Molecular Crystals and Liquid Crystals

Electronic States of a 2,3-Dicyanopyrazine Dye in Vacuum-deposited Films

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*A significant spectral change from solution to vacuum-deposited films was
observed in a 2,3-dicyanopyrazine dye, 5-t-butyl-6-[4-(dibutylamino)styryl]-2,3-
dicyanopyrazine. In absorption spectra, a large hypsochromic shift was recog-
nized. On the other hand, a large bathochromic shift occurred in fluorescence with
considerable fluorescence quenching. The dye films were characterized as the sin-
gle crystal phase, then estimation of exciton interaction was carried out on the
basis of the crystal data. The result indicated that the electronic states of the
dye films are considered to be similar to those of H-aggregates.*

1. INTRODUCTION

In recent years, organic dyes and pigments have been utilized for many
optical and optoelectronic applications, *e.g.*, an organic photoconductor,
optical recording materials, photovoltaic cells and electroluminescent

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devices. These dyes are called *"functional dyes"* [1–4] and novel dye systems have been developed with there expanding application fields as well as increasing demand for high-performance properties of functional dyes [3,4]. A pyrazine dye system is a newly-proposed chromophore developed in 1990s by Prof. Matsuoka's group [5]. Pyrazine dyes generally have vivid colors due to there strong fluorescence. The dyes with large substituents have been known to exhibit strong fluorescence even in the solid state. However, in the case of the dyes with small substituents, fluorescence quenching generally occurs in the solid state [6]. Some diaminodicyanopyrazine dyes with large substituents were also reported to have crystal polymorphs with different colors in single crystals [7]. 2,3-Dicyanopyrazine dye **1**, 5-*t*-butyl-6-[4-(dibutylamino)styryl]-2,3-dicyanopyrazine (Fig. 1), is one of the derivatives which were designed to investigate the effect of substituents on solid-state fluorescence [8]. Recently, we found that **1** exhibits a remarkable spectral change from solution to vacuum-deposited films. In this study, the electronic states of **1** in vacuum-deposited films was interpreted in terms of exciton interaction in order to explain its spectral change from solution to the solid state.

2. EXPERIMENTAL

Dye **1** was synthesized by a previously reported procedure [8]. Vacuum-deposited films for optical measurement were prepared onto a glass substrate by using a vacuum deposition equipment (ULVAC VPC-410) under high vacuum condition (*ca.* 3.0×10^{-4} Pa). A deposition rate and film thickness were monitored by a ULVAC CRTM-6000 quartz crystal deposition controller. Film thickness was controlled to be about 500 Å. For X-ray diffraction measurement, a thick film (thickness: *ca.* 10,000 Å) was prepared by a ULVAC
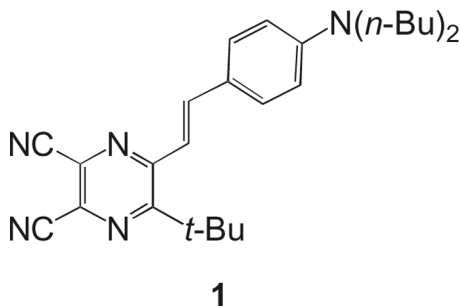

FIGURE 1 Chemical structure of dye **1**.

VPC-060 vacuum deposition equipment. UV/Vis absorption and fluorescent spectra were recorded on a Perkin Elmer Lambda 20 spectrophotometer and on a JASCO FP-6600 fluorescence spectrometer, respectively. The fluorescence excitation was performed at the wavelengths corresponding to each absorption maximum. Diffraction data was collected by a Rigaku RINT 2000 diffractometer using a graphite monochromated Cu$K\alpha$ radiation. Exciton interaction was estimated on the basis of a point dipole model [9]. An energy shift for a molecular dimer, which corresponds to the spectral shift, was calculated by $\Delta E = |\mu|^2$ $(1 - 3\cos^2\theta)/r^3$, where the transition dipole moment is denoted by μ, and the distance and angle between two transition dipoles by r and θ, respectively. The transition dipole moment was obtained by semi-empirical molecular orbital calculations [10,11] using the fractional coordinate sets of X-ray data [8]. The geometrical term, $(1 - 3\cos^2\theta)/r^3$, was determined from the geometrical relationship between the transition moments, which is correlated with the crystal structure. The total energy shift was estimated based on a nearest-neighbor approximation [12].

3. RESULTS AND DISCUSSION

Figure 2 shows the absorption and fluorescence spectra of **1** both in a toluene solution $(1 \times 10^{-5}\,\text{mol}\,\text{dm}^{-3})$ and in vacuum-deposited films.
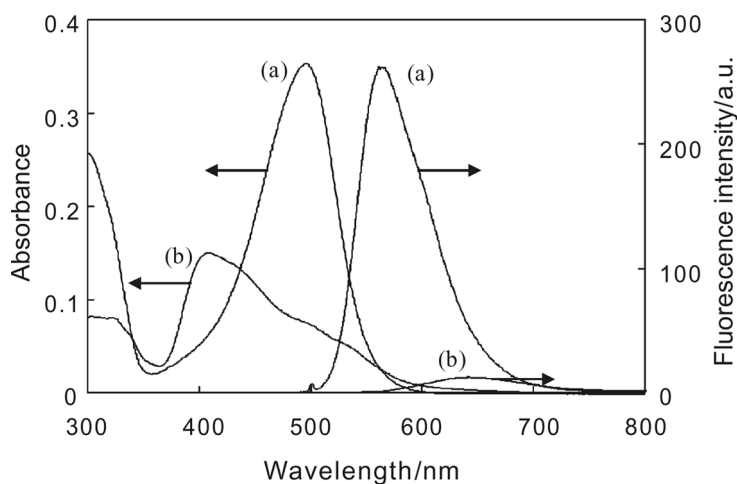

FIGURE 2 Absorption and fluorescence spectra of **1** (a) in toluene and (b) in vacuum-deposited films.

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The absorption maximum of **1** in the visible region appeared at 496 nm in toluene. In the vacuum-deposited films, the absorption maximum in the visible region was found to shift towards 409 nm. The energy displacement of this large hypsochromic shift is about $4289 \, cm^{-1}$. The spectral shift is accompanied by a color change from orange to pale yellow. **1** is also known to exhibit strong fluorescence in solution. In a toluene solution, its emission maximum is observed around 565 nm with 25% fluorescence quantum efficiency [8]. In contrast, fluorescence in the vacuum-deposited films is quite weak and its maximum is shifted towards 642 nm. These spectral changes are reminiscent of a spectral change due to H-aggregate formation, even though both absorption and fluorescent spectra of the films are relatively broad.

Figure 3 depicts the X-ray diffraction diagram of the thick vacuum-deposited film of **1**. Several diffraction peaks were detected and these peaks were well indexed by the crystallographic data of **1**: Triclinic, $P-1$ $(Z=2)$, $a = 7.022$ (1), $b = 9.586$ (2), $c = 19.272$ (3) Å, $\alpha = 96.34$ (2), $\beta = 101.85$ (2), $\gamma = 93.64$ (2)° [8]. Thus the films can be identified as the same crystalline phase as that of the single crystals. Most observed diffraction peaks were assigned to the (001) peak and its higher order peaks. As shown in Figure 4, the molecules are stacked along the a-axis to form a one-dimensional molecular column in single crystals. And this molecular column is two-dimensionally ordered along the b- and c-axes to form three-dimensional structure. The
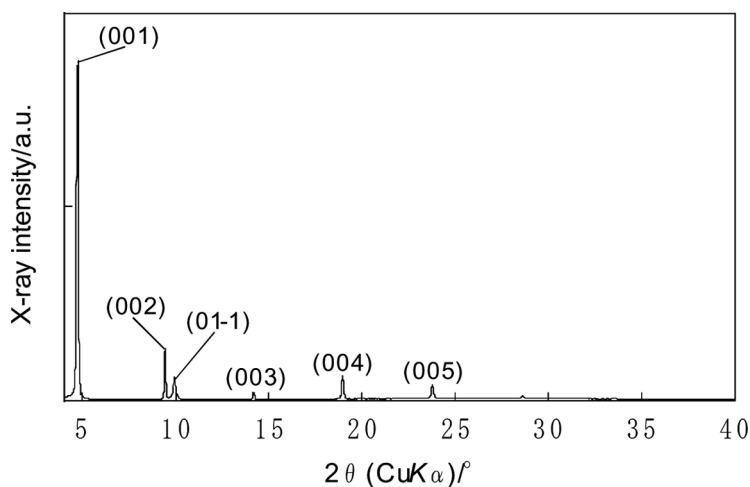

FIGURE 3 X-ray diffraction diagram of **1** in a thick vacuum-deposited film (thickness: ca. 10,000 Å).
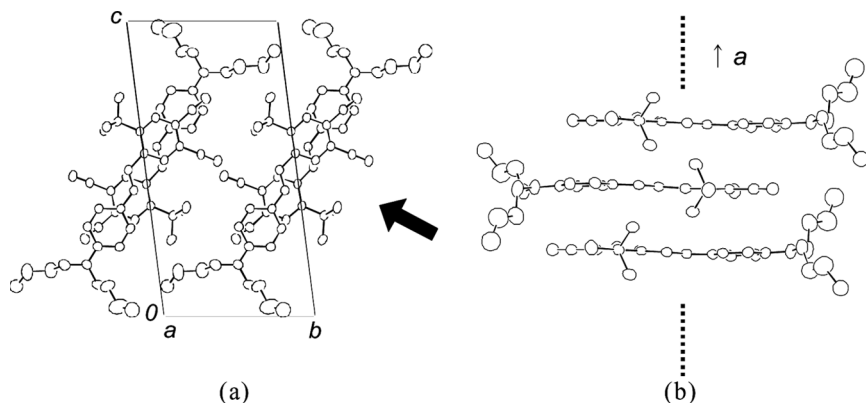
FIGURE 4 Crystal structure of **1**, (a) viewing from the *a*-axis and (b) the molecular stacking along the *a*-axis.

b- and *c*-axes are along the short and long molecular axes, respectively. The present experimental result is thus considered to indicate that the molecules in the vacuum-deposited films are arranged in such a way that the long molecular axis is almost perpendicular to the glass substrate. The definite appearance of the higher order diffraction peaks also suggests anisotropic film growth. The absorption intensity of **1** in the films were well interpreted from the present anisotropic film structure of **1**. The absorption coefficient of the films of **1** was found to be small for its molar absorption coefficient (3.33×10^4 at λ_{max}) [8]. It is about one-half to one-fifth of that of the vacuum-deposited films of common dyes with several tens of thousands of molar extinction coefficient. As shown in Figure 5, the calculated transition dipole moment of **1** for the visible absorption band was found on the π-conjugated plane along the long molecular axis. The transition
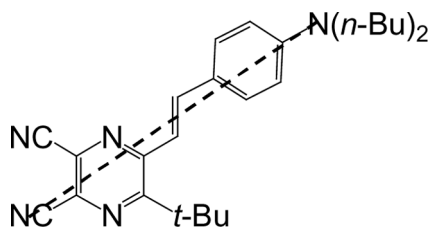

FIGURE 5 The calculated transition dipole moment of **1** for the visible absorption band.

moment is thus aligned in the above mentioned manner on the glass substrate to give relatively small absorption coefficient of the films.

In order to characterize the optical properties of organic dyes in the solid state, we must take into consideration two important effects on the electronic states of a crystalline molecular solid. One is a change in the electronic states of a molecule itself due to crystallization. We can find many examples in which a nonnegligible conformational change in a molecule is caused by crystallization. A given conformational change affects the electronic states of the molecule to have an efficient influence on the solid state properties. In dye **1**, a significant difference was not recognized between the electronic states of a molecule in single crystals and those of the optimized molecular structure [8]. The other important effect is exciton interaction, a quantum mechanical resonance effect due to molecular aggregation. An aggregation of molecules gives rise to a change in the electronic states depending on the molecular arrangement. In order to understand the spectral feature of molecular aggregates, an exciton band splitting in molecular dimers was described by Kasha [9]. An excitonic resonance state for a molecular dimer results in the splitting of the excited state. If two molecules are colinearly arranged in a head-to-tail fashion, the higher energy state is forbidden and the lower energy state is allowed due to the selection rule of exciton band transition. Therefore, the dimer absorption band will appear in the longer wavelength region than the monomer band and the fluorescence is observable. Optical properties of J-aggregates are well-explained on this basis [14]. On the other hand, in a parallel dimer case, in which two molecules are aligned completely parallel, the optical selection rule is different from the head-to-tail dimer case. The allowed and forbidden levels are changed to the higher and the lower levels, respectively. Accordingly, an absorption band of the dimer is blue-shifted relative to the monomer band and the fluorescence is expected to be quenched due to the forbidden lower singlet state. Optical properties of hypsochromic H-aggregates are generally interpreted in terms of this parallel dimer model [15].

The total energy shift for dye **1** was calculated to be $2602 \, \mathrm{cm}^{-1}$. This result indicates that the electronic states of **1** in the vacuum-deposited films are considered to be similar to H-aggregates. The hypsochromic shift in the absorption band as well as the bathochromic shift of the fluorescent band with significant fluorescent quenching are in good agreement with this estimation. The appearance of a relatively efficient phosphorescence is also expected due to H-type aggregation [9]. At room temperature, however, no phosphorescence was recognized in the films. Then emission measurement was also performed

at 6 K. The measurement showed fluorescence enhancement as well as the band sharpening of the fluorescent spectra, but phosphorescence was not detected. Basically, an absorption band of H-aggregates should be very narrow since the optical transition of H-aggregates is regarded as a pure electronic transition. In the present films, however, the absorption band involved several shoulder peaks and the shape of the fluorescence band is very broad. The films can thus be considered to include structural disorders. It is possible to take into account that structural disorders in the films contribute to the phosphorescence quenching.

Another remaining question is a difference in absorption properties between the vacuum-deposited films and a crystalline powder sample. In the crystalline powder of **1**, such a considerable hypsochromic shift was not observed in diffuse reflectance spectra: λ_{max} is 522 nm in Kubelka-Munk units, even though the sample emitted weak fluorescence around 625 nm [9]. It is difficult to find an exact answer to this question on the basis of the present data, but relatively high anisotropy in molecular arrangement in the films may be correlated with the difference in absorption properties.

4. CONCLUSIONS

The absorption and emission properties of vacuum-deposited films of pyrazine dye **1** were investigated from the viewpoint of exciton interaction. The calculation of exction interaction indicated that the electronic states of **1** in the films are similar to those of H-aggregates. The remarkable spectral change of **1** from solution to vacuum-deposited films was successfully interpreted in this calculation result.

REFERENCES

[1] Yoshida, Z. & Kitao, T. (Eds.) (1989). *Chemistry of Functional Dyes*, Mita Press: Tokyo, Japan.
[2] Zollinger, H. (2003). *Color Chemistry (3rd revised edition)*. Wiley VCH: Weinheim, Germany.
[3] Freeman, H. S. & Peters, A. T. (Eds.) (2000). *Colorants for Non-Textile Applications*, Elsevier: Amsterdam, Netherlands.
[4] Kim, S. H. (Ed.) (2006). *Functional Dyes*, Elsevier: Amsterdam, Netherlands.
[5] Matsuoka, M. (2000). *Colorants for Non-Textile Applications*, Freeman, H. S., Peters, A. T. (Eds.), Elsevier: Amsterdam, Netherlands, Chapter 8, p. 339.
[6] Shirai, K., Matsuoka, M., & Fukunishi, K. (1999). *Dyes Pigm.*, *42*, 95.
[7] Matsumoto, S., Uchida, Y., & Yanagita, M. (2006). *Chem. Lett.*, *35*, 654.
[8] Horiguchi, E., Matsumoto, S., Funabiki, K., & Matsui, M. (2006). *Bull. Chem. Soc. Jpn.*, *79*, 799.

[9] Kasha, M. (1976). *Spectroscopy of the Excited State*, Bartolo, B. D. (Ed.), Plenum Press: New York, London.

[10] Zerner, M. C. *ZINDO, A General Semi-Empirical Program Package*, Department of Chemistry, University of Florida: Gainesville, FL.

[11] (2001). *CAChe ver 5.0, Computer Aided Chemical Modeling Package*, Fujitsu Ltd.: Tokyo, Japan.

[12] Matsumoto, S., Tokkunaga, W., Miura, H., & Mizuguchi, J. (2001). *Bull. Chem. Soc. Jpn.*, *74*, 471.

[13] Preliminary measurement of the surface morphology by atomic force microscopy revealed that the films exhibit flat surface textures and on the surface there are smooth terraces separated by steps with a height roughly attributed to the cell constant of the *c*-axis. The details will be published as the second report.

[14] Czikkely, V., Försterling, H. D., & Kuhn, H. (1970). *Chem. Phys. Lett.*, *6*, 11.

[15] James, T. H. (Ed.). (1977). *The Theory of the Photographic Process*. Macmillan Publishing: New York.