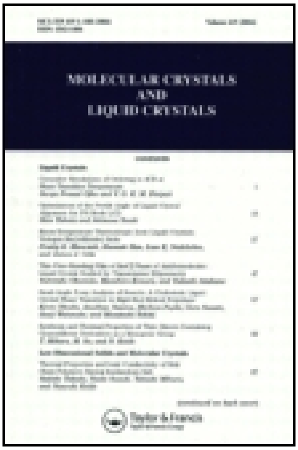

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Kaoru Okaniwa [a], Hiroshi Okamoto [a], Tadaoki Mitani [a], Tamotsu Inabe [a], Jiro Toyoda [a], Yasushi Morita [a], Kazuhiro Nakasuji [a], Hiroshi Yamamoto [b], Takashi Deno [b] & Seiji Honma [b]

[a] Grad. Univ. Advanced Studies, Institute for Molecular Science, Okazaki, 444, Japan

[b] Ciba-Geigy Japan Ltd., International Research Laboratories, Takarazuka, 665, Japan

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INTRA- AND INTER-MOLECULAR CHARGE TRANSFER INTERACTIONS IN H-BONDED DTPP CRYSTALS

KAORU OKANIWA, HIROSHI OKAMOTO, TADAOKI MITANI, TAMOTSU INABE, JIRO TOYODA, YASUSHI MORITA, KAZUHIRO NAKASUJI
Grad. Univ. Advanced Studies, Institute for Molecular Science, Okazaki 444, Japan

HIROSHI YAMAMOTO, TAKASHI DENO and SEIJI HONMA
Ciba-Geigy Japan Ltd., International Research Laboratories, Takarazuka 665, Japan

Abstract The spectra of polarized reflectivity and excitation of photoconductivity of β-DTPP crystal have been measured. Highly efficient photoconductivities were observed along the both directions of the stacking of the molecules and the intermolecular H-bond. These excitation spectra are considerably different and depend on the direction of applied electric field. These photoconducting properties are discussed in terms of charge transfer interaction along stacking axis and the electron-proton interactions.

INTRODUCTION

The DTPP(1,4-ditioketo-3,6-diphenyl-pyrrolo-[3,4c]-pyrrole) molecule consists of an acceptor part (a component around sulfur atoms) and a donner part (the rest part of molecule) as shown in FIGURE 1(a).[1,2] The crystals exist in three forms α, β and c. In the β-DTPP, which is monoclinic having a space group of $C_{2/c}$, molecular planes are perpendicular to the stacking axis (*b*). The intermolecular charge-transfer (CT) interaction is considerably large along the *b* axis. The H-bonds align in the form of N-H...S along the *c* axis.[3]

The β-DTPP crystals show a highly efficient photoconduction comparable to that of the phthalocyanines which have been practically used as a photoreceptor.[1,2] In such organic photoconductive materials, the process of photocarrier generation is generally discussed in terms of dissociation of electron-hole pair rather than direct band-to-band transition.[4] The CT excitation also plays an important role in the process of carrier generation.[5] Judging from the crystal structure of the β-DTPP, the CT interaction could not be neglected in the carrier generation processes. In addition, in the β-DTPP crystals, there exist the H-bond network closely interacting with the CT system. It is very interesting to study the correlation between the CT interaction and the H-bonds, presumably related to the high efficiency of photoconduction of this crystals.

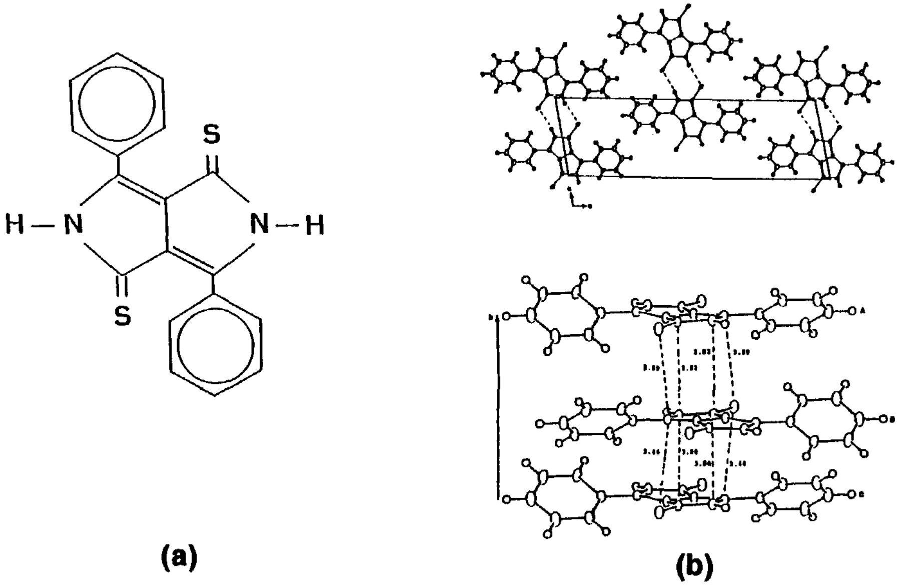

FIGURE 1 (a) DTPP molecule and (b) the crystal structure of β-DTPP.

EXPERIMENTAL

The single crystals of the DTPP were grown in vapor phase with carrier (argon) gas flow.[6] The dimension of the β-DTPP crystal was 0.4 x 0.4 x 0.08 mm^3. Polarized reflection spectra measurements were carried out using the light from a halogen-tungsten incandescent lamp through a polarizer (Glan-Taylor prism) and monochrometer (Jasco CT-25GD) with microscope technique. The reflection spectra were transformed to optical conductivity by using Kramers-Kronig analysis with Roessler correction. For the measurements of excitation spectra of the photocurrent, polarized and chopped monochromatic light was incident on the single crystals on which electrodes were made by carbon paste. An applied electric field in measurements of the excitation spectra of photoconduction was 1.5 x 10^3 V/cm. The photocurrent was recorded by a conventional lockin technique. Electric-field dependences of photocurrent were measured under the irradiation of monochromatic light at 10080 Å.

RESULTS AND DISCUSSION

OPTICAL PROPERTIES

The polarized reflection spectra on *bc* plane of the β-DTPP and the optical conductivity spectra obtained by Kramers-Kronig transformation of the reflection spectra are shown in FIGURE 2. In the figure, when an electric vector of light is parallel to the *b* axis (or the *c* axis), the spectrum is presented by solid (or broken) line. Strong structures are found at about 1.4 and 1.8 eV in the E//*c* spectra, which are labeled by A and B, respectively. Since the dipole moment of the intramolecular transition is parallel to the molecular plane, the strong structures A and B are assigned to the intramolecular transitions (the Frenkel exciton). Weak structures are found for both configuration of E//*c* and //*b* at about 1.2 and 1.3 eV, respectively, which are indicated by arrows in the figure.

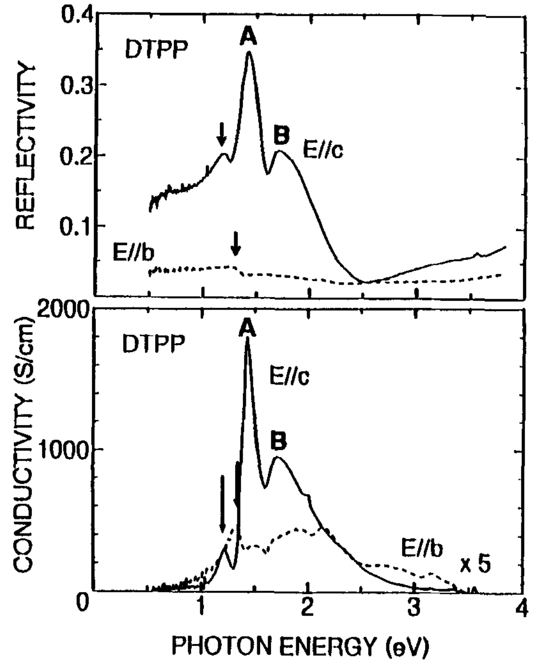

FIGURE 2 The polarized reflection (upper) and optical conductivity (lower) spectra of β-DTPP single crystals for the electric vectors of the light parallel to the *c* (solid line) and to the *b* (broken line) axes.

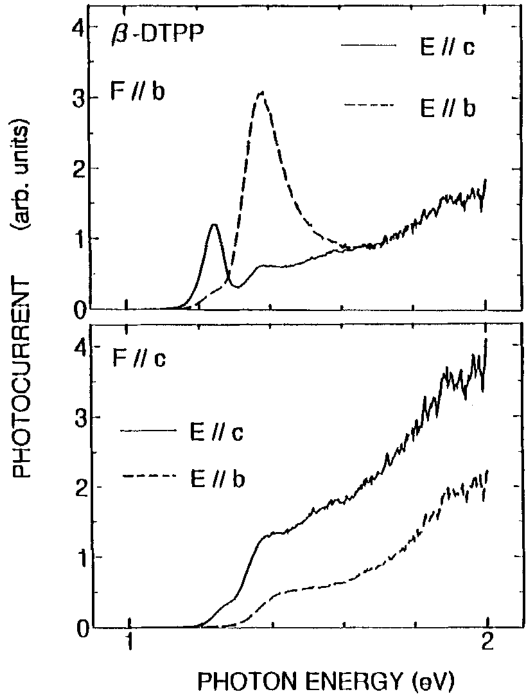

FIGURE 3 Excitation spectra of photocurrent for β-DTPP. An external electric field (**F**) is applied along the *b* axis (upper) or along the *c* axis (lower). Electric vector of incident light (**E**) is parallel to the *c* axis (solid line) or the *b* axis (broken line).

PHOTOCONDUCTIVITY

The excitation spectra of photocurrent of the β-DTPP single crystals are presented in FIGURE 3 for external fields (**F**) along the *b* and *c* axes. The excitation light is polarized parallel to the *c* axis (solid line) or the *b* axis (broken line). In the excitation spectra of the photocurrent for **F**//*b* (the upper figure), there exist sharp peaks in a near-IR region. The energy positions of these peaks are coincident with those of the conductivity spectra indicated by arrows for both polarizations. Spike-like spectral shape in the β-DTPP (the upper figure) are attributable to the reduction of photocurrent due to recombination of electron and hole in a higher energy region.[7-9] This interpretation is supported by the experimental results that luminescence was detectable in the same energy region. Unexpectedly, the efficiency of the photocurrent along the *c* axis is large in spite of a small overlapping between molecules. The efficiency is almost comparable to that along the *b* axis. Such a large efficiency of the photocurrent along the *c* axis suggests a unique photocarrier transport mechanism assisted by the intermolecular H-bonds. Taking account of a high photocurrent efficiency at the low energy region, the structures indicated by the arrows in FIGURE 2 might be assigned to the intermolecular CT transition.

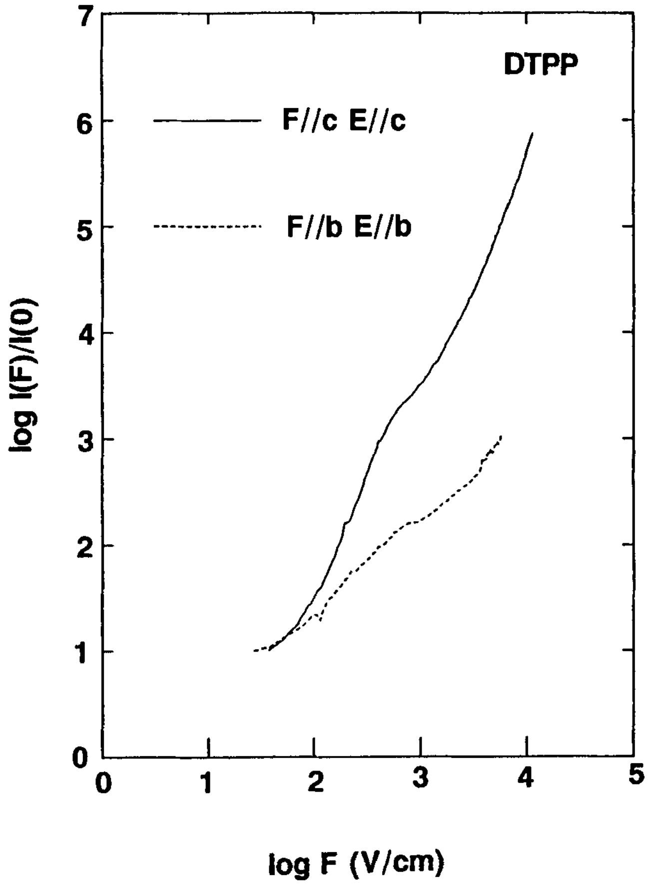

FIGURE 4 Electric-field dependence on photocurrent. The excitation energy was made at 1.23 eV. The direction of the external field (F) and electric vector of excitation light (E) is parallel to the *c* axis (solid line) in common or to the *b* axis (broken line).

FIGURE 4 shows an electric-field dependence of photocurrent of the β-DTPP crystals. A solid (or broken) line corresponds to F//*c* and E//*c* (or F//*b* and E//*b*), where E stands for an electric vector of incident light and F for an applied electric field. An excitation energy of the incident light in the both measurements is 1.23 eV. The photocurrent is found to follow the relation of $I \propto F^{\alpha}$. Approximate values of α are 2.5 and 1 for F//*c* and E//*c*, and F//*b* and

E//*b*, respectively. The value of α for **F**//*b* is independent of the polarizations and the excitation energy of the light. For **F**//*c*, however, the α's becomes smaller with increase of the excitation energy, and when the incident light is polarized in parallel to the stacking axis (**E**//*b*), the value of the α becomes relatively large. From these characteristic photocurrent-field relations, the photoconduction include many delicate problems in the processes of carrier generation and mobility of carriers. So that, it is difficult to give a conclusive interpretation of these problems. At present, it may be pointed out that the linear relation of the photocurrent for **F**//*b* implies an automatic dissociation of a photogenerated electron-hole pair (exciton): When the CT exciton is generated by light irradiation, the CT exciton might be easily relaxed into free electron and hole pair due to the strong screening effect via electron-proton interaction in the H-bonded system. This process is quite distinctive compared with the standard autoionization mechanism, in which electron-hole pair dissociate through the lattice depolarization effect.[10] More advanced studies are required to determine a definite picture of electron and proton motions concerning with the autoionization mechanism.

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