Electroluminescence from single layer molecularly doped polymer films

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Abstract:
Light emission from single layer thin film devices comprised of a hole transport
polymer, poly(N-vinylcarbazole) (PVK) doped with 2-(4-biphenyl)-5-(t.-butyl-
phenyl)-1,3,4-oxadiazole (Bu-PBD) and variety of emitter molecules is described.
The single layer nature and the use of soluble materials simplifies the
fabrication of devices by common solution coating techniques. The color of the
emitted light can be tuned across the visible spectrum by using appropriate dyes.
Evidence is presented that the luminance from any given device increases
linearly with the current density and that the luminance observed from different
devices is independent of the hole mobility. This shows that the critical
determinant of the light output is the quality of the injecting contact or the
number of injected carriers and not the speed with which the carriers migrate.
Some criteria for tuning the emission color are presented.

INTRODUCTION

The phenomenon of luminescence resulting from the recombination of injected
charge carriers, holes and electrons, has been studied extensively because of potential
commercial applications in a variety of devices such as simple illuminators, signs, or
eventually in flat panel displays. The clear advantage of organic electroluminescent (EL)
devices is the ease of fabrication, low operating voltages and the ability to tune the color of
the emitted light by appropriate dopants or by changing the bandgap of the active
polymer. Two basic types of organic EL devices have been under investigation. One type
of device is a thin bilayer structure made by sequential vapor deposition of hole transport
and electron transport molecules (1,2), optionally with a third layer of emitter molecule
sandwiched between these two layers (3). The hole transport molecules are typically
complex tertiary aromatic amines of the type currently used in charge transport layers in
electrophotographic photoreceptors for xerographic printers and copiers. The electron
transport molecule is a molecule with LUMO level sufficiently low to accept electrons
under strong electric fields from the cathode, which is a low work function metal. These
molecules bring the respective injected charge carriers to the recombination zone.

The second type of EL device employs thin films of hole transporting π-conjugated
polymers either created *in situ* from a precursor polymer by thermal conversion (4), or
cast from solutions (5). Recently described devices are also two layer structures in which

the second layer, typically not a medium for transport of holes, isolates the hole transport conjugated polymer from the cathode to prevent passage of holes to the cathode (6). The passage of charges without recombination in the bulk would be a loss process.

We describe here a simple single layer device using materials shown in Fig. 1: a well known hole transport polymer, poly(N-vinylcarbazole) (PVK), doped with 2-(4-biphenyl)-5-(t.-butylphenyl)-1,3,4-oxadiazole (Bu-PBD) and an emitter molecule and, eventually, when the control of the hole mobility in the device is desirable, also with N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1'-biphenyl]-4.4'-diamine (TPD) (7). First mention of an organic EL device with green emission using PVK appeared over twenty years ago (8) but those papers did not stimulate much activity even though they presented a number of important principles that control organic electroluminescence. The use of the oxadiazole derivative as electron transport material in layered EL devices has also been described previously (3). One of the objectives of this study was to elucidate the effect of variation of the hole mobility on the light output of the device. To vary the hole mobility of PVK, we used the well-known principle of single-trap controlled hopping transport (9), by doping PVK with another hole transport molecule with lower oxidation potential than the host. Doping with specific amounts of TPD is known to vary μ in PVK by many orders of magnitude without affecting the carrier range. Finally, some criteria for tuning the EL color are presented.
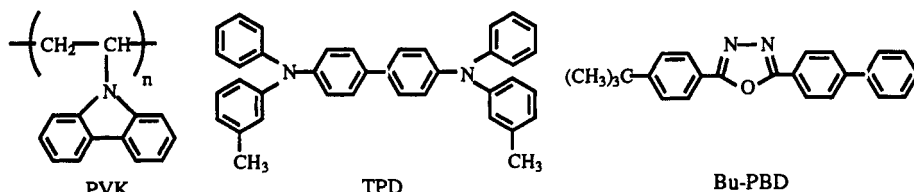

Fig. 1. Structures.

EXPERIMENTAL

Materials: Luvican®Poly(N-vinylcarbazole) was purified by 5x precipitation from THF in methanol. TPD was synthesized and purified by the methods described earlier (10). The oxadiazole derivative (Bu-PBD) and the emitter molecules were used as received.

Device fabrication: The polymer films were deposited on ITO-coated glass substrates of approximately 5x5 cm. The ITO serves as the anode. The substrates were cleaned in an ultrasonic detergent bath at 50°C, rinsed with deionized water, submerged successively in ultrasonic baths of acetone and ethanol at 50°C, then dried in an oven and then exposed to ozone in a glass chamber. The active layer was spin-coated from solutions (filtered through a 0.4μ glass filter and a polypropylene filter) containing typically (200 - x) mg of PVK, x mg of TPD, 100 mg of (Bu-PBD) and 0.3 - 0.7mg of the emitter in 10 mL of 1,1,2-trichloroethane. The resulting film thickness was 1,000 - 4,000Å. The films were uniform and pinhole free. The cathode was a 1500Å layer of vapor-deposited Mg, protected by a ~1000Å layer of Ag. The cathodes were deposited as 7x7 arrays of 4 mm diameter dots. The devices were stored under argon. The typical single layer device is schematically shown in Fig. 2.
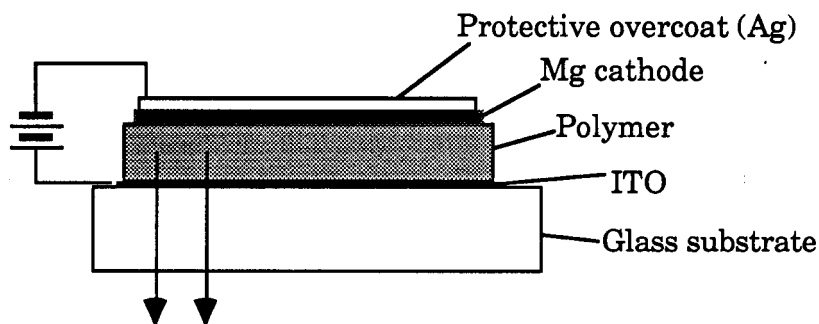
Fig. 2. Structure of the single layer device.

Measurements: All measurements were done in argon. The driving voltages were supplied by a HP 214B pulse generator. The devices were operated using 100μs pulse widths with a 10% duty cycle. Current was measured using a Tektronix 7904 oscilloscope with either a Tektronix 7A19 amplifier or, at low injection levels, with a Tektronix 7A22 differential amplifier shunted with a 50Ω resistor across its input. Luminance was measured with a EG&G silicon photovoltaic detector. The EL spectrum was measured on a McPherson Model 218, 0.3m focal length f/5.3 scanning monochromator. The photocurrent was measured with a Keithley 610B electrometer.

RESULTS AND DISCUSSION

Both PVK and TPD are known to exhibit essentially trap-free transport of holes (10, 11). Consequently, injected holes can reach the cathode without recombination, unless they encounter electrons injected from the cathode. On the other hand, electron transport in Bu-PBD molecularly dispersed in a binder polymer appears to be severely range-limited. The attempts to measure electron transport in Bu-PBD/binder by the Time-of-Flight technique only showed the current pulse signal following the excitation pulse which indicates that the average distance the electrons can travel in Bu-PBD / binder is much less than about 10 nm even at high electric fields. PVK and TPD are unipolar, hole transport media, and therefore injected electrons cannot reach the anode. The measured current in the single layer EL device described here is therefore a sum of the hole injection current and the current that leads to recombination of carriers.

The typical current - voltage characteristics of a device containing equal amounts of TPD, PVK and Bu-PBD and Coumarin-6 (C 6), and the dependence of the light output on the injection current are shown in Figs. 3 and 4, respectively. All other devices showed a similar behavior except that the lower the TPD concentration was, the higher applied voltage was necessary to sustain the same injection current. Apparently, decreasing the TPD concentration increased the barrier for injection from the ITO electrode. Fig. 4 shows that the luminance of the device depends linearly on the injected current density. Again, the same behavior was observed for all other devices with different concentration of TPD. The question of whether this linearity is a consequence of the bulk properties of the film or whether it reflects on the behavior of the ITO injecting contact can be resolved experimentally since the hole mobility can be varied over a range of more than 5 orders of magnitude by varying the TPD concentration in PVK (9).

Figure 5 shows the hole mobility behavior as a function of TPD concentration in PVK. This behavior is predicted in the framework of single trap controlled hopping
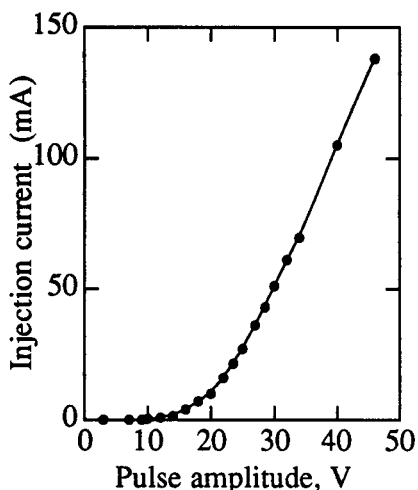
Fig. 3. I-V characteristics of a device
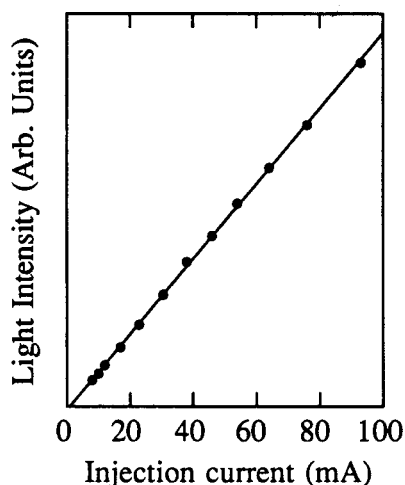containing equal amounts of TPD,PVK
and Bu-PBD, and 0.1wt% of C 6.

Fig. 4. Light output as a function of
injection current $J_{inj.}$ for the same
device as in Fig. 3.

transport (9). As the lower-oxidation potential charge transport molecule (TPD) is added
to PVK, the reduction in μ is proportional to its concentration, until the minimum μ is
reached. In this case the lowest mobility is reached at about 5 wt% of TPD. With further
increases in the TPD concentrations, the average separation distance of the TPD
molecules becomes smaller so that TPD gradually becomes the primary transport
channel, and PVK assumes the role of an inactive binder for TPD. In this range of TPD
concentrations, the mobility μ increases with increasing the concentration of TPD. At 50
wt.% TPD relative to PVK, the hole mobility μ of the layer is near 10^{-5} cm^2/V.sec at the
electric field of 10^5 V/cm, significantly higher than in undoped PVK. This indicates that
under these conditions TPD is already the primary transport medium and PVK acts only
as a binder. One would therefore expect the EL to come from TPD rather than from PVK,
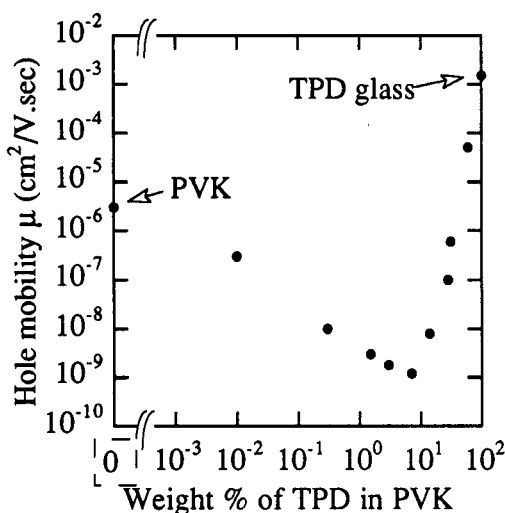which turned out to be the case.

Fig. 5. Hole drift mobility μ in PVK
doped with varying amounts of TPD at
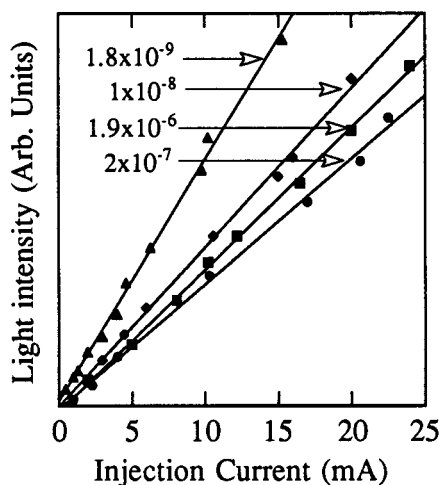$E = 5x10^5$ V/cm and 295K. Data replotted
from (9).

Fig. 6. The effect of hole mobility on
the luminance of TPD doped films

Figure 6 shows the EL intensity in four devices in which the hole mobility μ was modulated by varying the TPD concentration. In spite of the 3 orders of magnitude differences in μ at the same injection current levels, the EL intensity varies by no more than a factor of two. The near-independence of the light emission on μ shows that the injecting contacts to the doped polymer film are not ohmic but emission limited. The current density is determined by the rate of injection of carriers. The mobility becomes unimportant once the steady state conditions are reached. The time to reach the steady state obviously depends on the mobility since the steady state is achieved in times longer than the transit time of the first carriers. All this suggests that the performance of the devices can only be improved by increasing the rate of injection or ultimately by making the contacts ohmic. No serious attempt has been made to optimize the light output of these devices but luminances in excess of 2,000 cd/m^2 have been achieved at injection current density levels at around 500 mA/cm^2. This compares well with other published devices, based both on π-conjugated polymers and vapor deposited glasses of small molecules.

Without any other additive, the device containing PVK, TPD and Bu-PBD (1 weight part of each) emits blue light, but it is weaker than from emitter-doped layers. It has to be noted that the emission spectrum, even though it is from TPD, is considerably red-shifted and broadened compared to photoluminescence from TPD-doped films at much lower TPD concentration. This is perhaps due to the formation of TPD aggregates at these high concentrations which also may account for the lower EL output. The energy migration within the TPD phase could cause the molecular exciton to be trapped at a quenching site or quenched at the cathode. In either case, it is advisable to avoid high concentration of the emitter to minimize aggregation and exciton migration. The oxadiazole derivative, Bu-PBD, does not emit light in our devices, in contrast to the other type of electron transport materials frequently used in organic EL devices, such as 8-hydroxyquinoline aluminum (Alq$_3$) (1,2).

Tuning the color of the PVK based single layer devices is shown to be relatively easy, by adding small concentrations of emitter molecules. Selection of the emitter is based on the compound's photoluminescence in dilute solutions. For example, EL from the device containing 1 part PVK (by weight), 1 part TPD and 1 part Bu-PBD and as little as ~0.1wt% of Coumarin-6 was totally that from C-6; no fluorescence from TPD or PVK was detected. This is true even though the oxidation potential of C-6 is somewhat higher than that of TPD (+0.97V and +0.76V, respectively, vs. SCE), and therefore C-6 would be expected to be less effective in trapping holes than TPD. On the other hand, the reduction potential of C-6 is lower than that of Bu-PBD (-1.31V vs. -1.50V) and thus C-6 should act as an electron trap and serve as a recombination site. Also, there is very good overlap between the TPD emission and the absorption of C-6. Furthermore, the conditions for nonradiative energy transfer from TPD to C-6 via the Förster mechanism are satisfied.

Figure 7 shows the EL emission spectra of a number of devices containing different emitters. The spectra are normalized for visual comparison. Typically, the brightest devices (at the same injection current levels) were obtained with the "green" emitters, such as C-6. The efficiencies of these unoptimized devices tend to decrease towards both the blue edge of the spectrum as well as towards the red. The EL emission curves were obtained, in the order of increasing wavelength, using the following emitters: On the above examples we have shown that adjusting the EL color can be achieved by simple doping with emitter molecules, many of which are known as laser dyes. It is therefore

	Emitter	Peak λ (nm)	Color
1	TPD	465	blue
2	Coumarin 153	486	blue-green
3	Coumarin 6	495	green
4	4-(Dicyanomethylene)-2-methyl-6(p-dimethyl-aminostyryl)-4-H-pyran	558	yellow-green
5	Sulforhodamine B	581	orange
6	Sulforhodamine 101	603	red

Table 1. Tuning of EL color by additives. In the first case, TPD (same amount as PVK in the layer) was the emitter; no other additive was present. In all other cases, TPD was absent. The weight ratio of Bu-PBD to PVK (or to a 50:50 PVK:TPD mixture such as in case 1) was always 1:2.

reasonable to expect that white light can be produced by adjusting the concentrations of various emitter combinations. For example, addition of Rhodamine 6G to the film containing equal amounts of PVK, TPD and Bu-PBD resulted in EL which contained both TPD and R 6G emissions, giving the emitted light a redish-white visual appearance. Even though R 6G is more easily reduced than Bu-PBD (-0.92V and -1.50V, respectively, vs. SCE) and therefore acts as electron trap, the oxidation potential (+1.1V vs SCE) is too high for the compound to be a hole trap. Consequently, R 6G is not an efficient recombination site. Furthermore, the conditions for Förster nonradiative energy transfer from TPD to R 6G is considerably less favorable than in the case of C 6, which allows for parallel emissions from both R 6G and TPD.

On the other hand, we have found that the injection current density or the applied voltage may affect the color of EL. We have observed this effect on a device which contained equal amounts of Sulforhodamine 101 (with peak fluorescence at 603 nm) and Coumarin 153 (486 nm) in PVK. For example, at low injection currents (J_i = 30 μA/cm^2), instead of the expected near white-green emission, the EL visually appears much more red than it does at higher injection currents (J_i = 4 mA/cm^2). Similarly, Coumarin 152 (peak fluorescence at 470nm) and Sulforhodamine 101 in PVK showed red EL at low injection current density of 70μA/cm^2, and the combination of red and blue at J_i = 3.5 mA/cm^2. The EL spectra of the latter at low and high injection current densities (controlled by the applied voltage) are shown in Fig. 8. One possible explanation for this effect is that excitons generated by recombination of carriers in Sulforhodamine 101 undergo the electric field assisted charge separation rather than radiative decay - a process analogous to fluorescence quenching by an electric field. Another possibility is that the capture cross section is carrier-velocity dependent.

Based on some of the above experimental observations one can suggest criteria for selection of emitter molecules. In order to exhibit EL, the injected electrons and holes must be trapped on an emitter molecule. This can be a compound which supports injection and transport of holes such as TPD in the above case, or a compound which supports injection and transport of electrons such as 8-hydroxyquinoline Al (1, 2), or a dye molecule such as Coumarine 6. The trapped electron resides in the LUMO and the hole in the HOMO of the emitter, thus producing an excited molecule equivalent to an exciton
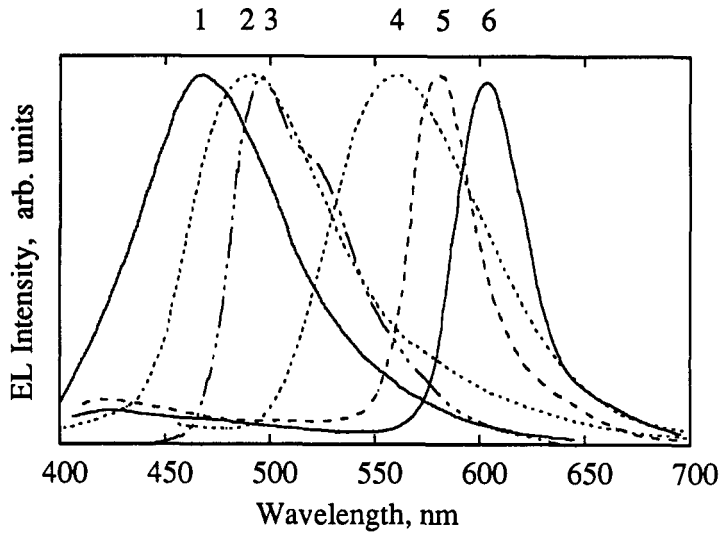
Fig. 7. EL from PVK doped with emitters from Table 1.

which would be produced by absorption of a photon. Radiative recombination of the carriers generates EL which is spectrally identical to fluorescence. One would wish that the internal electric field at this situation be minimal since the application of an electric field to (photo)excited molecules typically leads to separation of charges - a process which is desirable in photoconductors but is a loss process in EL devices. There is, of course, an opposite need for high electric fields to overcome injection barriers, especially for electrons. The necessity of trapping of holes and electrons in one molecule also suggests
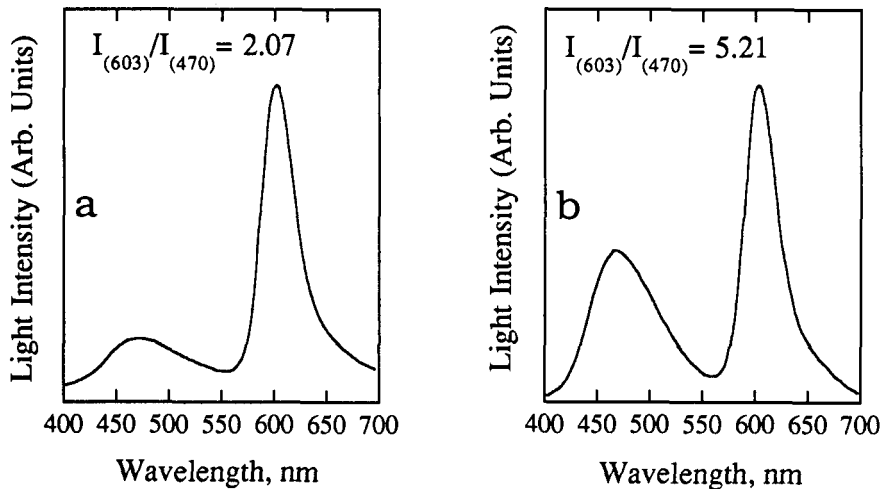

Fig. 8. Normalized EL spectra of the PVK/Bu-PBD (2:1) device doped with equal amounts of Coumarin 152 and Sulforhodamine 101 at (a) $J_i = 70 \mu A/cm^2$ and (b) $J_i = 3.5 mA/cm^2$.

that the emitter has lower or at least similar oxidation potential as the hole transport polymer, and should have higher or at least similar electron affinity as the electron transport molecule. This is illustrated in a simplistic scheme in Fig. 9. The requirement that the emitter just yields intense photoluminescence is not sufficient. Another requirement is that both reduction and oxidation steps are reversible, for reasons of stability. These criteria may be relaxed if energy transfer is an important process.

These preliminary data show that simple single-layer solvent-coated polymeric devices comprising charge transport moieties, compounds that facilitate electron injection and a trace of suitable emitter molecule produce EL which is comparable to that produced in other types of often more complex device architectures.
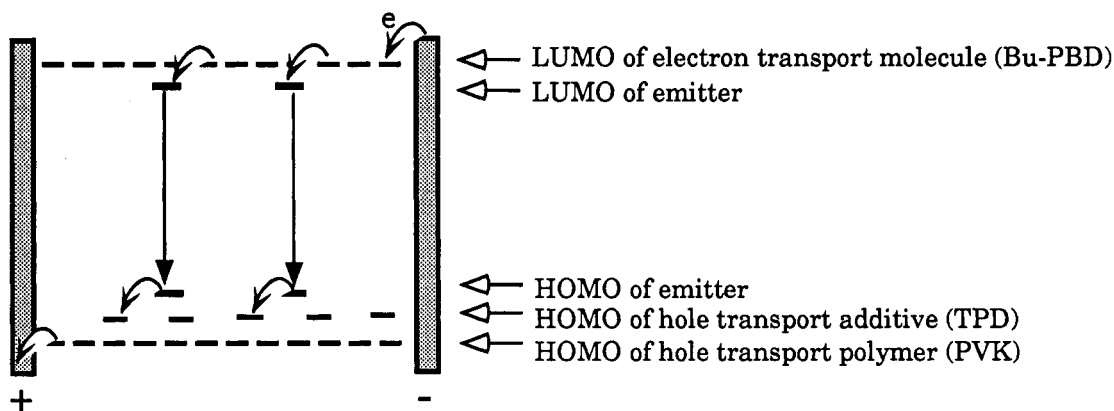
Fig. 9. *A diagram showing relative energy levels of the single-layer device.*

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