>
<td>$60.7 \times 10^5$</td>
</tr>
</tbody>
</table>

Next, an estimation will be provided for the force required to cause the reported deflection from each material layer from both devices individually. Deflection at the center of a beam from an applied force under 3 point bending can be estimated using eq. 11.
\[ d = \frac{PL^2}{48EI} \quad eq. 11 \]

This can be solved for \( P \), shown in eq. 12.

\[ P = \frac{48EId}{L^2} \quad eq. 12 \]

Setting deflection to the max set from testing, 1.4mm, estimations for the required forces for each individual layer for both devices are shown in tables 9 and 10.

**Table 9 - Estimated forces for deflection of individual Al OLED layers as simple beams**

<table>
<thead>
<tr>
<th>Material</th>
<th>( P ) (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>2.439</td>
</tr>
<tr>
<td>ITO</td>
<td>2.835x10^{-7}</td>
</tr>
<tr>
<td>Al</td>
<td>2.61x10^{-4}</td>
</tr>
<tr>
<td>Kapton Tape</td>
<td>0.0121</td>
</tr>
</tbody>
</table>

**Table 10 - Estimated forces for deflection of individual PET/ITO stock layers as simple beams**

<table>
<thead>
<tr>
<th>Material</th>
<th>( P ) (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>2.591</td>
</tr>
<tr>
<td>ITO</td>
<td>3.01x10^{-7}</td>
</tr>
</tbody>
</table>

PET and Kapton tape have the highest bending inertias and the lowest estimated stresses caused by the bending moment. All other layers have bending inertias multiple orders of magnitudes lower than the PET and Kapton tape, showing that these two would provide the most significant resistance to bending. Kapton tape was used in the Al OLED device as a separation layer between the ITO and Al electrodes. The Al OLED showed a higher max force than the PET/ITO stock pieces during the first 100
cycles of testing, and this analysis suggests that the main change is from the Kapton tape, not the deposited layers of PEDOT:PSS, MEH-PPV, or Al. Kapton tape was used as a low-cost solution to provide a separation layer between the two conducting electrodes, but can produce additional stresses from bending, which should be avoided. The tape’s thickness is also significant, meaning that the distance from the neutral axis used for the Kapton tape, and the Al on top, should be larger, resulting in larger stresses than the estimations reported here. If the Al device was made without the Kapton mask, it is likely that the tested forces would have been much more similar to the PET-ITO stock piece. If a separation layer is required, an alternative method will need to be explored to minimize bending stresses. The extremely small bending inertias for the three thinnest layers, ITO, MEH-PPV and PEDOT:PSS, resulted in extremely high bending stresses. These seem unrealistic, and show that standard bending mechanics are not a good estimation for films with nanometer range thicknesses.

5.13 Chapter Summary

Chapter 5 provides a flexibility analysis of the two structures created in Chapter 3. Cyclic loading is performed on each device, as well as the substrate used for both. Results show that cyclic loading has little effect on the functional layers, but does degrade the cathodes used in each structure. The polymer bunching occurring in the functional layer is also a point of concern for device flexibility. Results suggest that once a new cathode material is used, and improvements are made to functional layer deposition, the fabrication methods presented in this work are viable for fabrication of a flexible, thin film optoelectronic device.
Chapter 6: Optional Additional Fabrication Processes

Other fabrication processes were initially explored, but left out of the reported work in the interest of pursuing results from low cost fabrication techniques. A method for patterning the ITO layer on the PET was both considered and practiced. Patterning involves photolithography, which requires additional chemical materials such as photoresists, developers, and liftoff chemicals, as well as acids for etching. Because of the carcinogenic nature of some of these materials, the process is typically carried out in a clean room setting. ITO patterning can be one way to define the active area geometries of an optoelectronic device and may be beneficial for devices with more complicated architectures. This step was not necessary for the presented work, as simplistic architectures appeared more advantageous. Ligand exchange has also been reported to improve performance efficiencies in optoelectronic devices using QDs. While the process may provide improvements, they are not necessary for initial concept proofs, and were chosen to be left out of the presented work. Because it could provide improvements towards continued work, a brief ligand exchange background is introduced in this chapter.

6.1 ITO Patterning

Materials: Polyethylene Terephthalate (PET) coated Indium Tin Oxide (ITO) sheets have been purchased, along with a glass mask for the ITO pattern. A photolithographic process was carried out using AZ2020 negative photoresist, AZ-300MIF developer, an etching solution of hydrochloric acid (HCl) and water, and AZ-400T as a stripper. All steps for patterning in section 5.1 took place in the Egan microfabrication lab facility.
Step 1 - Coating: The ITO coated PET sheets are prepared with a protective plastic backing, so no pre-cleaning is necessary. The surface is ready to work with once the plastic is peeled off. AZ 2020 is dropped on the sheet and spin coated at 3000 RPM for 45 seconds, followed by a 2 minute soft bake at 115°C.

![Glass Photomask](image)

**Figure 67 - Glass Photomask**

Step 2 – UV Exposure: Photo mask is placed on top of the coated sheets, and manually exposed to UV light via mask aligner for 20 seconds. The sheet is again soft bakes at 115°C for 2 minutes.

Step 3 - Developer: The exposed sheet is soaked in AZ 300 MIF developer for 60 seconds, then rinsed with isopropanol alcohol (IPA) and DI water, and soft baked at 115°C for 2 minutes, then hard baked at 150°C for 45 minutes.
Step 4 – Etch: The developed film is submerged in a 4:1 solution of water and HCl for 30 seconds, and is then promptly rinsed with IPA and DI water.

Step 5 – Strip: The etched film is submerged in AZ 400t stripper, then promptly rinsed with IPA and DI water, followed by a soft bake at 115°C for 2 minutes, to strip off the remaining photoresist.

Figure 68 - Patterned ITO on PET

6.2 QDs and Ligands

The QDs used in the current work come capped with Oleic Acid ligands. These ligands are introduced during QD growth to help with stabilization, which improves size uniformity. While these ligands provide help during the QD growth process, they are viewed as a hindrance for optoelectronic QD applications. Considerable work with QDs as the active elements in photovoltaic devices have viewed Oleic Acid as insulating, inhibiting transport, and explored how the exchange of ligands can help
improve performance efficiency. This insulating nature comes from the ligand length, and an exchange with shorter ligands to decrease spacing between QDs is reported to improve dark and photocurrents (Konstantatos Howard et al, 2006). This work did report positive improvements, but the efforts seem to be a workaround for the real problem, that transport among QDs is poor. Work by Rauch et al. (2009) has reported that the issues with capped ligands are only present in pure QDs films. The work uses QDs suspended in a polymer matrix, and reports some of the highest photovoltaic efficiencies from QDs, noting that no ligand exchange was necessary - the QDs used were capped with Oleic Acid. Using QDs capped with Oleic Acid provides two distinct advantages: the first being simplicity in not needing to carry out any ligand exchange process. The second advantage is lifetime. Layers of pure QDs create a direct interface between the QDs and metal electrodes (Koleilat et al., 2008). This interface causes lifetime issues, for which ligand exchange has been explored as a solution. Suspending QDs in a polymer matrix eliminates the QD-metal interface. Work using QDs in a polymer matrix reports negligible changes in device performance after 120 days (Rauch et al., 2009).

![Figure 69 - Lifetime performance provided by Rauch et al., 2009](image-url)
Work exploring ligand exchange focuses on improving transport, as well as improving the QD-Metal interface. If QDs are suspended in a polymer matrix, the QD-metal interface is eliminated, and the polymer takes over the role of transport. With these two points of concern gone, there seems to be no need for ligand exchange. This idea is contradicted by Zhang et al., (2005), which reports that ligand exchange for QDs suspended in a MEH-PPV polymer matrix significantly increases the structure’s photovoltaic response. This provides evidence that when suspended in a polymer matrix, ligand exchange may not be necessary to improve QD performance lifetimes, but it can still provide significant performance improvements.

6.3 Chapter Summary

This chapter introduces two processing steps than can help improve optoelectronic device performance. These steps were left out of the present work, as they are considered not applicable at the current stage. Once light emission and detection are improved, the ITO patterning methods can be used to define active area geometry. Similarly, the ligand exchange process can be explored to improve performance efficiencies. While not relevant for the state of work currently reported, these are two process methods that should be considered when

Chapter 7: Conclusions and Recommendations

7.1 Conclusion

Low-cost fabrication methods with flexible materials have been explored through the development of two different device structures. The first structure proved that light emission using a polymer/QD blend can be achieved through simplified, large-area
fabrication techniques, but that emission areas are inconsistent. The second structure provided improved consistencies, but at the cost of a more complex process. This second structure also achieve lower turn-on voltages, around 3V, but fast device burnout, which prevented any substantial emission spectrum analyses to be observed.

By providing an external light source and treating the two developed device structures as photodiodes, an attempt to observe a photovoltaic response was made. Results from testing provided no measureable difference between dark and photo currents. To provide further insight, the device structures are compared to two previously reported, similar structures that produced more acceptable photoresponses. This analysis reveals the need for charge injection barriers and clear charge extraction paths, and how the two contribute to improved photo currents and reduced dark currents. This insight shows that the quantum dots used in the current devices have a built-in charge extraction barrier that inhibits photocurrent development, which provides a pinpoint explanation for why no difference could be observed between device dark and photo currents.

To explore flexibility, the two devices were put through bending cycles at a fixed radius of curvature. Results show that the first device’s structure is not suitable for flexibility, while the second structure could be an acceptably flexible device, with a few exceptions. The metal electrode used showed some resistance to bending, as well as some cracking. Clumping in the polymer layer was observed to cause inconsistencies in layer thickness. This could cause problems for thinner electrodes deposited on top, especially when bending stresses are applied.

The presented process has proven successful for creation of thin film light emitting devices using a QD-polymer blend active element. Low turn on voltages are observed,
but polymer clumping prevents realization of a reliably consistent emission area. Work towards discovering an ideal solution concentration, as well as better filtration methods, are needed to provide a more consistent emission area. This improvement area would help allow characterization of other factors including emission external quantum efficiency and photovoltaic efficiency. Evaporated Al provided more consistent contact compared to the EGaIn electrode, but requires a more complex deposition process. Further work is needed to improve the device architecture, but the MEH-PPV/QD blend was proven successful as an active layer.

The overall work presented has provided significant evidence that low-cost, large area fabrication techniques can be used to develop the functional structures required for a flexible, thin film optoelectronic devices. A QD-polymer blend can be used as the active layer for light emission. Similar materials can be used for photovoltaic applications, but a structure that can achieve efficient dark and photo currents require different Fermi energy levels than an emissive structure. All materials used in the device structure appear to handle flexibility fairly well, but better luminescence and photodetection need to be achieved before the effects of bending on device performance can be evaluated in greater detail.

7.2 Recommendations

Existing heart rate monitors use high-pass filters to keep track of the number of waveform peaks over time, which when done successfully results in tracking heart rate. Not enough information on performance is known about the prented device for a filter to be designed without fabrication and testing of the device. Fabrication will likely require testing with grown or purchased PbS NCs for a proper photovoltaic effect to be
observed. While the proper size NCs are commercially available, the size for the photosensitive layer will need to be determined to see if it can be purchased, or needs to be grown.

Pulse Oximeters take advantage of the different absorption spectra between oxygenated and deoxygenated hemoglobin in the blood, and are hence capable of measuring both heart rate and blood oxygen level simultaneously. The only difference between an infrared HR sensor and a pulse oximeter is a second wavelength of light that the pulse oximeter emits and detects. This wavelength falls within the infrared spectrum. Once the proposed HR sensor design is tested, little work will be required to add the additional components to operate at two wavelengths to develop and test a flexible film pulse oximeter.
APPENDIX

Appendix 1 – ITO on PET Deflection Data

Figure 70 - ITO on PET force and deflection data for 1k cycles

Figure 71 - ITO on PET force and deflection data for 1st set of 100 cycles
Figure 72 - ITO on PET force and deflection data for 2nd set of 100 cycles

Figure 73 - ITO on PET force and deflection data for 3rd set of 100 cycles

Figure 74 - ITO on PET force and deflection data for 4th set of 100 cycles
Figure 75 - ITO on PET force and deflection data for 5th set of 100 cycles

Figure 76 - ITO on PET force and deflection data for 6th set of 100 cycles

Figure 77 - ITO on PET force and deflection data for 7th set of 100 cycles
Figure 78 - ITO on PET force and deflection data for 8th set of 100 cycles

Figure 79 - ITO on PET force and deflection data for 9th set of 100 cycles

Figure 80 - ITO on PET force and deflection data for 10th set of 100 cycles
Appendix 2 – Al OLED Deflection Data

Figure 81 - Al OLED force and deflection data for full set of 1k cycles

Figure 82 - Al OLED force and deflection data for 1st set of 100 cycles

Figure 83 - Al OLED force and deflection data for 2nd set of 100 cycles
Figure 84 - Al OLED force and deflection data for 3rd set of 100 cycles

Figure 85 - Al OLED force and deflection data for 4th set of 100 cycles

Figure 86 - Al OLED force and deflection data for 5th set of 100 cycles
Figure 87 - Al OLED force and deflection data for 6th set of 100 cycles

Figure 88 - Al OLED force and deflection data for 7th set of 100 cycles

Figure 89 - Al OLED force and deflection data for 8th set of 100 cycles
Figure 90 - Al OLED force and deflection data for 9th set of 100 cycles

Figure 91 - Al OLED force and deflection data for 10th set of 100 cycles
Appendix 3 – EGaIn OLED Deflection Data

Figure 92 - EGaIn force and deflection data for full set of 1k cycles

Figure 93 - EGaIn OLED force and deflection data for 1st set of 100 cycles

Figure 94 - EGaIn OLED force and deflection data for 2nd set of 100 cycles
Figure 95 - EGaIn OLED force and deflection data for 3rd set of 100 cycles

Figure 96 - EGaIn OLED force and deflection data for 4th set of 100 cycles

Figure 97 - EGaIn OLED force and deflection data for 5th set of 100 cycles
Figure 98 - EGaIn OLED force and deflection data for 6th set of 100 cycles

Figure 99 - EGaIn OLED force and deflection data for 7th set of 100 cycles

Figure 100 - EGaIn OLED force and deflection data for 8th set of 100 cycles
Figure 101 - EGaIn OLED force and deflection data for 9th set of 100 cycles

Figure 102 - EGaIn OLED force and deflection data for 10th set of 100 cycles
Appendix 4 – Al OLED Center Images before and after bending cycles

Figure 103 - Al OLED structure image, Al side up, before bending cycles

Figure 104 - Al OLED structure image, PET side up, before bending cycles
Figure 105 - Al OLED structure image, Al side up, after 1k bending cycles

Figure 106 - Al OLED structure image, PET side up, after 1k bending cycles
REFERENCES


T. Saito, H. I. (2007). Development of Normally Closed Type of Magnetorheological Clutch and its Application to Safe Torque Control System of Human-


Related Publications & Academic Activities


