# Electronic Structure of Thioindigo Derivatives as Studied by Polarized Reflection Spectra on Single Crystals

*Jin Mizuguchi and Misato Mochizuki*
*Department of Applied Physics, Graduate School of Engineering*
*Yokohama National University*
*Hodogaya-ku, Yokohama, Japan*

## Abstract

4,4',7,7'-tetrachlorothioindigo (TCTI) is an industrially important red pigment and also used as a photoconductor for the electrophotographic photoreceptor. Although TCTI is quite similar in molecular and crystal structures to 4,4',5,5',7,7'-hexachlorothioindigo (HCTI), the electrophotographic gain of TCTI was reported to be about four times higher than that of HCTI. The high photosensitivity was interpreted in terms of the formation of weakly-bound intermolecular charge-transfer (CT) excitons and their subsequent electron-hole pair dissociation; whereas tightly-bound Frenkel excitons prevail in HCTI. In order to directly prove the formation of CT excitons in TCTI, an attempt has been made in the present investigation to observe the CT transition by means of polarized light using single crystals. No CT transition was, however, observed either in TCTI or HCTI and both electronic structures were quite similar. Furthermore, the photoconductivity of TCTI and HCTI is found to be equally high, but depends significantly on the electrode material. This indicates that the exciton is extrinsically dissociated at the Schottky barrier between TCTI (or HCTI) and the electrode. These results lead us to conclude that the difference in electrophotographic gain between TCTI and HCTI-based photoreceptors might presumably be attributed to the carrier formation or injection efficiency at the interface between the charge generation layer and charge transport layer.

## Introduction

4,4',7,7'-tetrachlorothioindigo (TCTI; Fig.1) is a thionated derivative of indigo and is an industrially important red pigment (Pigment Red 88[1]) on the market. Fukushima and others have investigated the electrophotographic properties of TCTI together with its analogue of 4,4',5,5',7,7'-hexachlorothioindigo (HCTI; Fig. 1) on the basis of the crystal structure.[2] They found an excellent electrophotographic photosensitivity of TCTI which is sufficient enough for practical applications. They reported further that although TCTI is very similar in molecular and crystal structures to HCTI, the electrophotographic gain of TCTI is about four times higher than that of HCTI. In addition, TCTI is more insoluble in organic solvents than HCTI by one order of magnitude. They attributed the high electrophotographic photosensitivity of TCTI to the formation of charge transfer (CT) excitons that involve an electron jump, upon light excitation, from one molecule to the neighboring molecule. The resulting weakly-bound CT excitons (*i.e.* excitons with a large Bohr radius) can subsequently be dissociated with ease into free electrons and holes as compared with tightly-bound Frenkel excitons in HCTI. Apart from the present outstanding performance of the TCTI-based photoreceptor, there remained two fundamental problems to be clarified. The first one concerns the experimental verification of the CT transition in TCTI by means of polarized light using single crystals. The other point is to elucidate the insoluble nature of TCTI in solvents (as characterized by stronger intermolecular forces) in comparison with HCTI. We have previously tackled the latter problem by means of energy partition analysis based on semi-empirical molecular orbital calculations.[3,4]

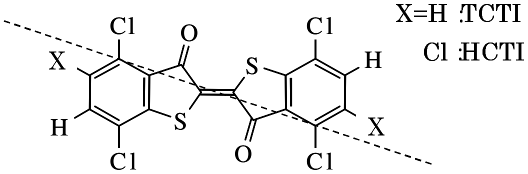

*Figure 1. Molecular structures of TCTI and HCTI. The direction of the transition dipole is depicted by a broken line.*

The purpose of the present investigation is to directly observe the CT transition in TCTI along the stacking axis by means of polarized light using single crystals and also to discuss the mechanism of the high electrophotographic gain of TCTI-based photoreceptors.

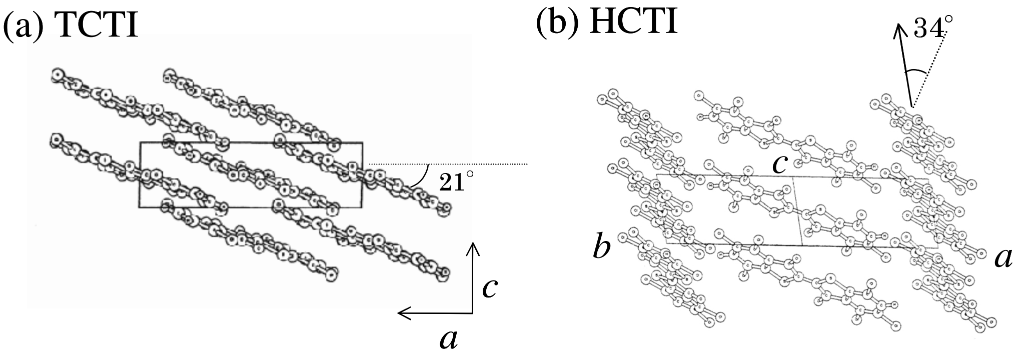

*Figure 2. Molecular arrangement along the stacking axis for TCTI and HCTI: (010) plane in TCTI and (1-10) plane in HCTI. Polarized light was introduced parallel or perpendicular to the molecular plane at an inclination angle of 21° measured from the a-axis in TCTI and 34° measured from the c-axis in HCTI.*

## Experiment

**Chemicals.** TCTI was obtained from BASF. HCTI was synthesized according to the method reported elsewhere.[5] The single crystals of TCTI and HCTI were grown from the vapor phase using a two-zone furnace.[6]

### Measurements for Polarized Reflection Spectra On Single Crystals

The crystallographic parameters for TCTI and HCTI are summarized as follows[2]: monoclinic, $P2_1/a$, $a$ = 13.090, $b$ = 15.368, $c$ = 3.799 Å , $\beta$ = 91.173° for TCTI; monoclinic, $P2_1/a$, $a$ = 12.011, $b$ = 15.323, $c$ = 4.878 Å, $\beta$ = 101.61° for HCTI.

Polarized reflection spectra in the visible region were measured by means of a microscope-spectrophotometer (UMSP 80 from Carl Zeiss). Figures 2 (a) and 2 (b) show the projection of the crystal structure onto the (010) and (1-10) planes of TCTI and HCTI, respectively. Polarized reflection measurements were carried out on the (010) plane of TCTI as shown in Fig. 2 (a), since this plane is most appropriate for measurements along the stacking axis as well as on the molecular plane. Polarized light was introduced with an angle of 21° with respect to the *a*-axis for polarization par-allel or perpendicular to the molecular plane. Similarly, polarized reflection spectra were measured on the (1-10) plane of HCTI (Fig. 2 (b)) for polarization parallel or per-pendicular to the molecular stack, where polarized light was introduced with an angle of 34° with respect to the *c*-axis.

Reflection measurements were also made on the molecular planes of (10-2) and (001) for TCTI and HCTI, respectively, in order to observe the Davydov splitting due to an oblique arrangement of transition dipoles (Fig.2). Polarized light was introduced parallel or perpendicular to the a-axis for both TCTI and HCTI.

### Photoconductivity Measurements

Photoconductivities were measured on evaporated thin films of TCTI and HCTI using interdigital electrodes made of transparent Al or ITO (indium-tin-oxide).

## Results and Discussion

### Molecular Properties

The absorption maxima observed in both compounds around 550 nm can be assigned to the HOMO (highest occupied molecular orbital)/LUMO (lowest unoccupied molecular orbital) $\pi$-$\pi^*$ transition on the basis of MO calculations. The transition moment points along the long-molecular axis as denoted by a broken line (Fig. 1).

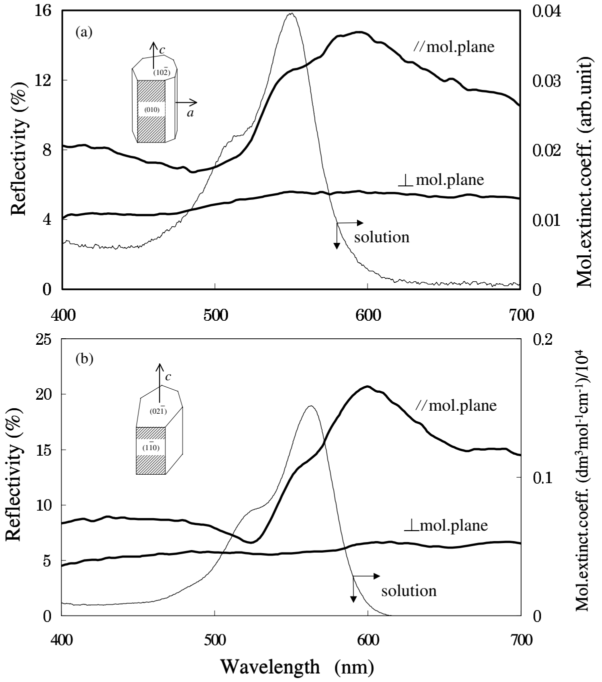

*Figure 3. Polarized reflection spectra together with solution spectra for TCTI and HCTI: (a) measured on the (010) plane for TCTI and (b) on the (1-10) plane for HCTI.*

### Polarized Reflection Spectra Measured on Single Crystals and Interactions Between Transition Dipoles

Figures 3 (a) and 3 (b) show the polarized reflection spectra measured on the (010) plane for TCTI and on the (1-

10) plane for HCTI (Fig. 2) together with their solution spectra, respectively. In TCTI, a prominent reflection band appears around 590 nm accompanied by a reflection shoulder around 540 nm for polarization parallel to the molecular plane. The spectral shape of the present band is very similar to that of the solution spectrum, although the absorption bands are displaced toward longer wavelengths by about 44.5 nm (about 1358 $cm^{-1}$). On the other hand, no noticeable reflection could be observed for polarization along the stacking axis. These results clearly indicate that transition dipole lies on the molecular plane along the long-molecular axis as characterized by the HOMO/LUMO $\pi$-$\pi$* transition as shown in Fig.1. The longer-wavelength band (590 nm) is then attributed to the 0-0 transition and the second longer-wavelength band (540 nm) to the 0-1 transition. On the other hand, the complete quenching of the reflection band for polarization perpendicular to the molecular plane (*i.e.* along the stacking axis) evidently indicates that no CT transition is operative along the stacking axis. This clearly rules out the formation of CT excitons, as opposed to the prediction given by Fukushima and others.[2]

In HCTI, the spectroscopic behavior is quite similar to that of TCTI. A strong reflection band is present around 600 nm together with a reflection shoulder around 550 nm for polarization parallel to the molecular plane. The bathochromic displacement of about 38 nm (1095 $cm^{-1}$) is also observed on going from solution to the solid state. On the other hand, no noticeable reflection could again be observed for polarization parallel to the stacking axis. The above results of HCTI lead us to the same conclusion as that of TCTI: the electronic transition is purely due to the HOMO/LUMO $\pi$-$\pi$* transition on the molecular plane and no CT transition is operative along the stacking axis.

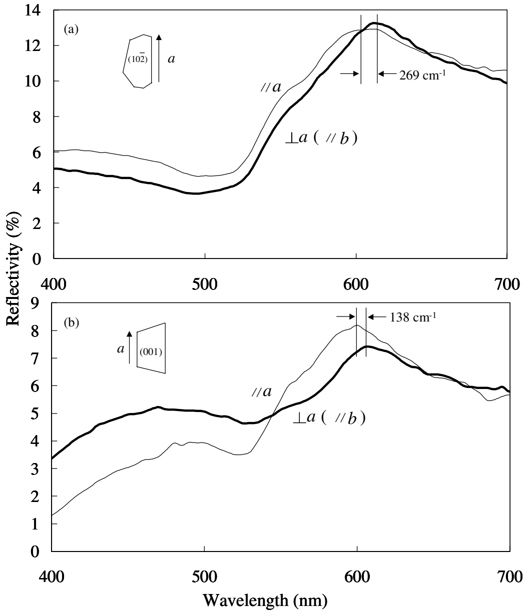

*Figure 4. Polarized reflection spectra: (a) measured on the (10-2) plane for TCTI using polarized light parallel to the a and b-axes. (b) measured on the (001) plane for HCTI using polarized light parallel to the a and b-axis.*

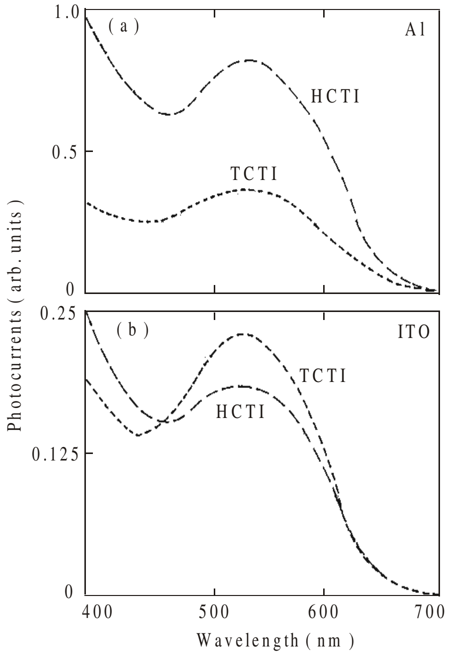

*Figure 5. Photoconduction spectra measured in evaporated thin films of TCTI and HCTI: (a) Al electrode and (b) ITO electrode.*

Since the molar extinction coefficient of thioindigo derivatives is in general quite large over 20000, the resonance interaction between transition diploes[7] is most likely to occur in the solid state. The bathochromic or hypsochromic shift will occur due to interactions between transition dipoles in translationally-equivalent molecules, depending on the slip angle of the transition dipoles where the critical angle is 54.7°. On the other hand, the Davydov splitting will result due to an oblique arrangement of the transition dipoles in translationally-inequivalent molecules. The Davydov splitting can easily be confirmed in polarization experiments based on single crystals and serves as evidence of short-range coherence of exciton packets. Furthermore, the existence of Davydov splitting acquires an extended significance that the excitonic interaction is also occurring between translationally-equivalent molecules. For this reason, measurements were also made on the (10-2) plane of TCTI (Fig.4(a)) and on the (001) plane of HCTI (Fig. 4(b)).

The polarized spectra shown in Figs. 4(a) and 4(b) clearly support the Davydov splitting as shown by the difference in reflection maxima for different polarizations around 605-615 nm in TCTI and around 600-605 nm in HCTI. In both TCTI and HCTI, the reflection bands are displaced toward longer wavelengths for polarization perpendicular to the *a*-axis (//*b*-axis) as compared with those for polarization parallel to the *a*-axis. The split energies for TCTI and HCTI are about 269 and 138 $cm^{-1}$ (Fig. 4), respectively. The existence of the Davydov splitting provides further evidence that the resonance interaction is also occurring between translationally-equivalent molecules. In reality, the resonance interactions between translationally-equivalent molecules as well as translationally-inequivalent ones are superimposed in complicated ways in the actual reflection spectra. Another important factor that governs the optical absorption in the solid state is the effect called "crystal shift" on going from solution to the solid state. This is due to the "van der Waals" stabilization energy in the ground state as well as in the excited state, leading to the spectral shift.[7] It is, however, an intractable task at the moment to analytically estimate the crystal shift as well as spectral displacements or band splitting due to resonance interactions between transition dipoles.

The discussions mentioned above suggest qualitatively that the interactions between transition dipoles as well as the crystal shift are responsible for the bathochromic displacement upon crystallization in TCTI and HCTI.

### Photoconductivity in Evaporated Thin Films

Figures 5(a) and 5(b) show the photoconduction spectra for TCTI and HCTI when Al and ITO electrodes were used, respectively. The photoconduction appears nearly in accordance with the reflection spectra shown in Fig. 3. The photoconductivity is four times higher when Al electrodes are used in both TCTI and HCTI as compared with that based on ITO electrodes. In addition, HCTI is more photoconductive with Al electrodes than TCTI while the reverse is the case with ITO electrodes. The present result that the photoconductivity depends greatly on the electrode material indicates that the dissociation of Frenkel excition takes place mostly at the Schottky barrier formed between TCTI (or HCTI) and the electrode.

The above results indicate that the dissociation of the Frenkel exciton in the photoreceptor plays the key role in the electrophotographic photosensitivity. Because the TCTI or HCTI-dispersed CGL is prepared on an Al electrode and the common CTL comprising *N,N'*-dipenyl-*N,N'*-bis(2,4-dimethylphenyl)-1,1'-biphenyl-4,4'-diamine is used in the photoreceptor (structure: Al/CGL/CTL), the interface between CGL and CTL is directly responsible for the difference in carrier formation between TCTI and HCTI-based photoreceptors. Then, we are forced to assume that the charge transport material that Fukushima used for the photoreceptor is quite appropriate for TCTI, but presumably not for HCTI. For this reason, even in HCTI-based photoreceptors, an equivalent electrophotographic gain to that of TCTI can basically be achieved if the charge transport material is optimized for HCTI.

## Conclusions

Electronic characterization of TCTI and HCTI has been investigated on the basis of the polarization measurements on single crystals. The conclusions of the present investigation can be summarized as follows.

1. The electronic transition of TCTI and HCTI in the solid state is totally due to the HOMO/LUMO $\pi$-$\pi$ * transition. No CT transition is operative along the stacking axis in both compounds. In addition, no noticeable difference in electronic structure is recognized between TCTI and HCTI.
2. The photoconductivity of TCTI and HCTI is found to be equally high and depend greatly on the electrode material, suggesting that the exciton can mostly be dissociated at the Schottky barrier between TCTI (or HCTI) and the electrode.
3. The high electrophotographic gain of TCTI is presumably due to an efficient carrier formation or injection at the CGL/CTL interface. An equivalent high photosensitivity can also be expected for HCTI-based photoreceptors if the charge transport material is optimized for HCTI.

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## Biography

Jin Mizuguchi obtained his B. Sc. in chemistry from Sophia University in 1970, Dr. of Science from the University of Tokyo in 1982 and Venia Docendi from the University of Bern in 1994. He worked at Sony Corporation Research Center from 1970 to 1985 and at Ciba-Geigy AG (Switzerland) from 1985 to 1995. Since 1995, Prof. Mizuguchi has been at Yokohama National University as professor of materials science.