

RAPID COMMUNICATION

Influence of Excimer Behavior on Photoluminescence and Electroluminescence of a Novel Conjugated Molecule Doped in Polymer

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Influence of excimer formation on photoluminescence and electroluminescence of a novel conjugated molecule, 1-(9-anthrylethynyl)-4-chloromethyl-2,5-dimethoxybenzene (ACDB), doped in polystyrene was investigated. The monomer emission decreased and the excimer emission increased when the concentration of ACDB in the doped film was increased for photoluminescence. This resulted from the energy migration to the trapping sites of excimer. The electroluminescent device with lower concentration of ACDB in the emitting layer exhibited only the exciton emission independent of the applied voltage. The device with higher concentration exhibits exciton emission at high drive voltages but excimer emission at low drive voltages. The electric field strength dependent electroluminescent behavior with higher concentration of ACDB was explained according to the fluorescence quenching effects caused by the field-enhanced thermal dissociation of excimer. Doping polymer is helpful in suppressing the formation of excimer. © 2000 Academic Press

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Electroluminescence (EL) devices based on organic thin layers have attracted much interest because of their possible application as large-area light-emitting displays (1–3). These devices operate by the injection of electrons and holes from negative and positive electrodes, respectively. Electrons and holes capture one another within the film and form neutral bound excited states (termed excitons). The exciton recom-

bination results in light emission. Besides the exciton emission from π^* to π , excimer emission can be observed sometimes due to the interaction between the small molecules or chromophores in polymer chain. Sometimes it is the only fluorescence (4–8). Formation of excimer is a key drawback because the color stability is an important basic requirement for the production of these devices. Such a problem could be partly solved by changing the molecular structure (9). A more simple method is using the molecularly doped polymer (MDP). MDP was first used in the fabrication of an EL device by Kido (10). It is a binary solid solution of emitting molecules molecularly dispersed in an inert, inactive polymer. By selecting the polymer, the mechanical properties of the film can be improved and this system may achieve an improvement of structural stability. In this communication, we report the excimer process in the single-layer organic EL device using molecularly doped polymer. The results indicate that MDP is a good method to suppress the excimer formation.

MDP used in this study is the molecular dispersion of a new conjugated molecule, 1-(9-anthrylethynyl)-4-chloromethyl-2,5-dimethoxybenzene (ACDB), dispersed in polystyrene (PS). ACDB was synthesized in our laboratory according to the method given in the literature (11) with a little modification. PS is an optic-electric inert material purchased from Aldrich.

Figure 1 shows the molecular structures of the materials used in this study. The EL device was a one-layer structure with doped PS film sandwiched between electrodes. The weight percentage of ACDB in the emitting layer was varied from 50 to 100%. A chloroform solution containing proper

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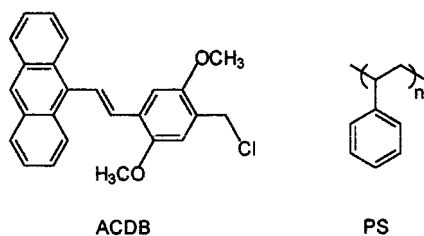


FIG. 1. Molecular structures of materials used (ACDB and PS).

amounts of ACDB and PS was spin coated on the indium-tin oxide (ITO) coated glass substrate at a rate of 2500 r/min, giving a homogeneous film. The thickness of the emitting layer of the device was controlled to be about 100 nm. The top aluminum electrode was prepared by thermal evaporation under 2×10^{-5} Pa. The PL film was made by the same method on quartz substrate. The photoluminescence and electroluminescence were measured with a Shimadzu RF-5000 spectrofluorophotometer.

Figure 2 presents the photoluminescence spectra of ACDB in chloroform solution (1×10^{-5} M) and in the doped film at room temperature. The solution exhibits only one emission band at 450 nm. The film with a 70% ACDB has two emission bands at 470 and 550 nm. As the concentration of ACDB in the film increased and the distance between ACDB decreased, the emission band at 470 nm decreased and the emission band at 550 nm increased. Figure 3 shows the ratios of emission intensity at shorter wavelength to that at longer wavelength, I_S/I_L , as a function of the concentration of ACDB in the film. I_S/I_L decreased when the concentration of ACDB increased. Above 95%

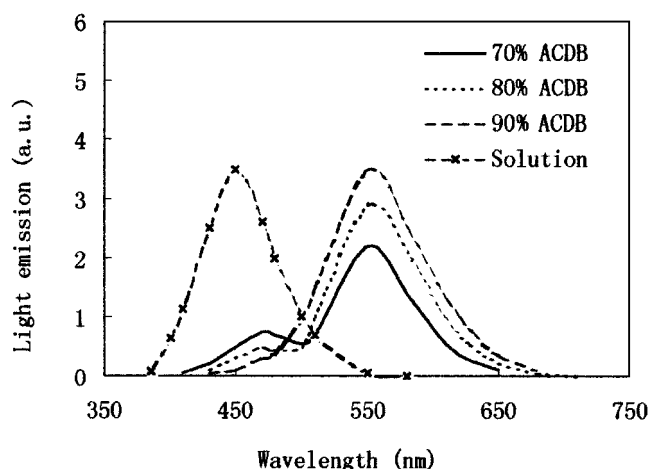


FIG. 2. Photoluminescent spectra of ACDB in solution (chloroform) and in doped polystyrene film with different weight concentrations of ACDB; excitation wavelength 370 nm.

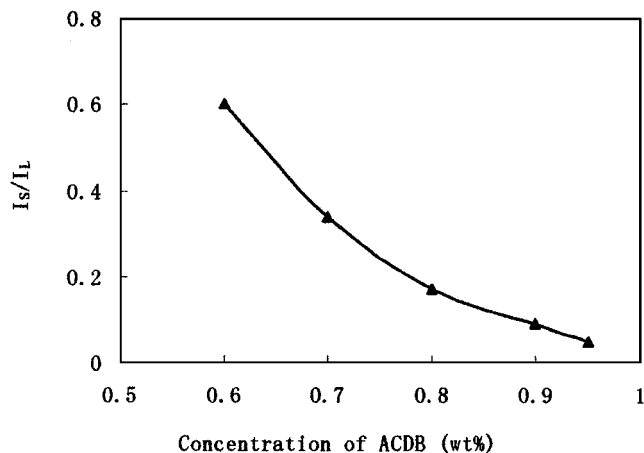


FIG. 3. Molecular fluorescence/excimer ratios as a function of ACDB concentration for films at room temperature; excitation wavelength 370 nm.

ACDB, no emission band at short wavelength was observed in the spectra of the film.

Figure 4 shows the EL spectra of ACDB. When the concentration of ACDB was 50%, the device exhibited a blue emission with a peak at 470 nm independent of the applied voltage (Fig. 4d). But when the concentration of ACDB was 95%, the EL spectra varied on different applied voltages. When the applied voltage was 15 V, the EL spectrum exhibited a green emission at 550 nm (Fig. 4a). When the applied voltage was increased to 20 V, the EL spectrum had two peaks at 470 and 550 nm (Fig. 4b). At a higher voltage 25 V, the spectrum exhibited a blue emission at 470 nm (Fig. 4c). In other words, the peak shifted toward the shorter wavelength range upon increasing applied voltage.

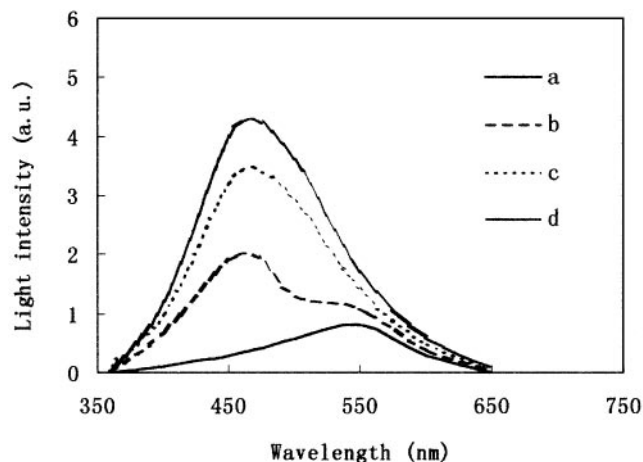


FIG. 4. Electroluminescent spectra of LEDs upon different applied voltage (a, ACDB 95%, 15 V; b, ACDB 95%, 20 V; c, ACDB 95%, 25 V; d, 50% ACDB).

This phenomenon has not been found before for organic-emitting diodes (OLEDs) with only one emitting molecule in the emitting layer.

Both photoluminescence and electroluminescence have two emission bands. The band at the shorter wavelength can be assigned to molecular fluorescence arising from a nonassociated excited molecule by comparing the PL of solution and that of film. The band at the longer wavelength can be assigned to an excimer arising from an excited singlet state molecule with another molecule in the ground state. The possibility of ground state aggregate emission can be excluded by comparing the absorption spectra of the doped films with different ratios of ACDB. Ground state aggregates represent new molecular species with an absorption spectrum different from that of the corresponding monomers. In contrast, because excimers only exist in the excited state, their absorption spectrum is the same as that of the monomers (12). In our experiments, the absorption spectra of films with different percentages of ACDB show no difference except a little red shift.

According to the general picture of excimer formation (13), excitation energy migrates through small molecules or the chromophores of a polymer chain until a site favorable to excimer formation is encountered. When no additional photophysical mechanisms are involved other than monomer and excimer emission, an increase in film concentration leads to an increase in monomer emission rather than in excimer emission. In our experiment, however, I_s/I_L decreased when the concentration was increased. This implies that the singlet energy migration is a possibility to be considered, since the associated species is already in a geometry suitable for pair formation, and it is generally accepted that excimers can act as traps for energy migration due to their lower energy level. As singlet energy trapping sites, the excimer is highly efficient for photoluminescence. It acts as a means of depleting singlet energy in the blend. The fact that excimer fluorescence becomes the main emission in the film when the concentration of ACDB was increased favors this hypothesis.

In the spectra for the device with a higher concentration of ACDB, a decrease in excimer emission is observed with increasing applied voltage. These electric-field-induced changes in the spectral distribution of the EL emission can be understood in terms of the fluorescence quenching effects attributed to the field-enhanced thermal dissociation of trapped charge-transfer excitons (excimer) (14). Excimer states can be more effectively quenched by external field than well-localized excitonic states. The results provide evidence that dopant molecules do not form exciton traps in the EL device as is the case in PL film.

For the device with a lower concentration of ACDB, only exciton emission was observed with no influence from the applied voltage. Excimer emission was thoroughly suppressed. This is because the ACDB molecule was dispersed

in PS matrix and could not associate for the formation of excimer under applied voltage. Since the color stability is an important basic requirement for the production of EL devices, the troublesome formation of excimers should be completely avoided. The introduction of small amounts inert polymer such as PS into the emitting layer provides a good selection.

In a summary, the differences in optical and electrical characteristics of molecularly doped polymer single-layer organic electroluminescent devices have been discussed. The monomer emission decreased and the excimer emission increased when the concentration of ACDB in the doped film was increased for photoluminescence. Energy migration existed in the process because excimer can act as trap sites due to its lower energy level. For EL devices with high concentrations of ACDB, the emission band shifted from the long-wavelength excimer emission to the short-wavelength exciton emission upon the increase in the applied voltage. These electric-field-induced changes in the spectral distribution of the EL emission can be attributed to the fluorescence quenching effects caused by the field-enhanced thermal dissociation of excimer. For EL devices with low concentrations of ACDB, the spectra exhibited only the exciton emission independent of the applied voltage. Doping polymer is helpful in suppressing the formation of the excimer.

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