LAB MODULE 2 OF 4: POLYMER LED

Fabrication and Characterization of a Polymer Light Emitting Diode

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Created by BL Conover, RK Komanduri, and MJ Escuti
North Carolina State University
Department of Electrical and Computer Engineering

Abstract

In this lab experiment you will fabricate your own **Polymer Light Emitting Diode** (pLED). You will start with a glass substrate coated with conductive indium tin oxide (ITO) as the anode and then spin-cast two polymer layers on top. The polymers will be the light-emitting polymer MEH-PPV (poly[2-methoxy-5-(2'-ethyl-hexyloxy)--1,4-phenylene vinylene]), and the hole transport layer PEDOT-PSS (poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)). Finally, you will employ a liquid metal (gallium-indium eutectic) on a second ITO-coated substrate to act as the cathode and you will seal the structure with optical adhesive. For characterization, you will measure and observe several aspects, including the color of electroluminescence, the color of photoluminescence, the turn-on voltage, the intensity vs. voltage curve, the current vs. voltage curve, and the power efficiency.

Part 1	Part 2	Part 3
Polymer Layers	Creating the Cathode and the pLED Cell	Device Characterization

Write-up Instructions

Your lab report (Lab Notebook) will minimally consist of the following *for each part*:

A. Statement of experimental objective
B. Sketches of experimental setup
C. Record of all measurements
D. All requested calculations

The following lab procedure will indicate specifically what to include and where. The purpose of this style of write-up is to force you to keep a technical record of your experiments in the way that many engineers and scientists are required to do (in industry and universities). The lab director(s) will provide you with blank technical notebook sheets in the lab (also available on the website). You are expected to follow the lab notebook guidelines introduced by the lab director(s) (also see the Appendix), and your lab grade will depend both on your experimental procedure and on how well you follow these guidelines. Note that the same pages you use during the lab experiment should also be the ones you complete at home and hand-in as your write-up — do not rewrite them.

A Brief History of Organic LEDs

Polymer light emitting diodes (pLEDs) fall into the more general category of organic light emitting diodes (OLEDs). Many of the early OLEDs consisted simply of an organic semiconductor layer sandwiched between two metal electrodes [1]. Even as improved organic materials and more complicated device structures have been identified, the operational principles of OLEDs remain the same [2]. pLEDs have attracted interest because all device layers can be easily processed in solution and with economically-attractive coating techniques (as opposed to inorganic LEDs). Moreover, the interfaces between the various layers do not have to be structurally regular at the atomic level.

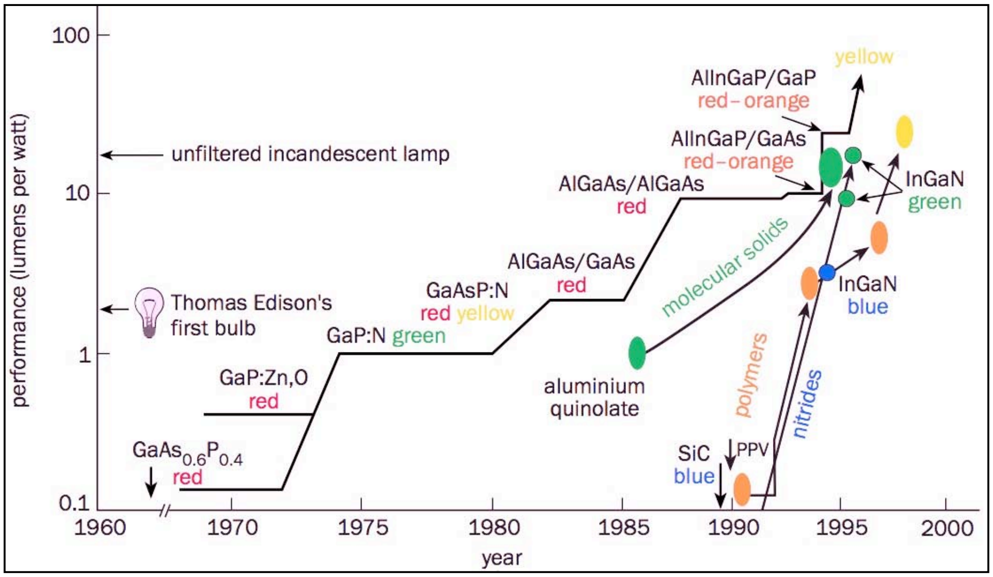

Figure 1. Evolution of LED/OLED luminous efficiency over time [3].

Initial results by Burroughes, Friend and coworkers in the 1990s were based on a structure that used the light-emitting-polymer poly(phenylene-vinylene) (PPV) enclosed between two electrodes [4]. These devices were very inefficient, limited to only a few percent external quantum efficiency (EQE). Several groups later discovered that including an additional organic layer as a hole transport layer (HTL) between the anode and the light-emitting layer improved the efficiency dramatically [1]. In particular, poly(ethylenedioxy)thiophene (PEDOT) was found to be very practical in this aspect. Fig. 1 shows the improvement in performance of various LED types over time. Most notably, high performance pLEDs now rival the efficiency of conventional incandescent filament lamps.

Basic Device Operation

In this lab, we will build a pLED using the layout depicted in Fig. 2(a). We will use poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) as the light-emitting polymer, which simultaneously serves as the electron transport layer (ETL). MEH-PPV, a variation of PPV, has additional alkyl groups attached to the basic phenylene ring as shown in Fig. 2(b). Generally these groups are added so that the material becomes soluble in common solvents, such as xylene, enabling spin-casting. For the HTL, we use the mixture poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS) with the chemical structure shown in Fig. 2(b). Clear glass coated with indium tin oxide (ITO) will act as the anode, while a liquid metal alloy (gallium-indium eutectic, work function ~4.2 eV) on a second piece of ITO-coated glass will be the cathode.

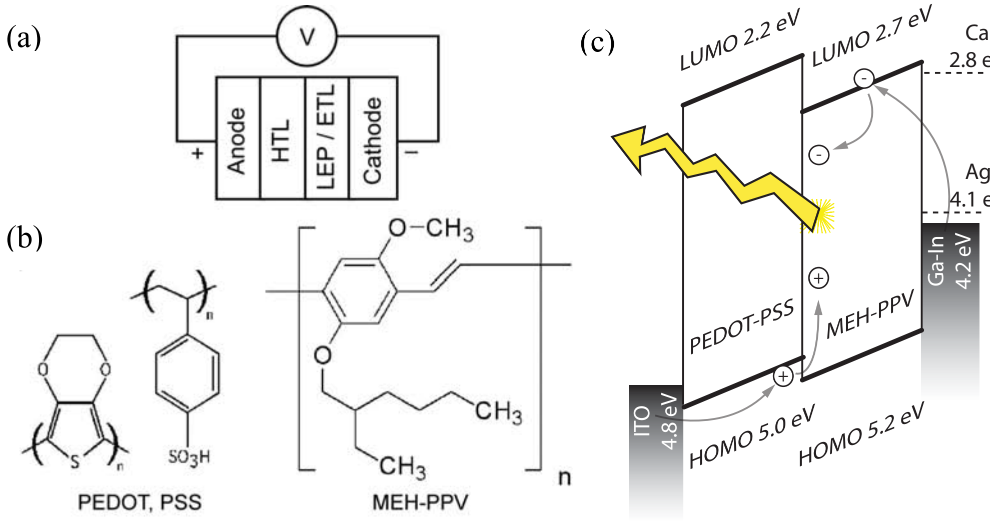

Figure 2. (a) pLED device layout; (b) Chemical structures for HTL and ETL materials; (c) Energy band diagram showing basic pLED device operation.

Fig 2(c) is an energy band diagram indicating the various energy levels for the individual layers. Many materials may be used as the cathode, and this diagram denotes two options, calcium and silver. Due to its reactivity, calcium is difficult to use. Aluminum and silver are sometimes used in commercial applications. We will use gallium-indium (GaIn) eutectic as it is quick and simple to apply, needs no special curing environment, and is cost-effective.

The basic pLED operation has similarities to that of an inorganic LED, but is based on molecular electroluminescence (EL). Electrons from the cathode and holes from the anode are injected into the light-emitting layer, where they recombine and release the energy in the form of a photon. This process is sometimes referred to as radiative recombination. The wavelength of light emitted depends on the band gap (E_g) of the polymer semiconductor – defined as the energy difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels, the HOMO energy of the HTL and the applied voltage.

In order to achieve emission from this device, a minimum voltage needs to be applied—the turn-on voltage of the pLED. This voltage should be large enough for the electrons and holes to overcome the barriers to LUMO and HUMO energy levels, indicated in Fig. 2(c) by ϕ_e and ϕ_h, respectively, and written as follows:

$$\phi_e = \phi_{cathode} - \phi_{LUMO}$$

$$\phi_h = \phi_{anode} - \phi_{HOMO} \, .$$

The purpose of the HTL layer here is to ease hole-injection into the light-emitting layer. This is achieved by materials such as PEDOT-PSS, which has a work function between that of

ITO and the HOMO energy levels. Additionally, this layer smoothes out the rough ITO surface, which would otherwise cause local short-circuits, causing the device to fail.

The built-in voltage is defined as the difference in the anode and cathode work functions. In the example of a Ga-In cathode,

$$V_{bi} = q(4.8\text{ eV} - 4.2\text{ eV}) = 0.6\text{ V}.$$

In the two-layer device (Fig. 2(c)), the absorption peak energy is best determined by the bandgap of the ETL (E_g = 2.5 eV) which leads to a peak emission of ~500 nm. However, for MEH-PPV the energy difference between the HOMO energy of the HTL and the LUMO energy of the ETL is ~2.3 eV, thereby dominating the emission. Therefore, the wavelength of photons emitted can be calculated as:

$$\frac{hc}{\lambda_{photon}} = 2.3\text{ eV} = 3.9\times10^{-19}\text{ J}$$

$$\Rightarrow \lambda_{photon} = \frac{1.24\text{ eV - }\mu\text{m}}{2.3\text{ eV}} = 540\text{ nm}$$

In fact, actual devices employing MEH-PPV will emit around 580 nm (yellow-orange color), since the above analysis does not incorporate all the key factors such as trap levels.

Finally, most of the metallic cathodes used in these devices are reflective. Since ITO-coated glass is transparent, the light is emitted from the anode side.

Electro-Optical Properties

The electrical characteristics of a pLED are similar to those of an inorganic LED. For instance, a minimum voltage is required to turn on the pLED. Once this value is exceeded, the current density (J) roughly follows a square law relation ($J \propto (V\text{-}V_{bi})^2$) as traced in Fig. 3(a).

Fig. 3(b) shows typical luminance (brightness) estimate for the same pLED as the voltage is varied. From these two plots, it is apparent that the device's quantum efficiency is constant with respect to voltage. In general, however, this is not true. In our lab, we will try to measure and calculate the parameters discussed in the previous sections and attempt to fit the data to the plots shown here.

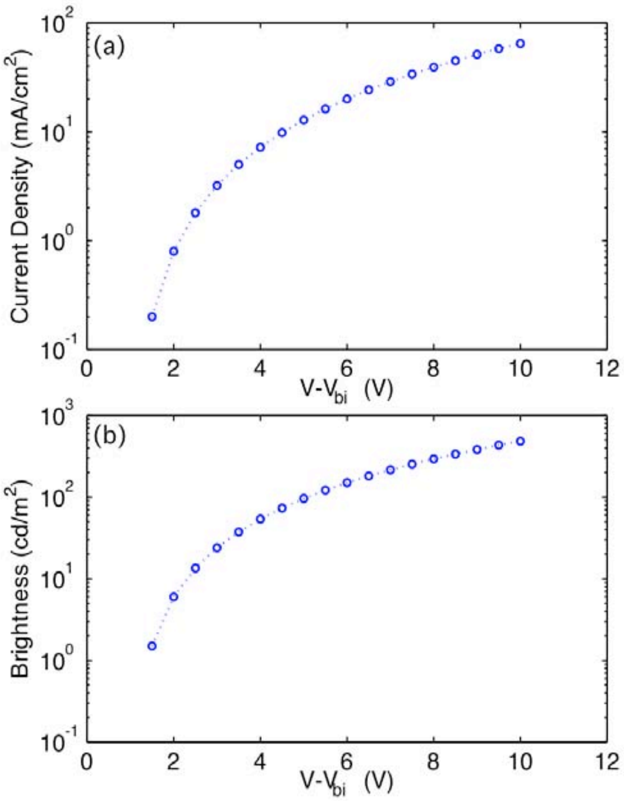

Figure 3. (a) Current Density vs Voltage for a typical pLED; (b) Brightness vs Voltage for the same pLED.

Construction and Characterization

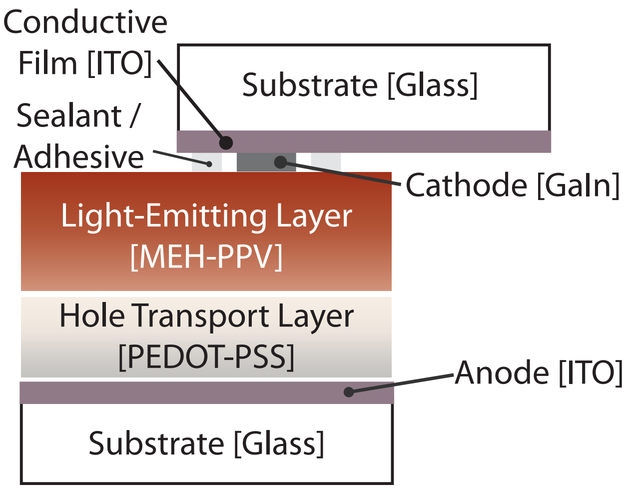

Figure 4. pLED Structure

In this lab, we will fabricate a pLED, with the construction shown in Fig. 4. We will start with two glass substrates coated with ITO, one of which will act as the anode. Upon this substrate we will spin-cast the two polymer layers, PEDOT-PSS and MEH-PPV. To the other substrate, we will apply a small amount of GaIn, which will act as the cathode. Since it is a liquid at room temperature, we can be very precise in its placement and in the amount we use. The Ga-In will be surrounded by a ring of optical adhesive having two purposes: securing the top substrate to the bottom and creating an air-tight seal virtually impenetrable to air and water vapor. This is considerably important since the organic films being used are particularly susceptible to decay when contacted by water molecules. Because of this, commercially produced pLEDs and OLEDs are fabricated in a water-free, often nitrogen-rich, environment.

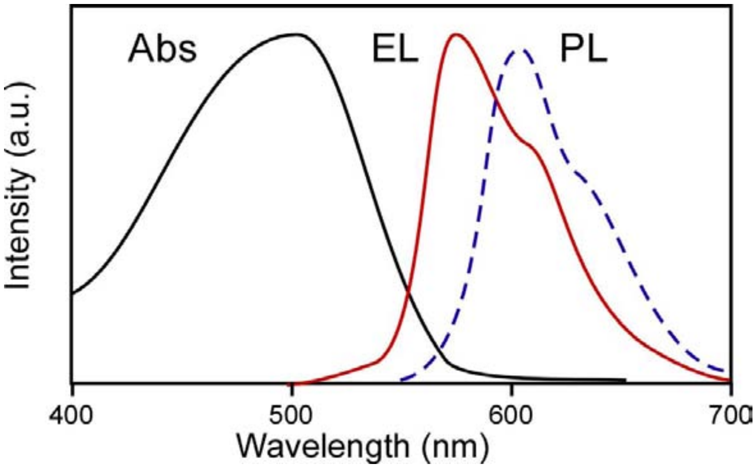

Figure 5. Spectral curve of MEH-PPV — Absorption (Abs), Electroluminescence (EL), and Photoluminescence (PL).

As with all light-emitting organic materials, the polymer used in this lab (MEH-PPV) can emit light via two mechanisms: electroluminescence (EL) and photoluminescence (PL). EL occurs when electrons and holes are injected from the corresponding electrodes and allowed to recombine as described above. PL occurs when the absorption of a photon of energy greater than the bandgap energy results in the creation of an electron-hole pair, which then quickly recombines. Because the process and bias conditions leading to the charge carrier creation is different for EL than for PL, the spectrum that results from each is also different. Fig. 5 shows an example of typical EL and PL spectra for MEH-PPV.

Further characterization of our pLEDs will be performed within a setup similar to that depicted in Fig. 6. A DC power supply will be used to vary the applied voltage, while an ammeter (multimeter) and optical power meter will measure the current and emitted optical intensity, respectively.

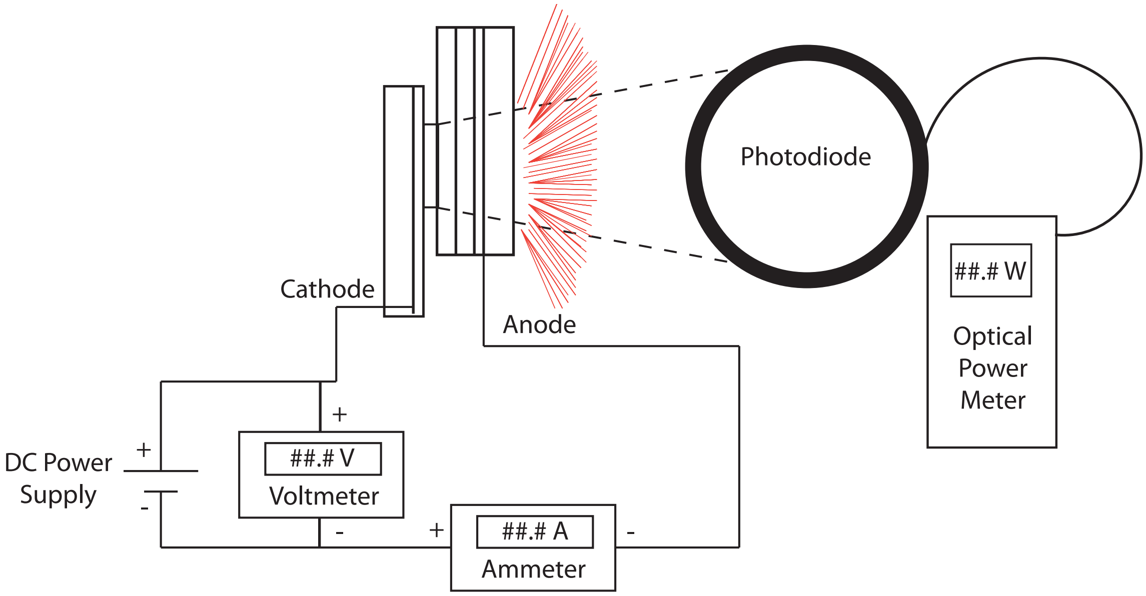

Figure 6. Measurement setup for characterizing a pLED.

Experimental Procedure

Important Notes:

•The option exists to perform this lab within a Glovebox designed to effectively evacuate harmful vapors, to provide a controlled environment in which to construct devices, and to provide a constant flow of nitrogen when necessary. Such is a good alternative to a fume hood or other controlled environment.

•Follow all of the instructions and precautions of your lab director(s) as variations from the procedures below may be in place.

•Always hold your samples along the edges and keep the ITO side of the substrates facing up.

Part 1 – Polymer Layers

EXPERIMENTAL OBJECTIVE:

To apply the two polymer layers of the pLED (PEDOT-PSS and MEH-PPV).

Procedure

1. Prepare your Lab Notebook
   a. Fill in your lab notebook headings (Lab #, Station Name, Page #, Name, Date).
   b. Briefly record the objective of this experiment.
   c. Sketch the complete cross-section of the pLED we are creating in this lab.

2. Prepare Two Substrates:
   a. Use a Multimeter (or similar device) in resistance mode to find the conductive side of the ITO-coated glass. The ITO side should measure a resistance of below 1 kΩ.
   b. Clean both substrates using an air gun and **methanol**.
   c. Transfer one substrate (called the anode substrate) to a hotplate set at 140 °C for ~10 minutes and the other (called the cathode substrate) to the worktable.

3. Spin-Cast the Polymer Layers:
   a. Secure the substrate in the spin-caster and, using a syringe, place ~12 drops of **PEDOT-PSS solution** onto the center of the substrate.
   b. Run Program B (see Appendix) unless instructed otherwise.
   c. When complete, place the substrate on a hotplate (140 °C) to dry for ~15 minutes.
   d. Return the substrate to the spin-caster and, using a syringe, place ~7 drops of **MEH-PPV solution** onto the substrate, attempting to cover the entire substrate.
   e. Run Program C (see Appendix) unless instructed otherwise.
   f. When complete, place the substrate on a hotplate at 140 °C to dry for ONLY ~3 minutes.

Part 2 — Create the Cathode Substrate and the pLED Cell

EXPERIMENTAL OBJECTIVES:

(1) To create the cathode substrate consisting of Gallium-Indium Eutectic, optical adhesive, and ITO-coated glass.
(2) To adhere the cathode substrate to the anode substrate consisting of the polymer layers.

Procedure

1. Prepare your Lab Notebook as before.

2. Apply the GaIn Eutectic and Optical Adhesive:
   a. Using a cotton swab applicator, apply a *small* quantity of **GaIn** Eutectic near the corner of the cathode substrate you earlier placed on the worktable.
   b. Using the syringe filled with **Optical Adhesive**, loosely encircle the GaIn spot.
   c. You should now have a cathode substrate as drawn in Fig. 7 below.

3. Create the pLED Cell:
   a. Place the anode substrate on the worktable.
   b. Invert the cathode substrate and gently place it onto the anode substrate with enough offset to attach alligator clips.
   c. Apply gentle pressure with a cotton swab applicator to spread the GaIn.
   d. Using the UV light, cure the optical adhesive for ~1 minute. *Be sure to have on your safety goggles in order to block the UV light from your eyes!*
   e. You should now have a completed and cured pLED cell as drawn in Fig. 8.

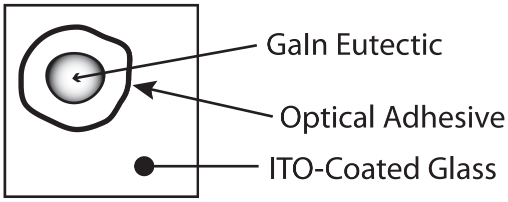

Figure 7. GaIn and Optical Adhesive applied to the cathode substrate.

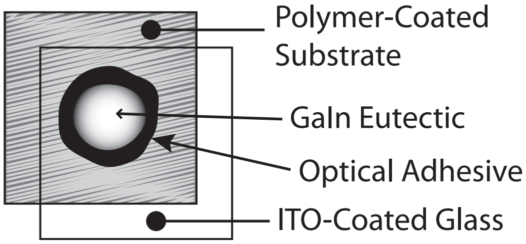

Figure 8. Cathode substrate inverted and sealed onto the anode substrate.

Calculations/Questions (Part 2)

These are to be written in your Lab Notebook.

1. Discuss two reasons why OLEDs have a limited lifetime (i.e. what causes them to fail?).
2. Comment on how the cathode created in Part 2 is different from *and similar to* what you might find in a typical commercial OLED. What about its properties and fabrication method make it unsuitable *yet still attractive* for commercial production? Think about bulk production requirements.

Part 3 — Device Characterization

EXPERIMENTAL OBJECTIVE:

Characterize the pLED by observing the electroluminescence by eye, and by simultaneously measuring current and emitted light as a function of voltage.

Procedure

1. Prepare your Lab Notebook as before, ensuring to sketch the characterization set-up.

2. Prepare the Power Supply and Connect the pLED to the Characterization Set-Up:
    a. With the DC power supply *not* connected, turn it ON and set to 10V. Turn it OFF.
    b. Attach the RED clip to the anode substrate and the BLACK to the cathode substrate.
    c. Turn ON the power supply. Do you see any illumination? Set the power supply to 0V.

3. Obtain Current and Optical Power vs Voltage Data:
    a. Place the photodiode directly over the sample and secure it in place.
    b. In steps of 1.0V from 5.0V to 20.0V, record the Optical Power and Current.
    c. When finished, return the power supply to 0V and turn it OFF. Remove your pLED.

Voltage (V)	Current (mA or uA)	Optical Power on Detector (mW or uW)
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Calculations/Questions (Part 3)

These are to be written in your Lab Notebook.

1. Create the following plots, and insert them into your Lab Notebook using tape or glue:
    a. Current (vertical) vs. Voltage (horizontal)
    b. Measured Optical Power (vertical) vs. Voltage (horizontal)
2. Describe, in terms of something real, the color of your pLED when the voltage was applied.
3. Identify the turn-on voltage of the diode.
4. Calculate the maximum radiant flux (mW or uW) and radiance (W/sr-m^2) emitted from your pLED. You should compensate for the fact that the photodiode does not actually measure the entire solid angle (i.e. remember the Prelab).
5. Calculate the electrical power (W) at the conditions for maximum radiance.
6. Calculate the maximum luminous flux (lm) and luminance (cd/m^2) produced by your pLED, assuming that all the light was emitted at 580 nm, so that 594 lm = 1 W.
7. Calculate the luminous efficiency of your pLED (lm/W).
8. Calculate the external quantum efficiency of your pLED (# photons / # charges injected).
9. Did your pLED fail while you were working with it? If so, describe what occurred.

Appendix A: Lab Notebook Guidelines

1. **Do** record entries *legibly*, *neatly*, and in *INK*.
2. **Do** sign and date every page.
3. **Do** fill in headings completely (Lab #, Station Name, Page #).
4. **Do** record your experimental objective and describe your experiment.
5. **Do** record your experimental setup, data, and all calculations in such a way that someone else could duplicate/verify your steps.
6. **Do** include extrinsic materials by **tape** or permanent glue (staples are acceptable but not preferred). This includes all raw data from recording instruments (e.g., microscope photos), **computer generated graphs**, drawings, specification sheets, etc.
7. **Do** work in chronological order, i.e., **Do Not** skip parts unless specifically told to do so.
8. **Do Not** erase or remove material. If you mess up, simply cross it out and start again! This is part of the experimental process. We will provide you with as many sheets as you need.

Appendix B: Spin-Caster Parameters

- The following programs were created on a *Laurell Technologies Model WS-40B-6NPP/LITE* Spin-Caster. Other spin-casters can be used but the lab director should ensure the parameters result in quality films.

Program B

Single Stage: Speed 2000 rpm
Acceleration 1870 rpm/second
Time 30 seconds

Program C

Stage One: Speed 550 rpm
Acceleration 595 rpm/second
Time 10 seconds

Stage Two: Speed 2000 rpm
Acceleration 4080 rpm/second
Time 30 seconds

Appendix C: Material Recommendations

- **3 mL Syringes with Luer-Lok Tips**, *Catalog No. 14-823-41*, distributed by Thermo Fisher Scientific, Inc., Pittsburgh, PA, USA.
- **23 Gauge Precision Dispense Tips**, *Part No. 5123-B-45*, distributed by EFD, Inc., East Providence, RI, USA.
- **UVS 91 Ultraviolet-Curable Optical Adhesive**, distributed by Norland Products, Inc., Cranbury, NJ, USA.
- **ITO-Coated Glass Substrates**, *Part No. CG – 40IN – 0115*; 25 x 25 x 1.1 mm unpolished float glass, SiO_2 passivated, indium tin oxide coated one surface, $R_S = 4 - 8$ ohms; distributed by Delta Technologies, Ltd., Stillwater, MN, USA. Two substrates are needed for each OLED.
- **PEDOT-PSS**, *Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate), Item # 483095, 1.3 wt % dispersion in* H_2O*, conductive grade*, distributed by Sigma-Aldrich, Inc., St. Louis, MO, USA. A single 100 gram bottle of PEDOT-PSS is adequate for ~90 OLEDs (assuming 1 mL per substrate and some loss due to filtering). This material should be filtered through a 0.45 µm filter prior to use.
- **MEH-PPV**, *Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene], Item # 541443, Molecular Weight 40,000 – 70,000*, distributed by Sigma-Aldrich, Inc., St. Louis, MO, USA. A single 1 gram bottle of MEH-PPV will produce enough polymer solution for ~200 OLEDs.
- **Xylene***, Anhydrous, 99.0%, Catalog # AC61047-1000*, distributed by Thermo Fisher Scientific, Inc., Pittsburgh, PA, USA. A single 100 mL bottle of Xylene will produce enough polymer solution for ~90 OLEDs
- **Gallium-Indium, Eutectic**: *Item # 495425, 99.99+ % trace metals basis*, distributed by Sigma-Aldrich, Inc., St. Louis, MO, USA. A single 5 gram bottle of Gallium-Indium is adequate for hundreds of OLEDs when used sparingly as suggested in the procedures.
- **5.0 µm Syringe Filters**: *Millex-LS 25mm Syringe Driven Filter Unit (PTFE), Catalog # SLLS025NS,* distributed by Thermo Fisher Scientific, Inc., Pittsburgh, PA, USA.
- **0.45 µm Syringe Filters**: *Fisherbrand 25mm Syringe Filter (PTFE), Catalog # 09-719H,* distributed by Thermo Fisher Scientific, Inc., Pittsburgh, PA, USA.
- **Other Useful Materials Include**: Methanol (for cleaning substrates), Acetone (for cleaning spin-caster, etc.), UV Lamp/UV LED Flashlight (for curing UV adhesive), Kimwipes (multitude of lint-free uses), Stirring Hot Plate and Ultrasonic Bath (for polymer preparation), Nitrogen Gun (for cleaning debris from substrates), Activated Charcoal Air Filter (for filtering hazardous solvent fumes), Electrical Tape, 20V Power Supply, Multimeters (for voltage and current measurements), Optical Power Meter, Assorted Hook-Up Cables.

Appendix D: Polymer Preparation Instructions

- **NOTE**: The instructions below prepare ~25-30 mL of polymer solution, enough for ~20 OLEDs (assuming <1 mL of polymer solution per substrate and some loss due to filtering).

- The solution described is intended to be used in conjunction with the spin-caster parameters in **Appendix B**. The lab director should ensure that alterations to ether the material preparation instructions or to the spin-caster parameters result in quality films and successful device fabrication.

MEH-PPV in Xylene

1. Clean one 40 mL vial (amber).
2. Add ~80 mg MEH-PPV to the vial.
3. Add enough Xylene for a total weight of ~30 g. The wt % of solids in solvent should be between 0.20 % and 0.275 %.
4. Add a stir bar to the vial, secure the cap, and wrap the seam with electrical tape.
5. Place the vial on a stirring hotplate at 80 °C and 500 RPM for 60 to 90 minutes.
6. Gently swirl the vial and place upright in an ultrasonic bath for 200 - 300 minutes or until well-mixed. NOTE: If heat is available in ultrasonic bath, set to 60 °C.
7. Process the solution through a 5.0 μm syringe filter. The filter will need to be changed every 5-6 mL or as the solution becomes difficult to process. NOTE: Filtering can be extremely messy as filters can break and solution can spatter. Solution is highly staining and xylene is harmful by skin contact and by inhalation. Filtering should take place in a fume hood with proper protections.
8. As necessary (depending on the wt % of the solution), repeat steps 5-7 until the solution is well-mixed and contains no visible particulate. It is rare to repeat more than once and zero repetitions is often acceptable. Variations will depend on type of ultrasonic bath in use, wt % of the solution, volume of solution compared to volume of vial, etc.
9. Total amount of prepared solution will vary depending on number of processing steps required.

Appendix E: Adhesive Material Preparation Instructions

A single 1 gram bottle of optical adhesive will be enough for thousands of OLEDs. A syringe of the mixture as described below will be adequate for hundreds.

Adhesive

1. Fill a 3 mL syringe 1/4 - 1/3 full of adhesive and remove most of the air with the plunger.
2. Screw a dispensing tip onto the syringe.
3. Wrap syringe with aluminum foil or electrical tape to prevent penetration by ultraviolet light.
4. Adhesive will expire on date marked on the original optical adhesive bottle.

Appendix F: Relevant Sources (Books, Links, Papers, etc.)

1. C. Adachi and T. Tsutsui, “Molecular LED: Design Concept of Molecular Materials for High-Performance OLED,” in *Organic Light-Emitting Devices: A Survey*, ed. by J. Shinar, (Springer, 2004), pp. 43 – 69.
2. I.H. Campbell, B.K. Crane, and D.L. Smith, “Physics of Organic Light-Emitting Diodes,” in *Semiconducting Polymers: Chemistry, Physics and Engineering*, 2nd edition, ed. by G. Hadziioannou and G.G. Malliaras, (Wiley-VCH, 2007), pp. 421 – 454.
3. J.R. Sheats, H. Antoniadis, M. Hueschen, W. Leonard, J. Miller, R. Moon, D. Roitman, and A. Stocking, “Organic electroluminescent devices,” *Science*, **vol. 273**, no. 5277, pp. 884 – 888, 1996.
4. J.H. Burroughes, D.D.C Bradley, A.R. Brown, R.N. Marks, K. Mackay, R.H. Friend, P.L. Burns, and A.B. Holmes, “Light-emitting diodes based on conjugated polymers,” *Nature*, **vol. 347**, pp. 539 – 541, 1990.
5. M. Jaiswal and R. Menon, “Polymer electronic materials: a review of charge transport,” *Polym. Int.*, **vol. 55**, pp. 1371 – 1384, 2006.