OLEDs:

Modifiability and Applications

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3.063- Polymer Physics

21 May 2007

> "The dream is to get to the point where you can roll out
> OLEDs or stick them up like Post-it notes,"
> --Janice Mahon, vice president of technical
> commercialization at Universal Display[1]

Take a look at your cell phone; do you see a display that saves your battery and doubles as a mirror? When you dream of your next TV, are you picturing an unbelievably thin screen that can be seen perfectly from any viewing angle? If you buy a movie two decades from now, will it come in a cheap, disposable box that continually plays the trailer? These three products are all applications of organic light emitting devices (OLEDs).   OLEDs are amazing devices that can be modified through even the smallest details of chemical structure or processing and that have a variety of applications, most notably lighting and flexible displays.

Overview of OLEDs: Structure and Operation

The OLED structure is similar to inorganic LEDs: an emitting layer between an anode and a cathode. Holes and electrons are injected from the anode and cathode; when the charge carriers annihilate in the middle organic layer, a photon is emitted. However, there is sometimes difficulty in injecting carriers into the organic layer from the usually inorganic contacts. To solve this problem, often the structure includes an electron transport layer (ETL) and/or a hole transport layer (HTL), which facilitate the injection of charge carriers. All of these layers must be grown on top of each other, with the first grown on a substrate (see Figure 1).

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Please see Fig. 2 in Remmers, Marcus, et al. “The Optical, Electronic, and Electroluminescent Properties of Novel Poly(p-phenylene)-Related Polymers.” *Macromolecules* 29 (1996): 7432-7445.

Figure 1: Heterostructure of an OLED with both ETL and HTL[2]

There are many choices of materials for each layer, depending upon the application. The substrate is usually glass but may also be made of Polyethylene for a flexible device[3] or even a thin metal foil for a flexible yet protective and durable layer[4]. The anode is usually transparent ITO but may be —for example—porous polyaniline[5], and the cathode is often calcium or another low work function metal[6]. The anode, of course, must be transparent so that the emitted photons can exit the device. Example materials of ETL and HTL are Alq3 and TPD[7], respectively. The emitting layer is discussed in depth below. There is great potential for this entire device to be easily processed, giving industry researchers a great reason to take a hard look at OLEDs.

The principles behind the emittance of photons can be fairly complicated, however even a simple knowledge of the physics behind OLEDs is enough to understand their potential. At a basic level of understanding: a hole is injected into one layer of the device and an electron is injected into the other side of the device. The two charge carriers move along the polymer chains in the emitting layer, and when these two charge carriers combine, they emit a photon (they produce light). There are many factors that determine the wavelength of the released photon: bonding energy of the polymers, conjugation length, etc. It is dependent on the specific material properties. A sketch of the energy bands for a tri-layer device is shown in Figure 2; an ETL or HTL would simply add another layer to the sketch.

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Please see Fig. 1 in Nuyken, Oskar, et al. “Modern Trends in Organic Light-Emitting Devices (OLEDs).” *Monatshefte fur Chemie* 137 (2006): 811-824.

Figure 2: Energy bands of a monolayer PLED[8]

Modifying the Emitted Wavelength

For the emitting layer, there are multiple choices of materials and of processing variables such that an emission of a very wide range of wavelengths is possible. Two commonly used polymers for the emitting layer are poly (paraphenylene), PPP and poly(p-phenylenevinylene), PPV (see Figure 3), which normally emit green and blue light, respectively[9]. However, sometimes it may be to our advantage to tailor the wavelength of an OLED while using the same emitting polymer. Modifications are possible since the band gap energy of the emitting layer can be radically changed by varying the morphology of the polymer thin film[10]. This transformation can be performed in multiple ways: changing the chemical structure, by changing the length of uninterrupted conjugation (possibly by forming a copolymer), by changing the concentration of the polymer solution during fabrication, or by changing the spin rate when using the spin-coating technique.

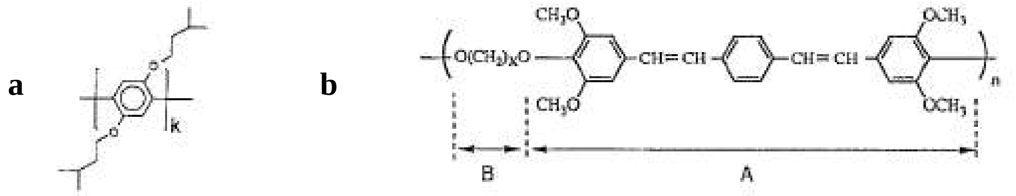

Figure 3: (a) Poly(paraphenylene) (PPP)[11], and (b) An example of a Poly(p-phenylenevinylene) (PPV) based copolymer, containing rigid (A) and flexible (B) blocks[12]

Modification of the Chemical Structure

One of the factors determining the band gap energy of the emitting layer is the planarity of the polymer. One way to adjust the planarity is to change the R groups attached to the phenyl group on the backbone of the polymer. Even though the equilibrium position is trans (R-groups opposite of each other), the angle of the R-group (and thus the phenyl group in the backbone) must change if the R-group is too large and there is stereo-hindrance. This change in planarity causes a change in the energy band gap—the determining factor for the wavelength of the emitted photon9.

Another factor determining the band gap energy is the length of conjugated segments in the polymer. The length of conjugated segments is the length along the backbone of connected, resonating π* electron orbitals. If this length is shorter than the conjugation length of the polymer (a material constant), then the chain will have a higher energy band gap[13] and thus a photon of shorter wavelength will be emitted when the electron recombines with a hole. The length of conjugated segments can either be the molecular weight of a straight polymer or the length of uninterrupted conjugation in a copolymer. For PPP-like polymers, the conjugation length is approximately 10-15 phenyl groups[14]. Thus, if the molecule length is greater than 15 phenyl groups, then the emitted photon will have the same wavelength for any fluctuation in molecular weight. However, if the polymer length is less than 10 phenyl groups, the wavelength of the emitted photon will vary dependent on the length of the polymer backbone. The same length dependence has been found in copolymers, where the determining length is the length of the emitting polymer segment (usually the stiff block). Yang et al.[15] demonstrated that shortening the length of the uninterrupted conjugated segment would cause the OLED to emit blue light rather than green light. Thus, co-polymerization is a potential process with which to alter the emitted wavelength of an OLED.

Modification of Processing

Not only does the chemical structure of the emitting material affect its emission, but the processing of the emitting layer has a strong effect on the emission spectrum as well. The processing can radically change the morphology of the polymer, which powerfully influences the electroluminescence.

There are multiple potential fabrication methods for organic thin films, however spin-coating is the most common. In spin-coating, a solution of polymer is placed on the previously grown layer and the device is rotated by a spinner. The centripetal force causes the solution to spread over the below layer, creating a thin film. After spinning, the device is annealed such that any liquid solvent that was still left in the polymer solution evaporates, leaving only the polymer in the emitting layer.

Spin-coating is the preferred fabrication technique for polymer thin films since it does not require very high temperatures and creates films of the necessary range of thickness. Polymers often decompose when heated, thus thermal vacuum evaporation is often not an option for growth. Also, spin-coating can produce very thin films, such as those needed for OLEDs. The procedure can't be used to create thicker films (greater than thousands of Angstroms), but rarely are such thick films used in OLEDs. A disadvantage of the spin-coating technique is the inability of pattering. Spin-coating creates a large plane of only one emitting polymer. Pixels can be created by patterning the cathode, however all pixels will be the same color[16]. Nevertheless, spin-coating is commonly used in the research field, and thus the processing variables discussed here apply mostly to this technique.

A simple method of changing the emission spectrum is to dissolve the polymer at different concentrations and/or into different solvents. Once the concentration of the polymer in solution is greater than the overlap concentration (c*), the polymer chains will begin to interact and aggregate. It is around this aggregation limit that the emission spectrum transforms. Liu et al[17] demonstrated that the emission spectra transformed as they changed concentration of poly(2-methoxy-5-(2'-ethyl-hexyloxy)- 1,4-phenylene vinylene) (MEH-PPV) dissolved in poly(9,9-dioctylfluorene) (PF) in solid-state. MEH-PPV at a concentration of 4% gave a very different spectrum than pure MEH-PPV, with λ_{max} at 4% MEH-PPV concentration approximately 100 nm less than λ_{max} at

100% (see Figure 4). This dramatic transformation can be attributed to the lack of interchain interactions (which give rise to the emission at approximately 650nm) in the dilute concentration[18]. Thus, the emitted color of an OLED can differ solely on the concentration of the emitting polymer within solid solution.

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Please see Fig. 1 in Liu, Jie, et al. “Improving the performance of polymer light-emitting diodes using polymer solid solutions.” *Applied Physics Letters* 79 (July 30, 2001): 578-580.

Figure 4: Dependence of emission spectrum on concentration of MEH-PPV mixed with PF in solid-state17.

The emission of a pure polymer thin film in the OLED can also be affected by the differences in morphology due to variation in spin-coating technique. For example, changing the concentration of the emitting polymer in solution (even when the solute entirely evaporates) can shift the emission spectrum. If the concentration of the polymer is below c*, then there are no (or very few) entanglements to prevent the elongation of the chains when spin-coated onto the device. The elongation of the chains increases the planarity of the carbon backbone, and thus increases the energy of an emitted photon. If the concentration of polymer is above c*, then the polymers will be overlapping and aggregated. When the solution is then spin-coated, the entangled polymers do not stretch radially to the extent of those below c*, and therefore the energy of an emitted photon from this system is slightly decreased[19].

Similarly, the spin rate can shift the emission spectrum of the polymer. As the spin rate increases, the centripetal force increases and causes greater radial extension of the chains. Again, this extension affects the planarity of the polymers, increasing their conjugation and thus decreasing the energy of emission. Changing the spin rate from 2000 rpm to 8000 rpm of MEH-PPV films gives a λ_{max} change of approximately 10 nm[20], and changing the concentration of polymer from 0.3% to 1% also shifts λ_{max} by approximately 10 nm19.

There are many ways to modify the emission spectrum of OLEDs to custom tailor the device to a specific application. There are also many applications for OLEDs which determine the socioeconomic effect of the above-mentioned research. Two of the most important applications are discussed below: residential lighting and televisions.

Application 1: Residential Lighting

One of the major applications for OLEDs is lighting, especially residential. The US Department of Energy reports that lighting consumes approximately 20% of the nation's energy, and residential lighting consumes about a quarter of that. For this reason, the DOE has formulated the Solid-State Lighting program with the goal of developing commercially acceptable lights that will use only half the energy used currently for residential lighting. Many of these lights will be OLEDs and will be mostly large displays. Figure 5 shows a prototype room lit with OLEDs (on a small scale).

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Please see http://tinyurl.com/yu3pb3

Figure 5: Prototype of a room lit with OLEDs[21]

As part of their Solid-State Lighting program, the DOE recently recognized a lab group shared between University of Southern California (USC) and Universal Display Corporation (UDC) for their substantial impact on the research of OLEDs. This group “was able to obtain an efficacy of 30 lumens per watt (lm/W), twice that of an incandescent bulb, at 70 CRI and this new record [external quantum efficiency].” A representative of the DOE stated: "The Department will continue to work with Universal Display and other lighting research partners to drive further technology advances and efficiency breakthroughs that will make solid-state lighting a cost-effective, energy-saving alternative for general lighting applications."[22] Obviously, the US government organization knows that OLEDs can do an amazing amount of good for our country: save space, money, and energy in the most common context. That is why government and industry alike continually research and support research on OLEDs and strive to create OLEDs that will transform the world. The UDC press release explained, “this achievement represents another important step toward DOE’s long-term SSL research goal of 160 lm/W in a cost-effective, market-ready white lighting OLED product.”[23]

This goal gives us insight into another great benefit of OLEDs: they will be much more efficient than the presently common in candescent bulbs. Thus, if OLEDs become prevalent, we will consume less energy, which is wonderful for numerous reasons (delaying global warming, conservation of fossil fuels, decreasing the trade imbalance, etc.). Ultimately, OLEDs are great for our economy and environment.

Application 2: OLED TVs

By the end of this year, OLED televisions will be sold commercially. There are a large number of advantages to OLED TVs, yet there are also many hindrances to their commercialization. OLED TVs are amazingly beautiful screens: they produce vivid color at nearly any viewing angle. As one forum member described, "LCD and plasma displays look faded in comparison."[24] However, the commercialization of OLED TVs has been delayed due to an immense need for more research in the field. Some examples of hindrances are the low lifetimes of the OLED pixels[25], the variability in manufacturing processes[26], and legal delays due to Kodak's patent on some of the basic technology[27].

One year ago, Samsung displayed a forty-inch television screen (http://tinyurl.com/2hpqle); however, there are not yet plans for commercial sale.[28] This January Sony unveiled their own OLED screens (Figure 7), and in May announced its plans to commercially distribute the smaller version of the OLED TVs by the end of this year24.

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Please see http://tinyurl.com/2hpqle

Figure 6: Samsung displays its 40'' OLED TV (May 2005) 28

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Please see http://tinyurl.com/2yxtre

Figure 7: Sony displays its OLED TVs (Jan 2007)[29]

There is obviously progress being made in the field of OLED TVs, however there are competitors for display technology. Some notable mentions are plasma, liquid crystal displays (LCDs), and even field emission displays (FEDs)[30], as well as inorganic LEDs. LCDs already have a very strong hold on the television market, so OLEDs would be best sold in a niche market. An example of this would be flexible OLEDs (FOLEDs)3. Since the emitting polymers or small organic molecules are flexible, the display itself can be flexible as long as it is deposited on a flexible substrate. In February 2006, UDC has introduced a rollable OLED with full-color and full-action[31], with a metal foil substrate and a multilayer thin film as encapsulation. FOLED applications can be anything from rollable TV screens to product wrappers to clothing. Surely they will soon be seen everywhere.

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Please see http://www.universaldisplay.com/video/2002foled257.wmv

Figure 8: Flexible OLED by UDC[32]

Conclusion

There are many advantages to using OLEDs in multiple applications. Most importantly, the color of the emitted light can be changed by a few modifications to morphology of the polymer. Since OLEDs can be very beneficial to our society both economically and environmentally, there is no doubt that their presence in the market will continue to increase.

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