

# Electroluminescence in Polymers

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## Abstract

Conjugated polymers and copolymers have been known to have electroluminescent properties for a number of years. This study examines the electroluminescent properties of a particular segmented block copolymer. This copolymer fluoresces quite well both in solution and as a thin film, but a single layer organic LED made from it does not work well. I investigate the effect of blending 1% PAN/CSA into the solution to facilitate the injection of charge into the copolymer.

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## 1 Introduction

For decades, we have taken advantage of the intriguing properties of semiconductors. Semiconductors make diodes, transistors, and a number of light-emitting devices possible because of the small band gap between their conduction band and valence band. When this gap is proportional to the energy of visible light, it becomes possible for single photons to excite the electrons from the conduction band to the valence band. Similarly, when electrons and holes recombine,

they emit visible light in a process known as electroluminescence.

Traditionally, the only materials which have exhibited such properties were inorganic, such as germanium and silicon. Other inorganic materials require doping in order to become semiconductors. However, it was recently discovered that a similar doping process could be applied to organic compounds to change, or completely remove, their band gap. The emeraldine-base form of polyaniline, when doped with camphor-sulphonic acid, becomes metallic (known as

PAN/CSA)[1]. A great number of other materials were discovered in the following years to have semiconducting properties.

Polymers are organic compounds which form in long chains of repeating organic units, called mers. They are often easier and cheaper to produce than metals and conventional semiconductors. In addition, they are more versatile than conventional materials. Polymers can be made on a wide variety of substrates, which allows the production of flexible polymeric devices.

Traditional polymers, however, are insulators. The discovery which now allows us to reduce the band gap is their extended  $\pi$ -conjugation. Most polymers consist of long chains of carbon atoms, often on aromatic rings. Most of the bonds form  $sp^2$  hybrids, which leaves the  $p_z$  orbitals unhybridized. This gives rise to the delocalization of the  $p_z$  orbitals, forming a continuous sea of electrons. In conjugated polymers, the distances between carbon atoms varies along the chain, which may cause conductivity. In addition, the  $\pi$  and  $\pi^*$  energy levels take on the role of the conduction band and valence band, respectively, of traditional semiconductors. Thus, we can tweak the polymer to produce nearly any band gap desired, and consequently, any color of light emission.

The first organic electroluminescent devices had unwieldy voltage requirements - often needing 100V to inject charge into the emissive layer. In 1987, a device with a driving voltage below 10V was developed using diamine as a hole transport layer to inject charge into *8-hydroxyquinoline aluminum* ( $Alq_3$ ) [2]. *Poly(9-vinyl carbazole)* (PVK)

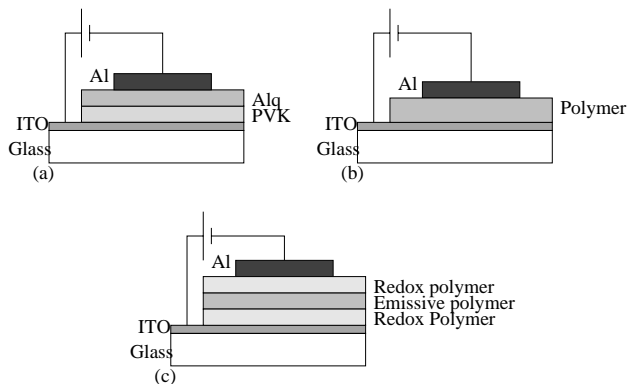


Figure 1: (a) Cross section of the ITO:PVK:Alq:Al device; (b) Cross section of a typical single layer device; (c) Cross section of a typical SCALE device

was also an effective hole transport layer[3]. Later it was discovered that *poly(phenylene vinylene)* (PPV) devices were effective as well[4]. This opened the way for other conjugated polymers such as *poly(p-pyridine)* (PPy)[5] and copolymers such as *poly(pyridyl vinylene phenylene vinylene)*, (PPyVPV)[6]. Later developments involved using blends with PVK and other materials to increase efficiency[7]. Figure 1 shows some typical devices.

The older devices only worked in forward bias. Recently, however, a number of devices were made which work in both forward and reverse bias. A number of them produce different color light when run in reverse[6]. In addition, many work with alternating current[8]. AC devices often have significantly longer lifetimes than their DC equivalents. In addition, they are made by sandwiching the emissive layer between two redox polymers. This construction allows us

to use any metal for either electrode, regardless of work function. In particular, we can use gold, which was previously unsuitable because of its high work function.

One particular class of AC device, symmetrically configured AC light-emitting (SCALE) devices, is made by sandwiching a conjugated polymer emissive layer between two layers of emeraldine base (EB) polyaniline. Most conjugated polymers which work in single layer devices will also work in SCALE configurations.

While there are a number of unique advantages found in organic electroluminescence, there is also a significant drawback. The quantum efficiency and power requirement of most polymers is still terrible compared to traditional materials. Thus, most of the research in recent years has been directed towards improving efficiency and power consumption. Generally, there is a correlation between the quantum efficiency of electroluminescence and of photoluminescence (emitting visible light when exposed to ultraviolet light). Several years ago in our lab, Dr. Daike Wang synthesized a material known as DW38 (as well as a closely related material called DW40). This is a PPy-derived segmented block copolymer (Fig 2) which has incredible photoluminescent efficiency. However, previous attempts at electroluminescence yielded very weak results.

## 2 Methods

This study consisted of building and testing a number of electroluminescent polymeric de-

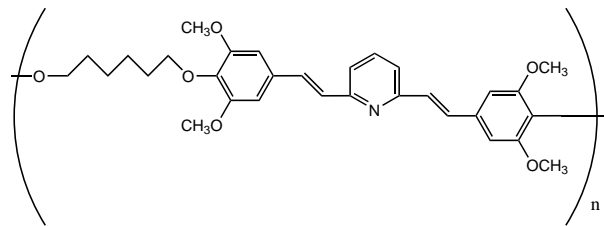


Figure 2: Molecular repeat unit of DW38

vices. Outlined below is the procedure used in making the devices.

### Fabrication

Start with a square (about 1 in<sup>2</sup>) of ITO coated glass ( $20 \Omega/\square$ ). Using single-sided clear tape, mask a strip in the center of the ITO. Then place the substrate in a solution of HCl and H<sub>2</sub>SO<sub>4</sub> and add Zn to etch the unmasked areas. See figure 3 for an overhead diagram of the device.

Next, clean the substrate. Sonicate the plates in a surfactant cleaner to remove any large particles. Then rinse with distilled water. Using cotton swabs, scrub the surface with acetone and toluene. Then sonicate in acetone to remove anything left over from the cotton swabs. Finally, sonicate in isopropanol to remove the acetone and dry with nitrogen.

After the substrates are clean, add the organic layers. This is done either by vacuum deposition or spincoating. Spincoated layers must be dried in a vacuum oven. The temperature is an important factor. If it is too hot, especially in the presence of oxygen, the C=C bonds can break and form O=C-C=O, which unconjugates the polymer. However, some applications require cross-

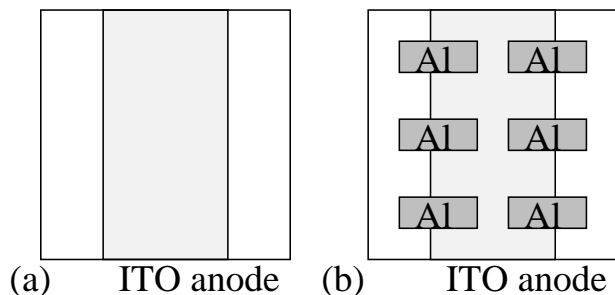


Figure 3: Overhead view of a device (a) after etching the ITO and (b) after depositing the aluminum

linking, which among other things is done with higher drying temperatures.

The target thickness for most layers is 50-120nm, depending on the application. Single layer devices tend to require a thicker layer than an individual layer of a multi-layer device. The solutions from which the layers are spun are filtered with  $5\mu\text{m}$  filters.

After the organic layers are added, evaporate about 100-120nm of aluminum into the top organic layer for the cathodes. The mask for the aluminum is set up so that there are a few devices on each plate (Fig 3).

## Testing

The devices are tested in a number of ways. First, with a working device, we gradually increase the voltage until the luminescence is clearly visible in a dark room. This is the turn-on voltage.

Next, we find the emission spectra of the light. Because of the devices' short lifetimes, we were forced to use a very short integration time, causing spectroscopy data to be very rough.

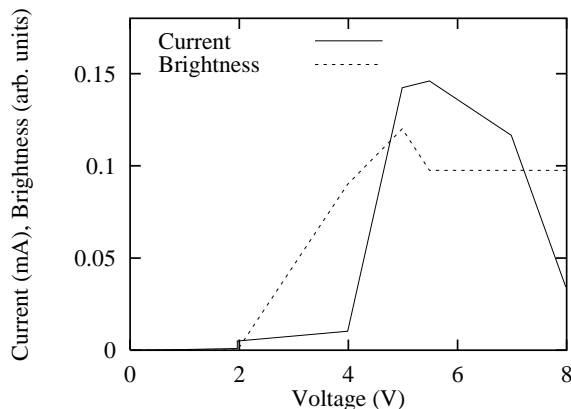


Figure 4: Current and brightness vs. voltage graph of device with 120nm layer of pure DW38

Finally, we use the LabView software with three digital multimeters and a phototransistor to generate graphs of current and brightness with respect to voltage.

## 3 Results

As a control, the first devices fabricated were PVK:Alq<sub>3</sub> devices[3]. After obtaining some good results, I moved on to some new materials. A number of materials either did not make good films or were not even photoluminescent. Finally, I began working with DW38 and DW40. Early results with each were weak (Fig 4).

I tried a number of things to increase the efficiency of the device. First, I attempted to use PVK to help inject charge into the copolymer. I tried it both as a separate layer and as a blend (1-3% PVK in the same solution). Neither of these worked. Figure 5

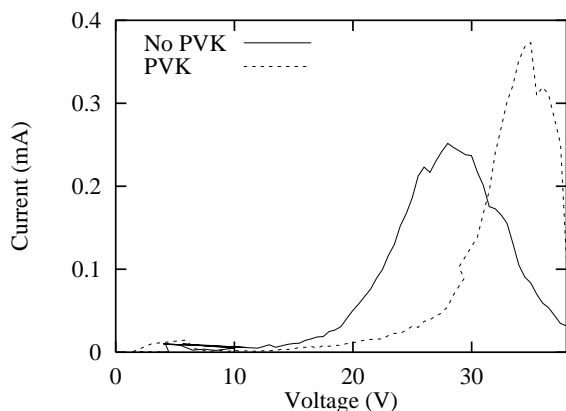


Figure 5: Current vs. voltage graph DW40 with and without a PVK layer

shows the effect of adding a 40nm layer of PVK beneath the 70nm layer of DW40.

Multi-layer devices are often difficult to make if adjacent layers have similar solubility properties. I believe some solubility issues may have arisen in the two layer PVK:DW40 and PVK:DW38 devices, in which the chloroform partly dissolved the already casted PVK layer. However, the PVK actually shifted the IV curve to the right, which suggests that the electrons may possibly be the problem.

Unfortunately, I did not have access to any substances which are effective electron transport layers, such as PPy. In addition, most electron transport layers are also good emissive layers, which causes ambiguity.

To work around this, I used PAN/CSA. PAN/CSA is a novel polymer because it responds to secondary doping[9]. It can be made either metallic or insulating, depending on the solution it is spun from. When spun from pure m-cresol, it is completely metal-

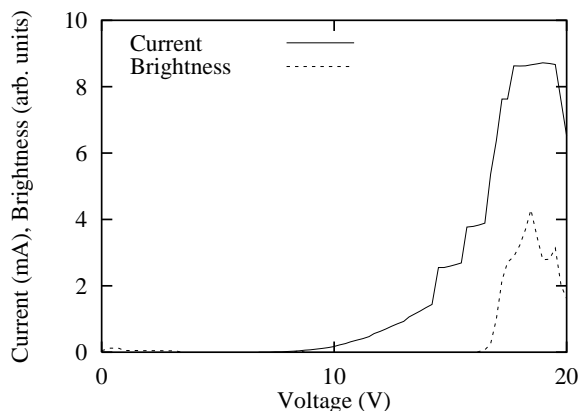


Figure 6: Current and brightness vs. voltage graph of 50nm, 99% DW38, 1% PAN/CSA blend

lic. When spun from chloroform or *1-methyl 2-pyrrolidone* (NMP), it is mostly insulating. A blend of solvents mixes these effects.

My first attempts involved sandwiching the DW38/DW40 between two layers of metallic PAN/CSA, spun from pure m-cresol. I also tried using a 5% m-cresol and 95% chloroform solution. Both attempts were unsuccessful.

One possible problem was the insolubility of PAN/CSA in chloroform. Even doped, the solubility is quite low, to the point that I was unable to get it to dissolve at all.

The most successful approach was to use NMP as the solvent. I made the initial solution with 30mg DW38 and .25mg PAN/CSA in 2mL NMP. Spincasting at 1,500rpm yielded a 50nm layer. The device emitted rather brightly and had a turn-on voltage of around 16V (Fig 6). The light was greenish, as shown by the emission spectra (Fig 7).

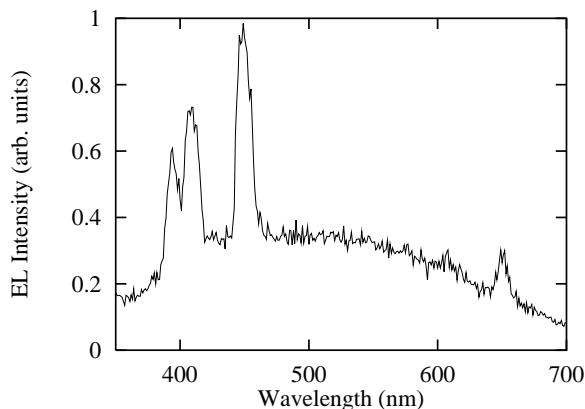


Figure 7: Electroluminescent emission spectroscopy for DW38 (1% PAN/CSA)

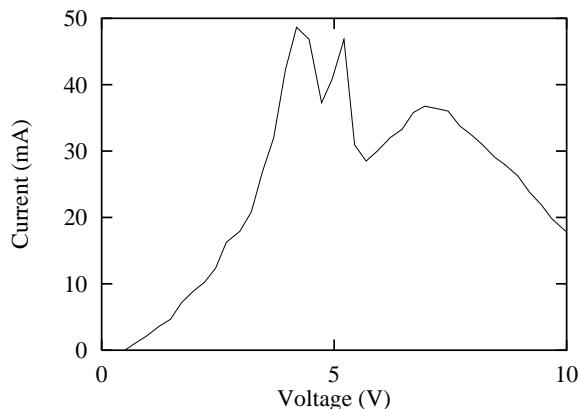


Figure 8: Current vs. voltage graph of 95nm, 99% DW38, 1% PAN/CSA blend

I made a thicker solution (probably 20-25mg/mL) with the same proportion of PAN/CSA. At 1,000rpm the film was 95nm thick. The resulting device was much better than the 50nm device, with a peak current of nearly 40mA and a turn-on voltage as low as 5V, but the brightness data was lost (Fig 8).

Unfortunately, I was unable to recreate the 95nm layer and have been unable to get results comparable to these.

I tried changing the amount of PAN/CSA to 3%, but the results were negative for both DW38 and DW40. In the end, I was unable to make any working devices with DW40.

Finally, I attempted to make a DW38 device in SCALE configuration. Because of solubility concerns, I used PAN/CSA spun from NMP as the bottom layer. However, I baked it at a higher temperature (70°C) to physically cross-link the polymer so that it wouldn't redissolve in the next layer of NMP[10]. The emissive layer was 99% DW38

with 1% PAN/CSA dissolved in NMP. The top layer was NSPAN dissolved in water. All layers were spun at 1,000rpm and the top two dried in a vacuum at 40°C. This device, unfortunately, did not work at all.

## 4 Conclusions

The copolymer DW38 is promising as an electroluminescent copolymer. With more work, it may become an efficient organic light source. It appears that the main problem with DW38 is the difficulty to get charge into the polymer itself. Once there, it seems to recombine and emit light quite well.

Further study should be conducted on thicker films of DW38. The one result I had with the 95nm film was quite a bit better than the thinner films, although I was unable to reproduce a film that thick again. Another noteworthy concern is the solubility of PAN/CSA in NMP. While it dissolves much

better in NMP than in chloroform, there are still many undissolved particles.

Because these particles are filtered out, it is difficult to know truly what the ratio of PAN/CSA to DW38 is. Additionally, an IR absorption spectra could have been used to determine the effectiveness of the drying process. A large concern was whether the drying was too hot and ruined the C=C bonds in the polymer, or not hot enough and left too much of the solvent in the layer. Finally, a more thorough investigation of the ideal amount of PAN/CSA would be beneficial as well.

This study provides more evidence that polymers may play an increasing role in light-emitting devices. Once the operating voltage and quantum efficiency is improved to the level of traditional materials, organics could be useful replacements for conventional semiconductors and metals.

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