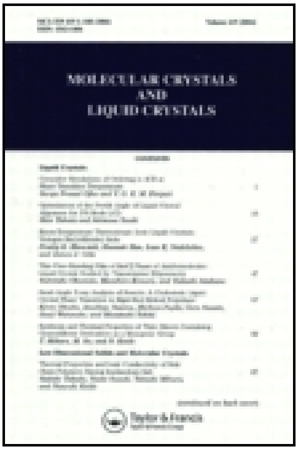

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Electronic Excitation Energy Transfer in a Novel Organic Electroluminescent Material

A. P. Pivovarov [a], M. G. Kaplunov [a], O. N. Efimov [a], I. K. Yakushchenko [a] & M. Yu. Belov [a]

[a] Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow Region, 142432, Russia

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Electronic Excitation Energy Transfer in a Novel Organic Electroluminescent Material

A.P. PIVOVAROV, M.G. KAPLUNOV, O.N. EFIMOV,
I.K. YAKUSHCHENKO and M. YU. BELOV

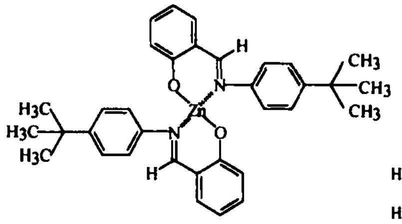
*Institute of Problems of Chemical Physics, Russian Academy of Sciences,
Chernogolovka, Moscow Region, 142432, Russia*

A new red light-emitting electroluminescent material of the dopant-host scheme is reported. A novel green light-emitting metal complex bis-(2-oxybenzylidene-4-tert-butylaniline)zinc(II), $Zn(OBBA)_2$, is used as a host material and Nile Red (NR) is used as a dopant. Evidences of the effective electronic excitation energy transfer from host to guest molecules are found. Exciton diffusion and single-step transfer are discussed as possible transfer mechanisms; the former process is considered to prevail in this system.

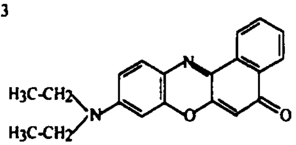
Keywords: luminescence; electroluminescence; energy transfer

INTRODUCTION

Electroluminescent devices comprising an emitting layer consisting of a host material doped with a small number of fluorescent molecules offer a simple means of producing efficient light emitters with a wide range of colors [1]. Some devices of red, green and blue colors based on Alq and distyrylarylene derivatives as a host materials were demonstrated [1-3]. In the present work, we report a new red light-emitting device of the dopant-host scheme. A novel green light-emitting metal complex bis-(2-oxybenzylidene-4-*tert*-butylaniline)zinc(II), $Zn(OBBA)_2$, is used as a host material and Nile Red (NR) is used as a dopant. We have



$Zn(OBBA)_2$



Nile Red

studied absorption, photoluminescence and luminescence excitation spectra of the films of $Zn(OBBA)_2$ and $Zn(OBBA)_2$ doped with Nile Red and found strong evidences of the effective electronic excitation energy transfer from host $Zn(OBBA)_2$ molecules to guest molecules of NR. We have also studied electroluminescent properties of this system and discussed possible mechanisms of the energy transfer in this system.

EXPERIMENTAL

$Zn(OBBA)_2$ was synthesized as described elsewhere [4]. NR was a commercial product (Aldrich). Films of $Zn(OBBA)_2$ and $Zn(OBBA)_2$ + NR were prepared by spin casting from benzene solutions. Concentrations of NR were determined from absorption spectra. Quantum yields of films fluorescence were determined relative to that of anthracene films by the method described in reference [5].

Electroluminescence properties were studied in the standard four-layered structure ITO/PTA/EML/Mg:Ag where ITO is the transparent anode of indium-tin oxide, PTA is the hole transporting layer of triphenylamine oligomers [6], EML is the emitting layer of doped with NR or undoped $Zn(OBBA)_2$ film and Mg:Ag is the cathode.

RESULTS AND DISCUSSION

Figure 1 shows the absorption, photoluminescence and photoluminescence excitation spectra of the $Zn(OBBA)_2$ film and of the doped $Zn(OBBA)_2$ film containing 0.001 mole NR / mole $Zn(OBBA)_2$. The absorption spectrum of the $Zn(OBBA)_2$ film contains three bands 410,

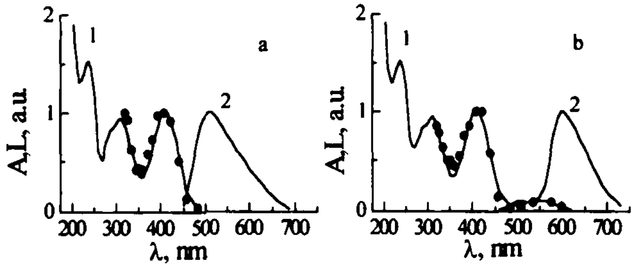


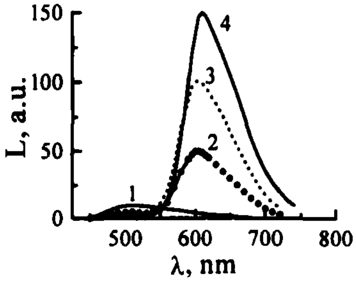
FIGURE 1 Spectra of the films of $Zn(OBBA)_2$: a - pure, b - doped with 0.1 mole % NR; 1 - absorption, 2 - fluorescence (exciting line 406 nm), circles - fluorescence excitation spectra.

311 and 235 nm. The fluorescence spectrum of the $Zn(OBBA)_2$ film exhibits a wide structureless band with a maximum at 510 nm and half-width 115 nm. The excitation spectrum of the film (i.e. the dependence of the integrated fluorescence intensity on the excitation wavelength) practically coincides with the absorption spectrum. This is an evidence of the fact that the fluorescence band is due to $Zn(OBBA)_2$ molecules and not to any impurity. The quantum yield of the film fluorescence is about 0.07±0.01 independently on excitation wavelength.

The absorption spectrum of the doped $Zn(OBBA)_2$+NR film coincides with that of pure $Zn(OBBA)_2$ film at wavelengths shorter than 500 nm. A weak additional band at 552 nm appears in the spectrum of the doped film due to absorption of NR molecules. The fluorescence spectrum of the doped film exhibits two bands: a weak band at 510 nm due to $Zn(OBBA)_2$ molecules and an intensive band with a maximum at 600 nm and half-width 84 nm due to NR molecules. At excitation wavelengths longer than 500 nm only the 600 nm band is observed. In the region of exciting wavelengths of 300-500 nm, the excitation spectrum of the doped film practically coincides with its absorption spectrum, i.e. with the absorption spectrum of $Zn(OBBA)_2$. The quantum yield of the red fluorescence at 600 nm is about 1 independently on excitation wavelength. This is an evidence of an effective non-radiative transfer of electronic excitation energy from host to guest molecules.

Electroluminescent device with the emitting layer of pure $Zn(OBBA)_2$ film emits green light with emission threshold about 5-6 V. Brightness is proportional to current and attains 350 cd/m^2 at 12.5 V and current density 2.5 mA/cm^2. Electroluminescent device with the emitting layer of doped Zn(OBBA)$_2$+NR film emits red light with brightness proportional to current giving 20 cd/m^2 at 19.5 V and current density 18 mA/cm^2.

Conclusions about the mechanism of the process of energy transfer can be drawn from its concentration dependence. Figure 2 shows the fluorescence spectra of the doped Zn(OBBA)$_2$+NR films for various concentrations of NR. Rising of the NR concentration leads to lowering of green fluorescence of Zn(OBBA)$_2$ matrix at 510 nm and to growth of red fluorescence of NR at 600 nm. Small changes of the spectral shape of the fluorescence band are due to reabsorption of radiation by NR molecules. The intensity of NR red fluorescence reaches its maximum value at molar relation about 0.01 mole NR / mole Zn(OBBA)$_2$ and falls at greater molar relations due to concentration quenching. The intensity of matrix green fluorescence continues to lower after this concentration.



FGURE 2 Fluorescence spectra of Zn(OBBA)$_2$ films:
1 - undoped, 2,3 and 4 - doped with 0.08, 0.14 and 0.26 mole% NR.

Figure 3 (filled circles) shows the concentration dependence of the quenching factor Q for green fluorescence of Zn(OBBA)$_2$ matrix:

$$Q = (L_0 - L)/L \tag{1}$$

where L_0 and L are the green fluorescence intensity for pure and doped films. The concentration dependence of Q is linear in all the range of concentrations studied up to 0.02 mole NR / mole Zn(OBBA)$_2$. Such

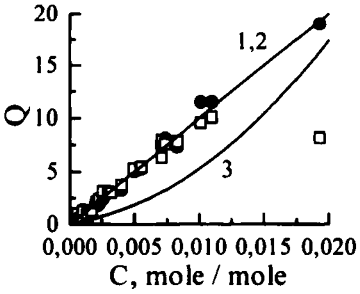


FIGURE 3 Concentration dependence of the quenching factor: 1,2 experimental values computed from the equations (1) (filled circles) and (3) (open squares); 3 - calculated from the dipole-dipole theory.

linear dependence is characteristic for the exciton diffusion mechanism of energy transfer [7,8]. It is assumed that the molecular excited state is propagated by random jumps between neighboring molecules, and each exciton that meets a guest molecule is trapped. According to this model, the quenching factor depends on concentration as

$$Q = 0.66Nc \tag{2}$$

where N is the number of jumps in the pure matrix during the lifetime of the excited state, c is the concentration of guest molecules (mole guest / mole host) and the factor 0.66 takes into account the probability of the exciton to return to its starting point [7]. The quenching factor can also be determined from the intensity of guest fluorescence: L_G:

$$Q = (L_G/L)(\eta_o/\eta_G) \tag{3}$$

where η_o is the quantum yield of the pure host matrix and η_G is the quantum yield of the guest molecules in the host matrix at direct excitation [7]. Figure 3 (open squares) shows the concentration dependence of Q obtained from the NR fluorescence intensity according to the equation (3) with $\eta_o/\eta_G = 0.07\pm0.01$. It is also linear like that obtained from equation (1) except the region of large NR concentrations were concentration quenching of NR takes place.

We have also discussed the alternative single-step mechanism of long - range dipole -dipole transfer treated by Förster [9]. For this mechanism, the quenching factor is expressed by [7,9]

$$Q = A/(1-A) \qquad (4)$$

Here $A = 2q\exp(q^2)\int_q^{\infty}\exp(-x^2)dx$ and q is the dimensionless parameter proportional to concentration: $q = (0.05/n^2)(\eta_0\alpha)^{1/2}c$ were n is the refraction index and α is the overlap integral of donor fluorescence and acceptor absorption $\alpha = \int f(\nu)\sigma(\nu)\nu^{-4}d\nu$. $f(\nu)$ is the donor's fluorescence distribution (relative quantum efficiency normalized to one on a wavenumber scale: $\int f(\nu)d\nu = 1$) and $\sigma(\nu)$ is the extinction coefficient of the acceptor (cm^2/molecule).

Figure 3 shows the theoretical curve for Q computed from the dipole-dipole theory according to equation (4) using the experimental values $n = 1.1$, $\eta_0 = 0.07$ and $\alpha = 7.5\times10^{-34}$ cm^6. It can be seen from the figure that the single-step dipole-dipole theory gives essentially nonlinear dependence of Q on concentration which is not consistent with the linear experimental dependence.

Thus, from our results it may be concluded that exciton diffusion predominates in this system. From the equation (2) and the experimental data of figure 3, the number of steps during the lifetime is calculated to be $N = 1.5\times10^3$. This is somewhat lower than the reported value 4.1×10^4 for the solid solution of perylene in N-isopropylcarbazole [7] which may due to at least partially amorphous structure of $Zn(OBBA)_2$ films in contrast with the crystalline system [7].

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