

Excitation mechanisms in dye-doped organic light-emitting devices

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In an organic light-emitting device with a polymeric matrix concurrently doped with two different dyes, the photoluminescence (PL) and electroluminescence (EL) spectra are observed to be very different, with both dyes emitting in PL and only one in EL at room temperature. A simple model based on charge trapping and thermal excitation is introduced to explain this observation. The EL spectral change of a device at 77 K is consistent with this model. In addition, using the same model, the strong dependence of the EL efficiency (but not PL) on the concentration of a single dye in an organic film can be understood. The materials used in this experiment are the polymer poly(9-vinylcarbazole) combined with electron transport molecules, and the dyes coumarin 47, coumarin 6, and Nile red. © 2001 American Institute of Physics. [DOI: 10.1063/1.1427746]

The concept of doping electroluminescent devices based on organic materials (OLED) to enhance the efficiency and to tune the emission color was first demonstrated by Tang *et al.*¹ In this experiment, a small number of molecules with very high fluorescence efficiency (dyes) were incorporated into the host material. Doping the device with several dopants is important, for example, to fabricate white emitting devices.^{2,3} Furthermore, using the method of patterned dye diffusion to locally change the emission color of the device, a second dye is introduced into a polymer film already doped with a first dye.⁴

In this letter, we show that the excitation mechanisms in photoluminescence (PL) and electroluminescence (EL) yield very different emission spectra when multiple dyes are present in the same location. A thermal excitation model explains the difference between these spectra. This model is then further applied to understand the rapid quenching of EL (but not PL) at high concentrations of a single dye in an OLED. In both the single and multiple dye case, the observed emission of a cooled device is consistent with the model.

Excitation of the dye can be accomplished by either energy transfer or charge transfer from the host to the dye. In the case of energy transfer, an exciton is formed at a host molecule, which is then transferred to the dye by either resonant coupling or by coherent charge exchange (Förster or Dexter transfer, respectively).⁵ For excitation by charge transfer, electrons and holes from the host are sequentially trapped by the dye, resulting in exciton formation on the dye and then photon emission due to exciton decay.

The materials used in this experiment are the polymer poly(9-vinylcarbazole) (PVK; $M_w \sim 1\,100\,000$ g/mole, obtained from Aldrich and used as-received) as a hole transport material and matrix forming host and 2-(4-biphenyl)-5-(4-*tert*-butyl-phenyl)-1,3,4-oxadiazole (PBD, also obtained from Aldrich and used as-received) as electron transport mol-

ecule. Furthermore, the dyes coumarin 47 (C47, emission peak at ~ 440 nm, Lambda Physik), coumarin 6 (C6, emission peak at ~ 505 nm, Lambda Physik), and Nile red (emission peak at ~ 600 nm, Aldrich) were used. Devices were made with PVK (100 mg), PBD (40 mg), and varying amounts of dye(s) dissolved in 7 ml chlorobenzene.⁶ The solution was deposited by spin coating on ITO-coated glass substrates (2000 rpm) resulting in an 80 nm thick film. A Mg:Ag (10:1) cathode was thermally evaporated (100 nm).

Figure 1 shows the EL and PL spectrum at room temperature of a device with 0.3 mg C47 (blue) and 0.3 mg Nile red added to the PVK/PBD/chlorobenzene solution. Whereas the EL spectrum is dominated by the emission from the Nile red, the PL spectrum shows two distinct peaks, one from each of the dyes. To first order, the EL spectrum does not depend on the current density over a range from 5 to 500 mA/cm². Qualitatively similar results were seen with C6 and Nile red mixtures, where again the EL occurs almost exclusively from the lower energy dye.

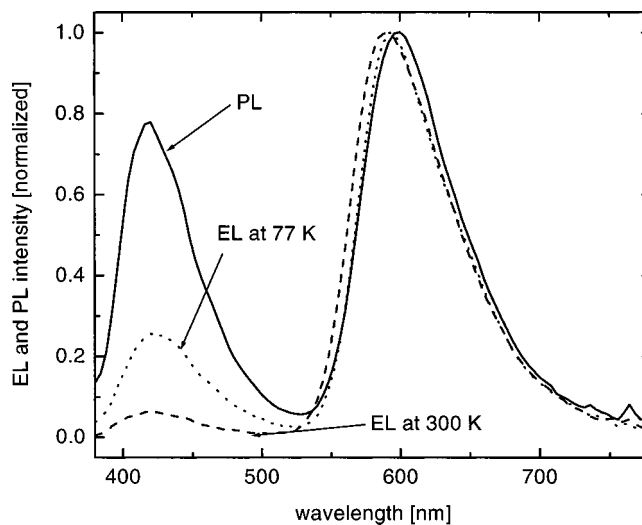


FIG. 1. Normalized photoluminescence spectrum (solid line), electroluminescence spectrum at room temperature (dashed line), and electroluminescence spectrum at 77 K (dotted line) of a PVK/PBD device containing the dyes C47 and Nile red.

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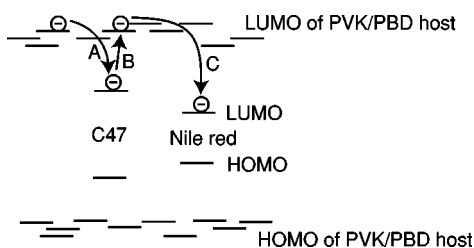


FIG. 2. Schematic energy level diagram showing electron capture (process A and C) and thermal reemission (process B) in a PVK device containing C47 and Nile red.

The photoluminescence process begins with the creation of singlet excitons in the host. That the emission occurs from both dyes but not from PVK implies that (i) the excitons created on the PVK are transferred to the dye much faster than the radiative lifetime of an exciton on PVK, and (ii) that once captured on the dye, no exchange of excitons between the dyes occurs (which would otherwise lead to emission from the lowest energy dye only). Excitons on the dyes presumably do not interact because either they are too far apart or the spectral overlap for Förster or Dexter is insufficient. Thus excitons initially captured by a dye (by Förster or Dexter transfer) leads to PL from this dye.⁷

That the EL spectrum is very different from the PL spectrum means that singlet excitons are not created in EL on the host, implying that the sequential capture of electrons and holes (and exciton formation followed by light emission) occurs directly on the dye. Similar observations have been reported.⁸ We hypothesize that the lifetime of the first captured electron in a LUMO state (or captured hole in a HOMO state) is long compared to the exciton lifetime because these carriers cannot recombine until a singlet exciton is formed, i.e., an electron and a hole of opposite spin are captured by the same molecule. Therefore the initially trapped carrier could be thermally reemitted back to the host (Fig. 2, process B), and recaptured by either dye after transport through the host. The release of carriers from the dye states will be slowest for dye states with the largest energy difference to the relevant host HOMO/LUMO levels. Therefore the accumulation of carriers in these deepest states will occur, leading to the eventual capture of the opposite carrier, and exciton formation followed by light emission. Assuming a level alignment such that the dye with the lowest exciton energy has its HOMO/LUMO levels farthest from the host level (see Fig. 2), light emission will preferably occur from the dye with the longest wavelength. Therefore, in EL, nearly all emission was observed from Nile red. (Figure 2 arbitrarily assumes that the initially trapped carrier is an electron.)

In support of this model, the EL emission from C47 increased significantly when the device was cooled (Fig. 1). This implies that carriers, which were reemitted from a C47 level (process B in Fig. 2) at 300 K to be retrapped by a Nile red state (process C), could not escape from the C47 level at lower temperatures. This, in turn, increases the probability that a singlet exciton can be formed on a C47 molecule, which explains the increased emission from this dye at lower temperatures.

A simple extension of this model allows one to explain why the EL efficiency depends much more on the dye con-

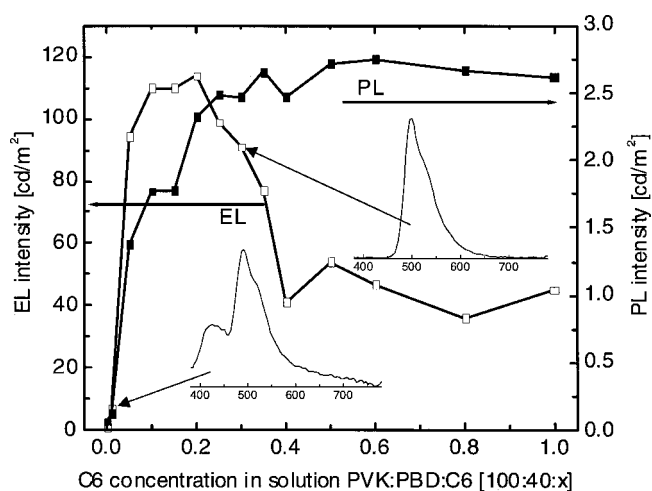


FIG. 3. Electroluminescence (open symbols at 50 mA/cm²) and photoluminescence (solid symbols) intensities as a function of C6 concentration in a PVK:PBD:C6 (100 mg:40 mg:x) device. The EL spectra for C6 concentrations of 0.01 and 0.3 mg are shown in the inset.

centration than the PL efficiency in devices with only a single dye. Figure 3 shows the EL intensity at current density of 50 mA/cm² as a function of C6 concentration in a PVK/PBD device (PVK:PBD:C6=100 mg:40 mg:x by weight). The luminance intensity increases with dye concentration, reaches a maximum and decreases sharply again for higher dye concentrations. Similar results were obtained in devices with either Nile red or C47. The initial rise is likely because more excitons can be formed on the dye due to the increased number of dye molecules. The two EL spectra at dye concentration of 0.01 mg C6 and 0.3 mg C6 shown in the inset illustrate this observation. Along with the EL intensity of the device, the PL intensity of the polymer film under constant illumination (254 nm) is depicted. The PL intensity also shows the initial increase due to the fact that more excitons are able to transfer to the dye. However, in contrast to the EL intensity, the PL intensity decreases only slightly at higher dye concentrations. The effect of EL luminescence quenching at higher dye concentrations has already been reported.⁸⁻¹³

It is well known that dyes aggregate and form excimer states at high dye concentrations. In this case, the exciton is delocalized over several molecules due to the increased intermolecular interaction. These states decay with a much smaller radiative efficiency, an effect referred to as “dye self-quenching.” In addition, the emission spectrum is redshifted compared to the emission of a single dye molecule. However, if this were the only effect at high dye concentrations, the EL and PL would be reduced similarly, which is not observed.

This difference in EL and PL efficiency at high dye concentrations may be explained using the same “two-dye” model (Fig. 2), but with levels of an isolated dye (efficient light emitters) and dye-dye complexes (excimers, which are inefficient light emitters) representing the two separate sets of levels (Fig. 4). At high dye concentrations, in PL singlet excitons are captured and immediately decay both on the C6 dye and on the C6 excimer, which explains the slight reduction of PL intensity. As previously shown, the main excitation mechanism in EL is sequential charge capture. Anal-

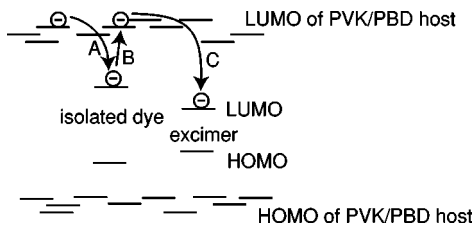


FIG. 4. Schematic energy level diagram showing electron capture (process A and C) and thermal reemission (process B) in a PVK device at high dye concentration with isolated dye molecules and excimer complexes.

gous to the argument that the dye with the smallest band gap dominates the EL spectrum, most of the excitons will in this case form at an excimer site with a low radiative efficiency, even if there are only a relatively small number of them. Due to this mechanism, the EL efficiency decays faster than the PL efficiency at high dye concentrations. The EL spectra of devices with various C6 concentrations immersed in liquid nitrogen (9 mA/cm²) (as shown in Fig. 5) supports this argu-

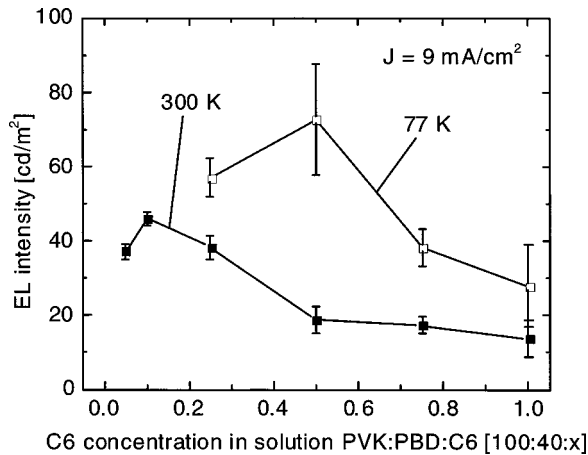


FIG. 5. Electroluminescence intensity of a PVK:PBD:C6 device as a function of C6 concentration at room temperature (solid squares) and at 77 K (open squares).

ment. Due to reduced reemission and thus less chance of excited carriers reaching the excimer, the EL intensity decay was much slower for the cooled device at high dye concentrations.

In conclusion, we have demonstrated that sequential capture of carriers into dye states is the prevalent EL excitation mechanism in dye-doped PVK devices. Unlike captured singlet excitons in PL, the captured carriers have enough time to be reemitted to the host level to be recaptured in another state. This leads to preferred emission from the dye with the longest wavelength when multiple dyes are present. Combined with the formation of excimer states, this concept also explains the surprisingly strong quenching of EL (but not PL) at high dye concentrations.

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- ¹C. W. Tang, S. A. VanSlyke, and C. H. Chen, *J. Appl. Phys.* **65**, 3610 (1989).
- ²J. Kido, H. Shionoya, and K. Nagai, *Appl. Phys. Lett.* **67**, 2281 (1995).
- ³T.-W. Lee, O. O. Park, H. N. Cho, J.-M. Hong, C. Y. Kim, and Y. C. Kim, *Synth. Met.* **122**, 437 (2001).
- ⁴F. Pschenitzka and J. C. Sturm, *Proc. SPIE* **4105**, 59 (2001).
- ⁵M. Pope and C. E. Swenberg, *Electronic Processes in Organic Crystals and Polymers*, 2nd ed. (Oxford University Press, New York, 1999).
- ⁶C. C. Wu, J. C. Sturm, R. A. Register, and M. E. Thompson, *Appl. Phys. Lett.* **69**, 3117 (1996).
- ⁷D. V. Roberts, B. P. Wittmershaus, Y.-Z. Zhang, S. Swan, and M. P. Klinosky, *J. Lumin.* **79**, 225 (1998).
- ⁸A. A. Shoustikov, Y. You, and M. E. Thompson, *IEEE J. Sel. Top. Quantum Electron.* **4**, 3 (1998).
- ⁹G. Yu, H. Nishino, A. J. Heeger, T.-A. Chen, and R. D. Rieke, *Synth. Met.* **72**, 249 (1995).
- ¹⁰J. Kalinowski, P. D. Marco, V. Fattori, L. Giulietti, and M. Cocchi, *J. Appl. Phys.* **83**, 4242 (1998).
- ¹¹M. Uchida, C. Adachi, T. Koyama, and Y. Taniguchi, *J. Appl. Phys.* **86**, 1680 (1999).
- ¹²S. Tasch, E. J. W. List, C. Hochfilzer, G. Leising, P. Schlichting, U. Rohr, Y. Geerts, U. Scherf, and K. Müllen, *Phys. Rev. B* **56**, 4479 (1997).
- ¹³H. Murata, C. D. Merritt, and Z. H. Kafafi, *IEEE J. Sel. Top. Quantum Electron.* **4**, 119 (1998).