

# Can Twisted Internal Charge-Transfer (TICT) State be Formed in Rigid Polymers?

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Absorption, emission and emission anisotropy spectra of 4-cyano-N,N-dimethylaniline (CDMA) and 4-cyano-2,6,N,N-tetramethylaniline (CTMA) were investigated in poly(vinyl alcohol) (PVA) films. It was found that the CDMA and CTMA molecules in PVA films at room temperature display phosphorescence, the emission band of which overlaps with the longwave fluorescence band **a**. The low value of the emission anisotropy shows that in the rigid PVA matrix there are microscopic defects in the form of empty spaces in which a certain fraction of the CDMA or CTMA molecules can attain twisted intramolecular charge-transfer states (TICT) due to rotational relaxation. The emission anisotropies in the shortwave, **b**, and longwave, **a**, fluorescence bands of CDMA in propylene glycol were found to be distinctly different, this indicating that the directions of the transition moments are not parallel.

## 1. Introduction

Lippert et al. [1] have found that p-cyano-dimethylaniline (I, CDMA) emits two fluorescence bands in liquid polar solvents, a low-energy emission **a** and a high-energy emission **b**. They have attributed this phenomenon to the inversion of closely situated  $^1L_a$  and  $^1L_b$  states due to the reorientation of polar solvent molecules, the strongly polar  $^1L_a$  state being better stabilized.

The measurements of the emission anisotropy (polarization degree) spectra of I in ethanol at 90 K showed that the shortwave fluorescence **b** is polarized perpendicular to the longwave fluorescence **a**, i.e. to the long axis of molecule I [2]. However, as demonstrated in later measurements of the emission anisotropy carried out by Rotkiewicz et al. [3], the emission anisotropy is high and assumes positive values for both **a** and **b** bands, irrespective of the excitation wavelength  $\lambda_{exc}$ . This is in apparent contradiction to the mechanism proposed by Lippert [1, 2], since the **a** and **b** emissions are polarized parallel and not perpendicular to each other, as required for the  $^1L_a$  and  $^1L_b$  emitting states.

The fact that the two transition moments are parallel encouraged Grabowski and coworkers [3] to assume an internal rotamer structure for the polar excited state [3–5]. Since the fluorescence **a** can be attributed neither to the  $^1L_a$  nor the  $^1L_b$  state, these

new electronically excited states have been called twisted intramolecular charge-transfer states (TICT), (see Fig. 1, II), [4, 5].

The TICT fluorescence is polarized in the same direction as in the absorption, i.e. the transition moment is polarized along the molecule's axis, but in rigid glasses no TICT state can be formed [4].

However, dual fluorescence was observed for I in a rigid PVA matrix at room temperature [6]. It was also found that such a dual emission vanishes at low temperatures. At liquid nitrogen temperature only normal fluorescence **b** and phosphorescence were observed.

On the other hand, in our experiment molecule I in PVA at room temperature displayed both fluorescence and phosphorescence, the band of which lies within

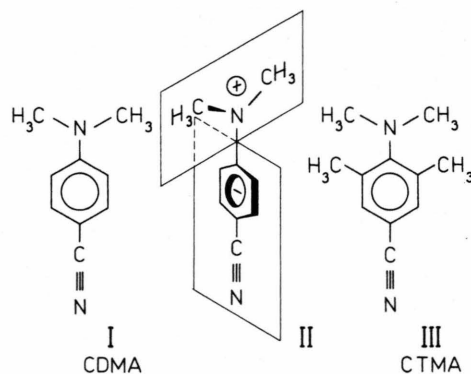


Fig. 1. Structural formulae of 4-cyano-N,N-dimethylaniline (CDMA) and 4-cyano-2,6,N,N-tetramethylaniline (CTMA).

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the band of fluorescence **a**. In the present paper, the results of our spectroscopic investigations are reported for 4-cyano-N,N-dimethylaniline (CDMA, I) and 4-cyano-2,6,N,N-tetra-methylaniline (CTMA, III) in poly(vinyl alcohol) (PVA) films.

## 2. Experimental

Isotropic poly(vinyl alcohol) (PVA) films were prepared at room temperature by the method described in [7, 8]. The molecules I and III are relatively poorly soluble in aqueous PVA and were therefore introduced to the solutions through methanol.

Absorption spectra were measured on a Specord-M40 (Carl Zeiss, Jena) spectrophotometer. Fluorescence and phosphorescence spectra were recorded by means of a fully corrected spectrophotometer designed and built in our laboratory [9]. Absorption and fluorescence spectra were measured in a special thermostatic cell enabling the temperature of the sample to be maintained with an accuracy of  $\pm 0.5$  K.

Absorption and fluorescence anisotropy spectra ( $r$ ) were measured by the photon counting technique as described in [10]. Phosphorescence anisotropy spectra were recorded by means of a spectrophotometer fitted with two Glan prisms [9].

## 3. Result and Discussion

### 3.1 Absorption, Emission and Anisotropy Spectra of CDMA in PVA Film

Figure 2 shows absorption, emission and emission anisotropy spectra of CDMA in PVA at 296 K in a freshly prepared film. Two intense **a** and **b** emission bands can be observed: band **b** corresponds to the fluorescence and band **a** to the global emission (phosphorescence and weak fluorescence). The emission anisotropy in band **a** distinctly differs from that in band **b**. For the wavelength  $\lambda_{em} = 415$  nm it even assumes a negative value. Figure 2 shows also the anisotropy spectrum of phosphorescence alone, measured at 296 K. The mean phosphorescence lifetime,  $\tau_{ph}$ , amounts to 1.2 s. The character of the run of the emission anisotropy in a freshly prepared and in a previously heated film does not differ essentially. In both cases, fairly low values of the emission anisotropy are observed (they markedly differ from the limiting val-

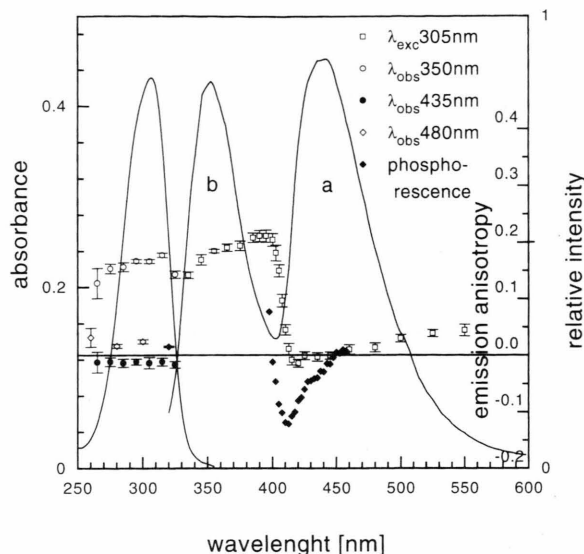


Fig. 2. Absorption, emission and emission anisotropy spectra of CDMA in fresh PVA film measured at 296 K.

ues of 0.4 and  $-0.2$ ), thus indicating the existence of microscopic defects in PVA. Therefore, irrespective of the rigidity of the medium, restricted rotational motions may occur. The CDMA molecule is small compared to the molecules of diphenylpolyenes and para-substituted stilbenes, for which markedly higher emission anisotropies were measured [11, 12]. As seen in Fig. 3, the phosphorescence spectrum coincides with the longwave emission band **a** both at room temperature and at 84 K. When lowering the temperature, the intensity of the shortwave fluorescence band **b** increases. The contribution of the intensity of the fluorescence **a** is small compared to that of the phosphorescence intensity. Thus, in a rigid PVA medium, in view of the presence of some empty free spaces, a certain, very small fraction of the CDMA molecules may be responsible for the formation of the TICT state due to rotation of molecular fragments and rotational relaxation (Figure 1, II).

### 3.2 Absorption, Emission and Anisotropy Spectra of CTMA in PVA Film

In the CTMA molecule (Fig. 1, III) the planes of the amino group and the ring make an angle of about  $60^\circ$  in the ground state [13]. Characteristic of a non-planar molecule in a polar solvent (e.g. methyl alcohol) is a single fluorescence band in the energy region

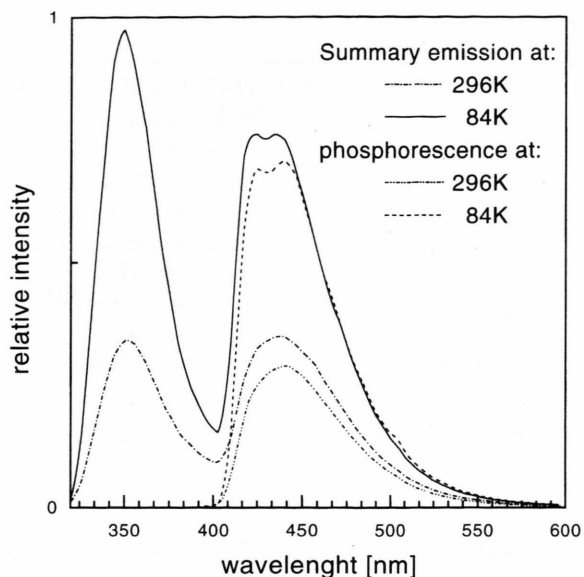


Fig. 3. Summary and phosphorescence spectra of CDMA in PVA film at 296 K and 84 K.

of CDMA's fluorescence **a** [14]. Nonetheless, the CTMA molecule in PVA film, which is a weakly polar medium, has two emission bands, **a** and **b** (Figure 4). Like in the case of CDMA, the band **a** comprises phosphorescence and weak fluorescence. The run of the emission anisotropy in the absorption band, as well as in the **a** and **b** emission bands, resembles that in the CDMA molecule. The strong drop in the emission anisotropy of band **a** is in both cases due to the effect of phosphorescence. In other polymers, such as polyvinylchloride (PVC), no phosphorescence of the molecules was observed at room temperature.

### 3.3 Absorption, Fluorescence and Anisotropy Spectra of CDMA in Propylene Glycol

The CDMA molecule in propylene glycol has two fluorescence bands, **a** and **b**. The intensity of the short-wave band **b** is markedly higher than that of the long-wave band **a** (Figure 5). The dielectric constant of polar propylene glycol is 32, and its viscosity at 25°C is 40.4 mPa · s [15]. Although the viscosity of propylene glycol is moderate compared with the rigid PVA film, the anisotropy observed in band **b** is considerably higher in propylene glycol (cf. Figs. 2 and 5). This clearly demonstrates the existence of free empty spaces in PVA films. The case of the change in emis-

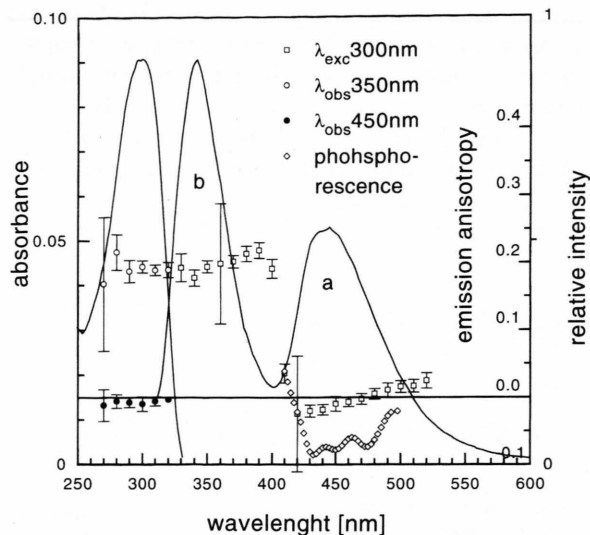


Fig. 4. Absorption, emission and emission anisotropy spectra of CTMA in fresh PVA film measured at 296 K.

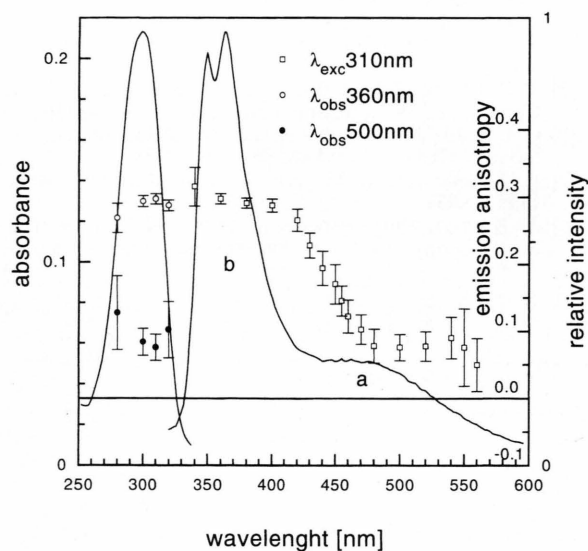


Fig. 5. Absorption, fluorescence and emission anisotropy spectra of CDMA in propylene glycol (con.  $10^{-5}$  M) measured at 296 K.

sion anisotropy when passing from the shortwave band **b** to the longwave band **a** is worth of interest (Figure 5). A marked drop in the emission anisotropy value is observed, similar as for CDMA in PVA film. In propylene glycol, however, no phosphorescence oc-

curs in the **a** band. Propylene glycol was purposefully chosen as a viscous solvent, since attempts to use glycerin with a markedly higher viscosity have shown that upon excitation at  $\lambda = 310$  nm glycerin is strongly luminescent. A similar behaviour of the emission anisotropy in the region of the two **a** and **b** bands was observed by Heldt *et al.* [16] for aminosalicylate derivatives in hexanol.

#### 4. Conclusions

- a) The molecules of CDMA and CTMA in PVA films display phosphorescence at 296 K, the emission band of which overlaps with the longwave fluorescence **a**.
- b) In the rigid PVA matrix, microscopic defects are present in the form of empty spaces, in which some of the CDMA or CTMA molecules can initiate the TICT state due to rotational relaxation.
- c) The different behaviour of the CDMA emission anisotropy in propylene glycol in the **a** and **b** fluorescence bands shows that the directions of the transition moments are different, and not parallel as has conventionally been assumed.

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