Organic Light Emitting Devices

A really short intro...

DRAFT COPY

Isaac Leung

1. Introduction

Organic light emitting devices are made from organic compounds, unlike standard light emitting diodes (LED's) which are usually made from materials such as GaAs, AlGaAs, InP, etc.

Photoluminescence from an organic material was first demonstrated on poly(p-phenylene vinylene) or PPV. This lends itself to use as LED's or other display applications. More recently, not just LED's, but lasers based on solid polymer films have been demonstrated. These usually make use of π-conjugated (conducting) polymers. There are both luminescent and nonluminescent types of π-conjugated polymers , and of course, only the luminescent variety is of interest in making light emitting devices.

1.1 Materials

Recipes for Organic LED's usually use PPV (poly(p-phenylene vinylene)). For lasers, some materials include dioctyloxy-PPV (DOO-PPV) or poly (1-phenyl-2-p-n-butylphenylacetylene) (PDPA-nBu) because they have particularly high photoluminscence yields.

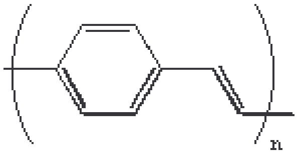
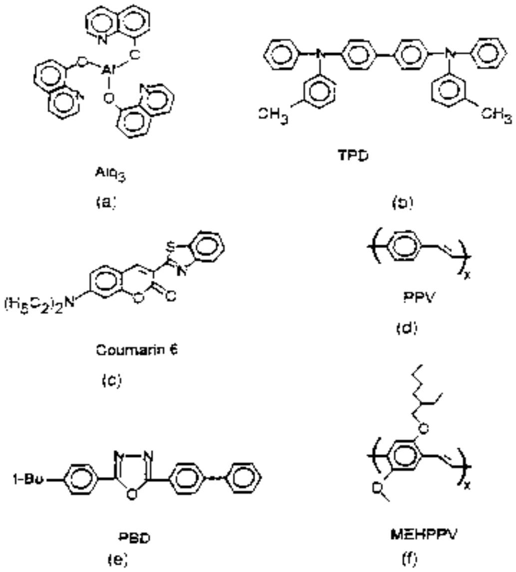


Figure 1: PPV monomer

Figure 1 hows a simple representation of PPV molecule. There is still on-going work in trying to find ideal materails for organic light emitting devices. PPV was the first and is very easy to work with.



Structures of the common organic materials used in EL devices
(a) tris-8-hydroxyquinolinealuminum
(b) N,N'-diphenyl-N,N'-(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine
(c) 3-(2'-Benzthiazolyl)-7-N,N-diethylaminocoumarin
(d) poly(para-phenylenevinylene)
(e) 2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole
(f) poly(2-methoxy-5-(2-ethylhexoxy)-1,4-phenylenevinylene)

*Figure reproduced from L J Rothberg et al., J. Mater. Res.(1996), Vol. 11

Figure 2: Common organic materials of light emitting devices

1.2 Using organic materials

The organic materials, of course, differ in various characteristics when compared their inorganic counterparts. So, while the same end result can be achieved, the strategies on how to achieve this with organic compounds will be different.

For example, at this point, organic semiconductors are **not** doped. This is because it is very difficult to achieve a stable junction with doped organic compounds. So, only intrinsic materials are used.

In addition, unlike silicon or other types of doped semiconductors, electron mobility is quite poor in organic materials. It is typically less than the hole mobility, quite the reverse situation.

2. Physics of Organic LED's

This is not intended to be an extensive description of the processes that occur. But, it will hopefully give enough of an understanding of what occurs so that potential applications can be further investigated.

The materials we are interested in are π-conjugated polymers. They have a delocalised π-electron system along the polymer backbone, which is essentially for it to have semiconductor like properties. These properties arise because of double or triple bonds that cause the overlap of pz orbitals.

π-conjugated polymers: a conjugated system consists of carbon atoms bonded by alternating single and double bonds. This arrangment results in some highly mobile electrons, which are called p-electrons. Unlike the regular electrons which are "stuck" with the chemical bond, p-electrons get to wander all over the place.

The carrier transport here is different than in traditional inorganic semiconductors. In the polymer, the electrons end up "hopping" from one chain to another.

2.1 Basic Operation

The basic idea of organic LED (OLED) operation is fairly simple and similar to that of inorganic LED's. Electrons and holes are injected into an "active" region. There, they recombine resulting in photon emission.

In an OLED, the electrons are provided by the cathode, usually some metal such as aluminum. In addition to providing the electron source, it is also used as an optical reflector to ensure the photons emit only from the side of the transparent anode.

The hole source is, of course, provided by the anode, typically a glass or plastic substrate with a thin film of IndiumTinOxide (ITO). This layer is required to be optically transparent.

Electrons are injected in the the conduction band of the polymer and holes are injected into the valence band. These carriers then move by diffusion across the polymer until they meet and recombine to form excitons. When these excitons decay to their ground state, photon emission occurs. This is the same process as in fluorescence.

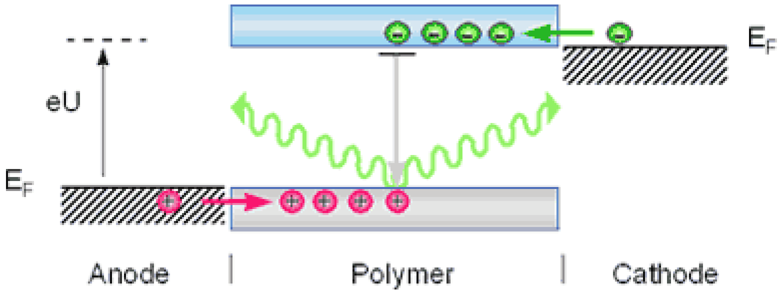


Figure 3: Injection of carriers across a LED (*Source: Covion, GmbH*)

The excitons which are generated can be in a singlet state or a triplet state. The singlet state ones decay immediately to generate the fluorescence. On the other hand, the triplet state excitons tend to have a very long lifetime (due to spin selection rules), and even when they decay, photon generation efficiency is relatively low.

It appears at the current time that there isn't yet very good agreement about what happens with these excitons and why or how many singlet excitons occur. I have seen an argument based on simple spin statistics that calculates the singlet state to occur with 25% probability, which would limit the maximum quantum efficiency of the polymer. This argument assumes that electron spins recombine into either one singlet state or three triplet states with equal probability and that the triplet to singlet state transition has a very low probability.

This argument may not be entirely correct, as there has been observation of triplet-triplet annihilation resulting in fluorescence.

2.2 Complications

The process described above is, of course, in a perfect world. In the real world, there are several complications that arise. These not necessarily stop light emission, but contribute to various inefficiencies of the process.

2.2.1 Mismatched carrier currents

One problem that can occur is that the energy levels of the cathod and anode material may not be well matched to the valence/conduction bands of the polymer (or whatever organic compound is being used). This results in an imbalance of the electron and hole currents.

This won't prevent light emission, but the dominant carriers end up diffusing across the entire junction without recombining. This is clearly very inefficient, but most importantly, leads to increased power and heat dissipation.

Of course, there are solutions to this problem. One method is to make use of 2 organic materials, each one matched to the anode or cathode. This succeeds in optimizing the carrier transport for both holes and electrons, but they may still be mismatched. Fortunately, there is a secondary effect. At the interface between the 2 organic layers, the carriers tend to get "stalled", so they wait around until a carrier arrives to recombine with. This performs the same purpose as a quantum well in a traditional inorganic LED.

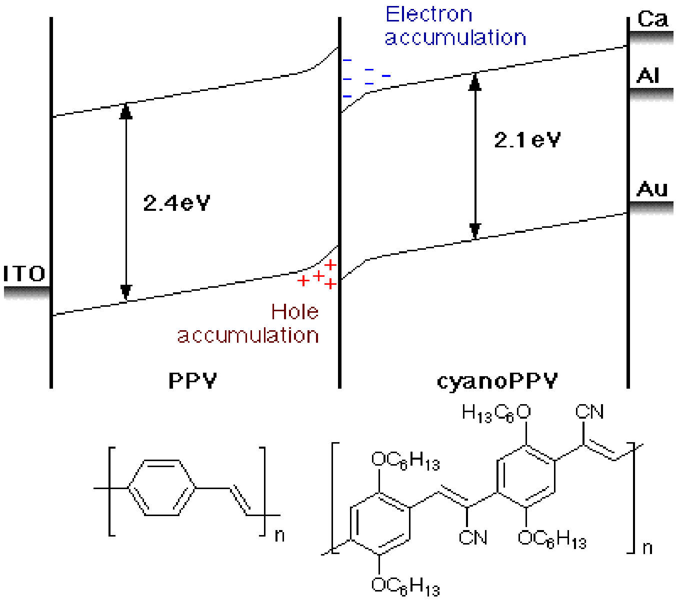


Figure 4: 2 layer OLED (*Source: Cambridge Display Technology*)

You can carry this idea further and introduce a 3rd layer optimized for luminescence. But this will of course introduce more complexity into the fabrication.

2.2.2 Quenching

Quenching simply means that the luminescence is suppressed in some means. The process is unclear yet, but it seems that some inter-chain interactions can quench the luminescence. Other known sources of quenching include processing "errors" in the PPV which result in carbonyl defects in the chain.

Also, some quenching processes are reversible whereas some have been observed to be irreversible. This likely means some permanent reaction has taken place to inhibit the recombination processes or the carrier transport.

3. Organic LED Recipes

Making organic LED's are ridiculously cheap and easy compare to their inorganic counterparts. In fact, it is straightforward enough to be included as part of undergraduate laboratory courses in Electrical Engineering.

3.1 Ingredients required

The list of materials is short, and most are easily acquired.

- PPV poly(p-phenylene vinylene) typical thickness is approximately 100nm for spin cast film, 1μm for drop cast.
- Aluminum (cathode)
- ITO - Indium Tin Oxide (anode) approximately 20 nm or so.
- Glass (substrate). Thickness doesn't really matter too much here.

Suitable substitutions, of course, can be made. There's no guarantee that it will work, as the process probably isn't fully understood. So, if you're not in the business of investigating organic LED's, it's probably safest to stick with a tried and true method.

The cathode is normally aluminum, and there probably isn't much reason to switch. It is cheap and easy to work with. Other materials which can be used are magnesium and calcium. Theoretically, any metal with low work function will suffice.

ITO is also pretty much standard, although there are practical problems, such as figure out how to properly etch it so that it will bind nicely to the organic polymer. Some tricks involve a secondary layer of another material. However, ITO has been used so much, any problems are likely well known.

The substrate material can be glass, or even a flexible sheet of plastic. Once could conceivably use a microscope slide for the task (properly cleaned, of course).

3.2 Making the organic LED

The equipment and process required is easy. Total time for completion is about 1 day or so, which includes time spent pumping out vacuum chambers and such. The steps aren't terribly complicated either, not if you can get a reasonably bright class of undergraduates to complete it year after year.

1) Prepare substrate in dust free work area. This can be a clean room, or clean "glove box" or whatever.
2) Coat substrate with thin film of ITO
3) Spin-coat polymer film (PPV).
4) Deposit top metal electrode in vacuum evaporator.

That's it. There are, of course, practical issues (as there are with any laboratory techniques), but these are relatively minor, and with a bit of practice, these can be easily overcome.

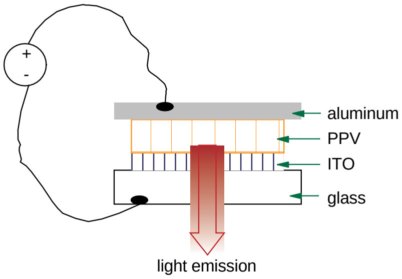


Figure 5: Simple organic LED

Figure 5 shows a simple diagram of the completed LED. For a real LED, it will actually be pretty much the same! That is because unlike traditional LED's, there is no patterning required. (Another money and time saving feature). As long as the layers exist (and have been deposited correctly), photon emission should occur once a voltage has been applied. It doesn't particularly matter which shape it is.

Originally, one of the limiting factors of organic light emission devices was the high voltage required. The most recent crop of organic LED's have lowered the voltage requirements to "normal" electronics levels, in the order of 5 volts or even less.

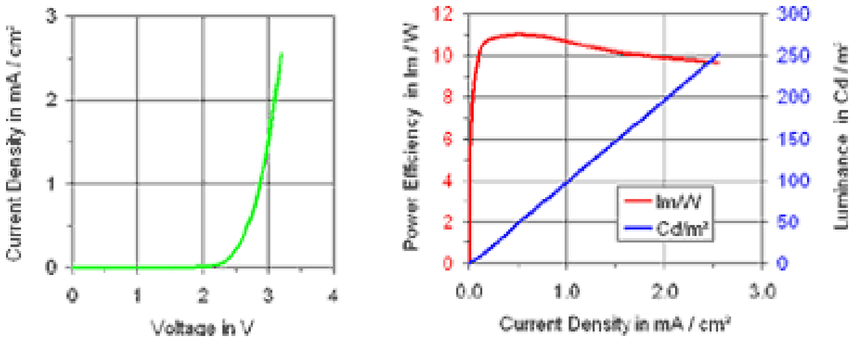


Figure 5: I-V and intensity curves for a typical organic LED (*Source: Covion, GmbH*)

Figure 5 above shows a graph of the I-V characteristic for a production organic LED. You can see that it turns on at a relatively low voltage in this case, even less than 5 Volts. At an operating voltage of 3V, power dissipation is approximately 6mW for a $1cm^2$ device. That sort of size should be easily sufficient for our needs, so a smaller device will have even less power dissipation. Low power dissipation will be important if we need to operate these LED's in a cryostat.

4. Sources of organic LED's

4.1 Labs at UBC

There is some work going on at UBC related to organic LED's.

4.1.1 Materials Chemistry Research Group

Headed by Dr. Michael O. Wolf, Associate Professor from the Dept. of Chemistry.

Contact Information
Office: Chemistry D420 *(604) 822-1702*
Lab(s): Chemistry D430/D418/D416/D320 *(604) 822-1673/0496*
FAX: (604) 822-2847
Email: `mwolf@chem.ubc.ca`
Web page: <`http://137.82.7.114/`>

This lab does a bunch of stuff, but one of them involves investigation of the materials used in making organic LED's, so indirectly, they are involved in making them.

The graduate student involved in the project is Andras G. Pattantyus-Abraham.

Part of the work, photophysical characterization of conjugated polymer/porous host hybrids, has photoluminescence studies are done by the Photonics and Nanofabrication Lab (Dr. Jeff Young) in the Department of Physics.

4.2 Commerical Companies

Most of the companies listed here are concerned with developing display devices using organic LED technology, rather than individual devices. However, organic LED (OLED) display technology is such that most of the commercially viable products are still relatively small (i.e. possibly suitable for use in a NMR).

- Covion <http://www.covion.com/>
- Cambridge Display Technologies <http://www.cdtltd.co.uk/>
- eMagin <http://www.emagincorp.com/>
- Kodak <http://www.kodak.com/US/en/corp/display/index.jhtml>
- Dupont Uniax <http://www.uniax.com/>
- Phillips

5. Potential Applications

While there are many interesting aspects of organic LED's, we must not lose sight of the fact that we are not in the business of investigating physical properties of LED's, or trying to develop new LED manufacturing techniques, or anything of that nature. (Of course, this may change in the future).

We are simply interested in using organic LED's or laser diodes simply as a method of increasing the spin polarization of target materials (e.g. spider silk) in order that it can be easily "imaged" using NMR.

Organic light emitting devices offer the promise of being used here because:

- Easily manufactured (relative to normal semiconductor devices)
- Can be easily custom designed to emit at a specified wavelength.
- Can manufacture one with relatively large surface area
- Possible to have easier spin transfer between organic-biologic material.
- Materials are non-magnetic (work nicely inside NMR)

The LED can be made to emit at various wavelengths relatively easily. (Any particular LED emits only at the designed frequency. i.e. these are not tunable LED's). This is accomplished by chemically varying the side chains on the PPV used in making the LED. (However, in the case of blue emission, we may have to move beyond PPV and use instead poly(p-phenylenes) or PPP.

5.1 Direct optical pumping

Original purpose is to optically enhance the spin polarize population of a material, and then have that transferred into our target material. With an organic light source, we could conceivably generate photons which enhance the atoms in the polymer itself, which would then transfer spin to the target material which is presumably physically on top of the polymer.

5.2 Organic LED/laser diode characterization

Well, it's not our original intent. But we have access to low temperature and a big magnet. I don't think many people have done this sort of investigation before. It might be interesting to see what happens. Might be worth a paper or two, but more importantly, we'll need to know how it performs, in case, for example, we do want to go to low temperatures in a large magnetic field.

5.2.1 General Characteristics

The wavelength of the LED can be customized to the region we are interested in. Lifetime of the LED's can be in the order of 50 hours (for a poorly made one) to several thousand hours. While probably at least an order of magnitude less than what is required for commercialization, even several hundred hours worth of operation should be sufficient for our needs.

References

S. Noach, E.Z. Faraggi, G. Cohen, Y. Avny, R. Neumann, D. Davidov, A. Lewis, "Microfabrication of an electroluminescent polymer light emitting diode pixel array", *Appl. Phys. Lett.*, Vol. 69, No. 24, pp. 3650-3652, December 1996

S. V. Frolov, M. Shkunov, A. Fujii, K. Yoshino and Z.V. Vardeny, "Lasing and Stimulated Emission in p-Conjugated polymers", *IEEE Journal of Quantum Electronics*, Vol. 36, No. 1, pp. 2-11, January 2000

G.E. Jabbour, S.E. Shaheen, M.M. Morrell, J.D. Anderson, P.Lee, S. Thayumanavan, S. Barlow, E. Bellmann, R.H. Grubbs, B. Kippelen, S. Marder, N.R. Armstrong and N. Peyghambarian, "High T_g Hole Transport Polymers for the Fabrication of Bright and Efficient Organic Light-Emitting Devices with an Air-Stable Cathode", *IEEE Journal of Quantum Electronics*, Vol. 36, No. 1, pp. 12-17, January 2000

S. Forrest, P. Burrows, M. Thompson, "The dawn of organic electronics", *IEEE Spectrum*, pp. 29-34, August 2000

M. Pope and C. Swenberg (1999), *Electronic Processes in Organic Crystals and Polymers*, Oxford University Press

http://www.chemsoc.org/exemplarchem/entries/2001/williamson/development.html

http://udel.edu/~subbu/OLED.htm

http://www.ee.calpoly.edu/~dbraun/papers/MRS00BraunKingsbVanasHH8-4.html

http://www.covion.com/technology/tech_summary.html

http://www.almaden.ibm.com/st/projects/oleds/physics/index.html

http://www.emagincorp.com/oledpri.htm

Notes: