BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (12), 3737—3738 (1979)

# The Singlet-excitation-energy Migration in an Amorphous-state Film of 1,3-Di(9-carbazolyl)propane

Akira ITAYA,* Ken-ichi OKAMOTO, and Shigekazu KUSABAYASHI

*Department of Chemical Engineering, Faculty of Engineering, Yamaguchi University, Tokiwadai, Ube 755*

(Received May 1, 1979)

**Synopsis.** The singlet-excitation-energy migration in an amorphous film of 1,3-di(9-carbazolyl)propane(DCzP(a)) was studied by means of a fluorescene-quenching experiment. The results were compared with those of amorphous poly(9-vinylcarbazole)(PVCz) and poly[2-(9-carbazolyl)ethyl vinyl ether](PCzEVE) films. The numbers of carbazolyl chromophores covered by a singlet exciton during the lifetime were in the following order: DCzP(a)>PCzEVE>PVCz.

1,3-Di(9-carbazolyl)propane (DCzP) is known as a dimeric model compound of poly(9-vinylcarbazole) (PVCz), which has received considerable interest in recent years in connection with the highly photoconductive vinyl polymers. DCzP forms an amorphous state by the fast evaporation of the solvent.[1] It is important to investigate singlet exciton migration in a DCzP(a) film and to compare it with that in a PVCz film, because the efficiency of the singlet exciton migration in a vinyl polymer is known as one of the factors determining whether or not the polymer has a large photoconductivity.

A few investigations have been carried out to ascertain how the efficiency of the singlet exciton migration changes when going from a crystalline to an amorphous state.[2] However, a comparison of the optical properties of an amorphous film of a model compound with the optical properties of an amorphous film of a corresponding vinyl polymer has not hitherto been performed.

In a previous paper,[1] the absorption and fluorescence spectra of a DCzP(a) film were investigated and compared with those of polycrystalline DCzP(DCzP(c)) and amorphous PVCz films. In the present work, the migration of the singlet excitation energy in a DCzP(a) film has been investigated in comparison with that of an amorphous PVCz film.

## Experimental

The model compound (DCzP) and polymers (PVCz and poly[2-(9-carbazolyl)ethyl vinyl ether](PCzEVE)) were the same as those used before.[1,3] The dimethyl terephthalate (DMTP)and perylene were recrystallized twice from benzene and *p*-bis(trichloromethyl)benzene (TCB) from hexane. Subsequently, they were sublimed *in vacuo*. The DCzP(a) and polymer films were cast onto quartz or Pyrex-glass plates from a benzene solution. The fluorescence spectra were observed by front-surface excitation with the apparatus described in a previous paper.[4]

## Results and Discussion

In a previous paper[1] we reported that the fluorescence spectrum of a DCzP(a) film seems to be composed of three components, monomer-like, second excimer ($\tilde{\nu}_{\max}$: *ca.* 26700 cm$^{-1}$), and sandwich-like excimer ($\tilde{\nu}_{\max}$: 23900 cm$^{-1}$) fluorescences, while a DCzP(c) film seems to show the monomer-like and second excimer fluorescences.

The presence of the second excimer and monomer fluorescences was supported also by the investigation of the temperature dependence of the fluorescence spectrum of a DCzP(a) film. As is shown in Fig. 1, the intensity of the second excimer fluorescence of a PVCz film increased with a decrease in the temperature, showing that the second excimer site is a shallow trap and acts more effectively as a trap at low temperatures. This is consistent with the results obtained by the investigation of the excitation-energy-migration.[4] The temperature dependence of the fluorescence spectrum of a DCzP(a) film was similar to that of a PVCz film, as is shown in Fig. 2. In the case of a DCzP(a) film, the structure band in the shorter-wavelength region, which appears with an increase in the temperature, is the monomer fluorescence, which increases with a decrease in the concentration of the trap sites.

By the doping of perylene, TCB, and DMTP, the host fluorescence decreased. The fluorescence spectra of DCzP(a) films doped with various concentrations of DMTP are shown in Fig. 3. The fluorescence in the longer-wavelength region ($\tilde{\nu}_{\max}$: 21620 cm$^{-1}$) is attributable to the exciplex formed between DMTP and an excited Cz chromophore. The dipole-dipole resonance cannot be responsible for the energy transfer to TCB and DMTP, because these guest molecules have no absorption in the wavelength region where the fluores-

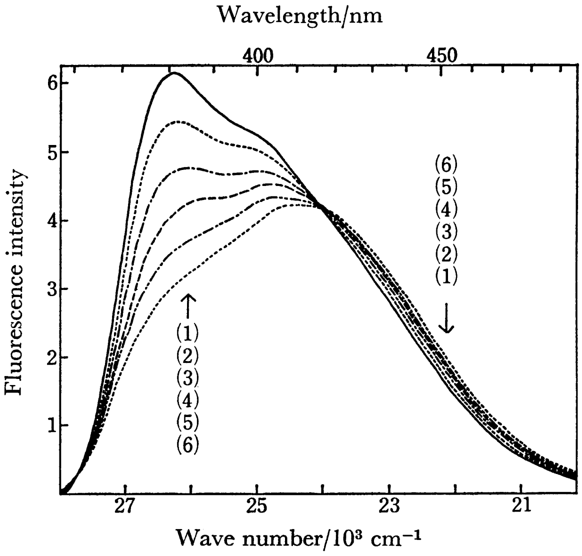

Fig. 1. Temperature dependence of the fluorescence spectra of a PVCz film. Excitation wavelength; 330 nm. (1) 121 K, (2) 140 K, (3) 163 K, (4) 187 K, (5) 210 K, and (6) 234 K.

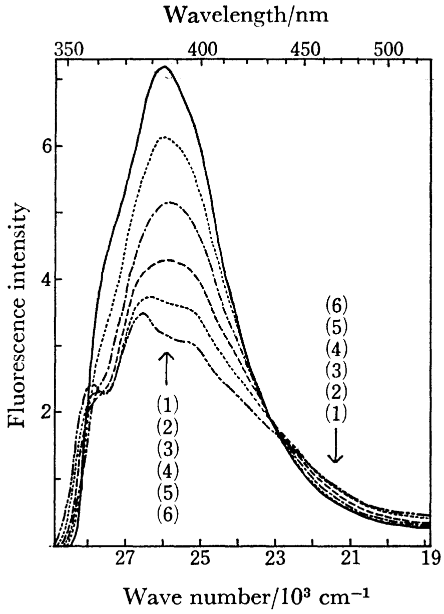

Fig. 2. Temperature dependence of the fluorescence spectra of a DCzP(a) film. Excitation wavelength; 330 nm. (1) 129 K, (2) 144 K, (3) 163 K, (4) 192 K, (5) 213 K, and (6) 236 K.

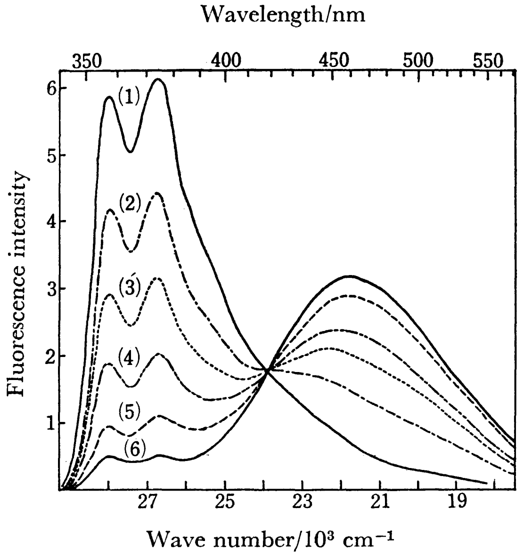

Fig. 3. Fluorescence spectra of DCzP(a) films doped with DMTP at room temperature. Excitation wavelength; 335 nm. DMTP concentration; (1) 0, (2) $3.54\times10^{-4}$, (3) $8.85\times10^{-4}$, (4) $1.80\times10^{-3}$, (5) $3.02\times10^{-3}$, and (6) $8.85\times10^{-3}$ (mol/mol basic unit).

cense of the host film is observed. Therefore, the random-hopping model of monomer-exciton migration, in which both the intrinsic trap site and the guest molecule act competitively as exciton traps, is applicable. Then, the quenching factor of the host fluorescence, $Q_H$, is expressed by the following equation:[4,5]

$$Q_H = (\eta_{H0}-\eta_H)/\eta_H = nc/(1+nc_T) = n'c, \qquad (1)$$

where $\eta_{H0}$ and $\eta_H$ are the quantum efficiencies of the host fluorescence in the absence and in the presence of the guest molecule in a concentration of $c$ (mol/mol basic unit); $n$ and $n'$ are the numbers of Cz chromophores covered by an exciton during the lifetime in the absence and in the presence of the intrinsic trap sites (second and sandwich-like excimer sites) in a concentration of $c_T$ (mol/mol basic unit). The quenching factor of monomer fluorescence, $Q_M$, is expressed by

$$Q_M = nc_T. \qquad (2)$$

The bilogarithmic plots of $Q_H$ and $c$ gave a straight line with a slope of 1.0. The values of $n'$ were obtained from the lines according to Eq. 1; they are listed in Table 1. The value of $n'$ is dependent on the guest molecule. In the case of perylene, an energy migration with a subsequent long-range energy transfer seems to be observed.[6] This is why the value of $n'$ for perylene is larger than those for the others.

In the case of polymer film, where no monomer fluorescence was observed, $Q_M \gg 1$, as has previously been reported.[4,5] Therefore, $Q_H = c/c_T$. Then, $c_T = 1/n'$. Although $Q_M$ could not be obtained for a DCzP(a) film, the value of $c_T$ for the film seems to be smaller than $1/n'$. The values of $c_T$ are also listed in Table 1.

Table 1. Energy transefr by the exciton-diffusion process

| No. | Host | Guest | $n'$ | $c_T\times10^3$ (mol/mol basic unit) |
|---|---|---|---|---|
| 1 | PVCz | Perylene | 1200 | 0.83 |
| 2 | PCzEVE | Perylene | 3700 | 0.27 |
| 3 | DCzP(a) | Perylene | 5900 | $<0.17$ |
| 4 | PVCz | TCB | 690 | 1.4 |
| 5 | PCzEVE | TCB | 2000 | 0.50 |
| 6 | DCzP(a) | TCB | 3600 | $<0.28$ |
| 7 | PVCz | DMTP | 420 | 2.4 |
| 8 | PCzEVE | DMTP | 2900 | 0.34 |
| 9 | DCzP(a) | DMTP | 1300 | $<0.77$ |

Concerning amorphous films, the value of $c_T$ increases in the following order, irrespective of the guest molecule, except for PCzEVE film doped with DMTP: DCzP(a) $<$ PCzEVE $<$ PVCz. That is, the concentration of the trap sites for a DCzP(a) film is smaller than that for a PVCz film and that for a PCzEVE film, where it is difficult for Cz chromophores to form the intrinsic trap sites because of the large distance between neighboring Cz chromophores. This suggests that the excimer sites in a polymer film are formed with greater ease than the excimer sites in an amorphous film of the model compound, even if Cz chromophores are widely spaced on the skeletal chain.

## References

1) A. Itaya, K. Okamoto, and S. Kusabayashi, *Chem. Lett.*, **1978**, 131.

2) K. P. Seefeld, H. Müller, and H. Bässler, *J. Luminescence*, **16**, 359 (1978); Y. Sano, M. Yokoyama, Y. Shirota, and H. Mikawa, *Mol. Cryst. Liq. Cryst.*, in press.

3) K. Okamoto, A. Itaya, and S. Kusabayashi, *Polym. J.*, **7**, 662 (1975).

4) A. Itaya, K. Okamoto, and S. Kusabayashi, *Bull. Chem. Soc. Jpn.*, **50**, 22 (1977).

5) W. Klöpffer, *J. Chem. Phys.*, **50**, 2337 (1969).

6) R. C. Powell and Q. Kim, *J. Luminescence*, **6**, 351 (1973).