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Extrinsic Photoconductivity of *N*-Ethylcarbazole Single Crystals

Keishi Kato, Masaaki Yokoyama, and Hiroshi Mikawa
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadakami, Suita, Osaka 565

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Synopsis. An extrinsic photocurrent was observed in pure *N*-ethylcarbazole single crystal, contrary to the current view that it does not exist in *N*-isopropylcarbazole.[8] It was reduced to a great extent in anthracene-containing crystal due to the decrease in carrier quantum yield caused by the energy transfer from *N*-ethylcarbazole (host) to anthracene (guest) molecules.

Studies have been made on the photoconductivity of poly-*N*-vinylcarbazole (PVCz),[1-7] as regards application to electrophotography. For a better understanding of the photoconductive properties of this polymer, it is desirable to investigate the differences in photoconductive property of the polymer and the corresponding molecular crystals. *N*-Ethylcarbazole (EtCz) and *N*-isopropylcarbazole (IPCz) were chosen as suitable model compounds, each corresponding to the monomeric unit of PVCz.

The photoconductivity of IPCz was studied by Sharp who reported that the compound exhibits no extrinsic photoconduction in the lowest π-π^* absorption region in contrast to the presence of both extrinsic and intrinsic photoconduction in PVCz. In view of current aspects of the photoconductivity of anthracene, the absence of extrinsic photoconduction in IPCz seems unusual. It seems necessary to reinvestigate the photoconductive properties of molecular crystals of the model compounds.

The present paper gives the results concerning the photoconductivity of EtCz single crystal. EtCz exhibits extrinsic photoconduction in the lowest π-π^* absorption region which could be largely reduced by the presence of a small amount of anthracene.

Experimental

Commercial EtCz contains anthracene as an impurity which is very difficult to remove by the usual methods of purification.[9] EtCz of high purity could be obtained only when synthesized EtCz was used as a starting material.

In our present work we used two kinds of EtCz crystal, one obtained from commercial EtCz purified first by repeated recrystallization and finally by vacuum distillation followed by zone melting, and containing about 2×10^{-3} mol/mol anthracene, the other a zone-refined EtCz crystal prepared from synthetic carbazole, the purity of the crystal being confirmed by the fact that the fluorescence lifetimes remained constant (about 20 ns) over the whole spectral region. Single crystals were obtained in a Bridgman furnace. Pillar crystals (about 2 mm×2 mm×5 mm) cut from the ingot along the a-axis (crystallographical) were used for the DC steady-state measurements, the surfaces of both ends being painted with silver-paste (Du Pont). A 500 W-xenon light source was used together with a prism-monochromator. Monochromatic light was cast onto the crystal perpendicular to the applied electric field. The photocurrent was measured with a vibrating-reed electrometer (Takeda Riken TR-81).

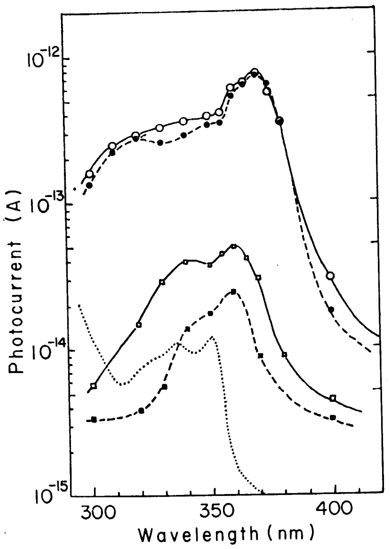

Fig. 1. The spectral dependence of the photocurrent for both pure and anthracene-containing EtCz crystals, applied field strength being 5000 V/cm.
(—○—); pure EtCz crystal in high vacuum, (--●--); pure EtCz crystal in air, (—□—); anthracene-containing EtCz crystal in high vaccum, (--■--); anthracene-containing EtCz crystal in air. The dashed line indicates the absorption spectrum of EtCz solid (KBr disk).

Results and Discussion

Figure 1 shows the spectral dependence of the photocurrent for both pure and anthracene-containing crystals of EtCz. The photocurrent was proportional to the light intensity irrespective of the exciting wavelength.

The pure EtCz crystal shows a relatively large photocurrent, nearly equal to that of PVCz. The photocurrent rises at the onset of the lowest singlet absorption, its peak being located at about 370 nm. This antibatic behaviour of the action spectrum of the photocurrent is similar to that of PVCz reported by Bauser and Klöpffer[1] and Okamoto *et al.*,[3] carriers are generated by extrinsic processes involving the interaction of singlet excitons with impurity or defects in the bulk of the crystal.

In anthracene-containing crystals, a considerable reduction of the photocurrent is observed over the whole spectral range by factor of about 10. This results is similar to the case of tetracene-doped and acridine-doped anthracene crystals.[10] The reduction of the photocurrent might be due to either the decrease of the quantum efficiency of the charge-carrier formation process or the decrease of the effective mobility of the carriers. The latter effect can be neglected for the following reasons. (1) Carrier mobility is independent of the wavelength of the incident light. In spite of

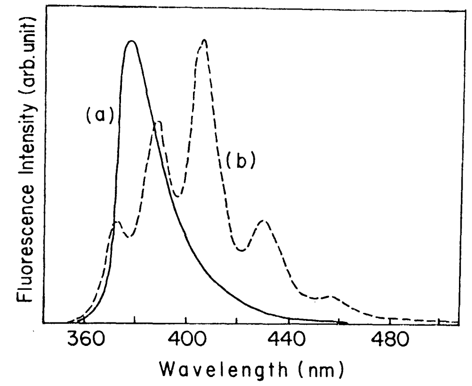

Fig. 2. The fluorescence spectra of pure and anthracene-containing crystals of EtCz at room temperature. (a); pure EtCz single crystal, (b); anthracene-containing crystal of EtCz (2×10^{-3} mol/mol).

this, the spectral dependence of the photocurrent changes in anthracene-containing crystals, the photocurrent peak showing a blue shift to 360 nm. (2) In anthracene-containing crystals, the fluorescence of EtCz is remarkably quenched and the intensive fluorescence of anthracene is observed as shown in Fig. 2. This is due to an efficient energy transfer from the lowest excited singlet state of EtCz (3.5 eV) to that of anthracene (3.3 eV). Thus it can be concluded that the reduction of the photocurrent in anthracene-containing crystals is mainly due to the decrease in the carrier-generation efficiency due to the energy transfer. The shift of the photocurrent peak to about 360 nm can be interpreted as follows. Since anthracene molecules are distributed uniformly in the crystal, anthracene molecules available as the dissipating center of the singlet-excitation energy decrease if the light is absorbed near the surface of the crystal, thus causing a blue-shift of the action spectrum of photoconductivity.

Preliminary experiments on the transient photoconductivity of EtCz single crystal with a pulsed light of the π-π^* absorption region showed that the hole photocurrent was remarkably larger than the electron photocurrent. Hence, the photocurrent measured with pillar crystals is mainly due to the hole photocurrent in the lowest π-π^* absorption region.

Thus the photoconductivity of EtCz crystal can be described as follows: The photocarrier (mainly holes) are generated by an extrinsic process involving the interaction of singlet excitons with impurity or defects in the bulk of the crystal. The small contribution of photocarrier generation on the surface of the crystal is explained by the experimental result in which the photocurrent was not affected, or only a little, by the atmosphere. If the crystal contains anthracene molecules, they act as traps of the singlet-excitation energy in EtCz crystal causing a decrease in carrier generation efficiency. Complete quenching of the photoconductivity may thus occur in the lowest π-π^* absorption region, if the crystal contains a considerable amount of impurity which quenches the excited energy of the host EtCz molecules. The result obtained by Sharp[8] showing no photoconduction in the lowest π-π^* absorption region, a sharp contrast to the present results of EtCz crystal, might be attributed to the presence of some impurity such as anthracene in the crystal.

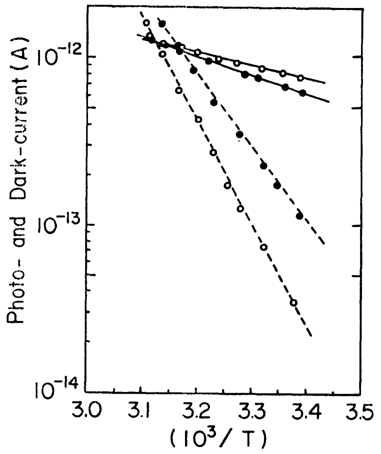

Fig. 3. The temperature dependence of the photo- and dark-currents of pure EtCz single crystal. (—○—); photocurrent in high vacuum, (—●—); photocurrent in air, (--○--); dark-current in high vacuum, (--●--); dark-current in air.

Table 1. The activation energies of EtCz crystal and PVCz film (eV)

Current	EtCz crystal		PVCz film[2]	
	photo-	dark-	photo-	dark-
In vacuum	0.06	0.5	0.1—0.3	1.0—1.3
In air	0.08	0.45	0.5—0.6	0.7—0.8

Figure 3 shows the temperature dependence of the photo- and dark-currents in pure EtCz crystal. The relation $i \propto \exp(-E_a/kT)$ holds for dark- and photocurrents. The activation energies (E_a) are given in Table 1, compared with those of PVCz. The activation energies of both dark- and photo-current in EtCz crystal are smaller than those of PVCz. Since it is expected that carrier-generation process requires a very small activation energy, these differences in activation energy seem to reflect the differences of the behaviours in carrier transport between molecular crystals and polymers.

References

1) H. Bauser and W. Klöpffer, *Chem. Phys. Lett.*, **7**, 137 (1970).

2) K. Okamoto, S. Kusabayashi, and H. Mikawa, This Bulletin, **46**, 1948 (1973).

3) K. Okamoto, S. Kusabayashi, and H. Mikawa, *ibid.*, **46**, 2324 (1973).

4) K. Okamoto, K. Kato, K. Murao, S. Kusabayashi, and H. Mikawa, *ibid.*, **46**, 2883 (1973).

5) D. M. Pai, *J. Chem. Phys.*, **52**, 2285 (1970).

6) A. Szymanski and M. M. Labes, *ibid.*, **50**, 3568 (1969).

7) J. Mort, *Phys. Rev.*, **B5**, 3329 (1972).

8) J. H. Sharp, *J. Phys. Chem.*, **71**, 2587 (1967).

9) K. Kato, M. Yokoyama, K. Okamoto, S. Kusabayashi, H. Mikawa, K. Yoshihara, and S. Nagakura, *Mol. Cryst. and Liq. Cryst.*, in press.

10) R. F. Chaiken and D. R. Kearns, *J. Chem. Phys.*, **45**, 3966 (1966).