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Reflection and Photoconduction Spectra of the Single Crystals of Perylene-TCNQ 1:1 and 3:1 Molecular Complexes

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Crystal absorption spectra of the two modifications of the perylene-TCNQ (7,7,8,8-tetracyanoquinodimethan) complex were derived from reflection spectra by the Kramers-Kronig transformation and are discussed in relation to the differences in the crystal structures. The spectral response of photoconduction does not show any efficient photocarrier generation in the lowest charge-transfer band region in either modification. However, the rise of the photocurrent of both modifications was found to obey an empirical equation, $Y \propto (E-E_{\mathrm{th}})^{2.5}$, where Y is the quantum yield of the photocarrier generation, E is the photon energy, and E_{th} is the threshold energy. E_{th} of the two modifications is almost the same and falls in the energy region a little above the lowest charge-transfer band. Efficiencies of the carrier generation, on the other hand, are quite different for the two modifications. These photoelectrical characters are discussed in connection with the optical spectra and also with the data of photoelectron emission.

Photoconduction in the charge-transfer (CT) complex has been studied for a number of complexes since Akamatu and Kuroda reported the photoconduction in the complexes of pyrene with some electron acceptors.[1–17] As for the mobility of the charge carriers, some features arising from the one-dimensionality of the crystal structure have been observed for some complexes.[15–17] However much less has been known about the mechanism of the carrier generation.[14] Photoelectric responses have been observed for some complexes in the region of the lowest CT-band, while some other complexes show photoelectric response only in the higher-energy regions. It has been inferred that the higher CT-states, in which the charge transfer occurs to acceptor molecules farther than the nearest neighbor of a donor, play an important role in the carrier generation.[10] However, no clear evidence has been obtained for such an inference.

Perylene and TCNQ have been found to form a 3:1 complex[18] as well as the well known 1:1 modification.[7,19] The crystal structure of the former (Fig. 1b)[20] has two characteristics as compared with the usual CT-complexes. First, the stacks of perylene–the donor(D)– and TCNQ–the acceptor(A)– are composed of DAD units. The CT-interaction between the donor and acceptor molecules seems to be confined within a DAD unit. Secondly, there are additional arrays of perylene molecules between the stacks of perylene and TCNQ, the orientation of those perylene molecules being almost perpendicular to the molecules forming the stacks. Consequently, the interaction between the stacks is blocked by those additional perylene molecules, which are hereafter called *interstitial* perylene molecules.

In this paper, we report the reflection and photoconduction spectra of the single crystals of the two modifi-

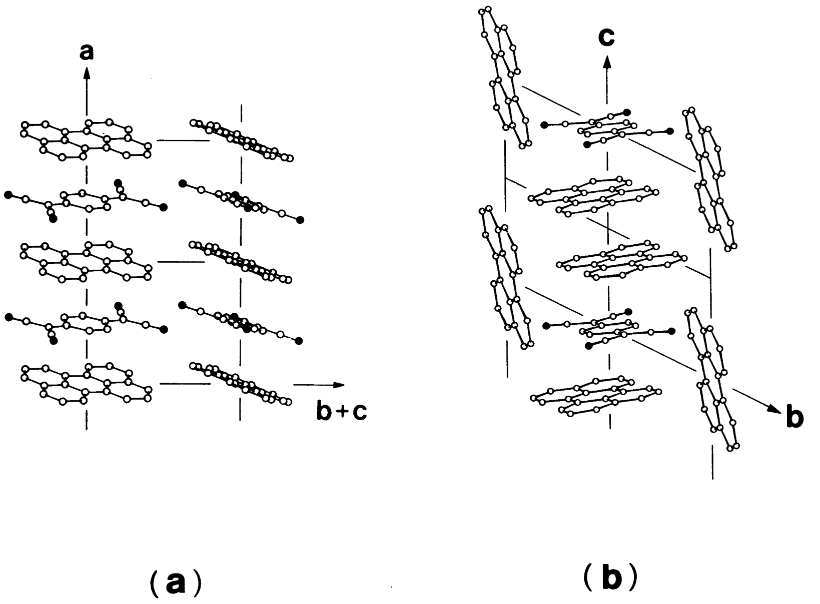

Fig. 1. Crystal structures of the two modifications of the perylene-TCNQ complex, (a) 1 : 1, (b) 3 : 1.

cations of the perylene-TCNQ complex, and discuss the threshold energies of the photocarrier generation in these crystals. The nature of the higher CT-states and the process of the carrier generation through those states are also discussed in connection with the crystal structures.

Experimental

Perylene was purified from Aldrich gold-label reagent by column chromatography on active alumina using xylene as the eluent, and then by the sublimation in the vacuum. TCNQ obtained from Tokyo Kasei was purified successively by the recrystallization from acetonitrile and by the repeated sublimation in the vacuum.

Crystals of the 1:1 modification were obtained by the recrystallization from an equimolar solution in tetrahydrofuran or by the sublimation in the vacuum. Crystals of the 3:1 modification were obtained by the diffusion method in benzene or by the recrystallization in the same solvent. In the diffusion method, perylene and TCNQ were separately charged in two branches of a sealed U-shaped tube filled with benzene, and then it was maintained at about 30 °C for several weeks. The 3:1 modification was also obtained by slowly evaporating the benzene solution containing an excess amount of perylene.

Both the 1:1 and 3:1 crystals were dark-blue crystals with metallic lusters, but their crystal-formation habits were totally different. The 1:1 modification usually crystallizes as needle-like crystals elongated along the c-axis, whereas the 3:1 modification crystallizes as small blocks. The above-mentioned two kinds of crystals were confirmed by X-ray diffraction to be identical with the known 1:1 and 3:1 modifications.[19,20]

Polarized reflection spectra of single crystals of the two modifications were measured at room temperature with a microspectrophotometer, details of which have been previously reported.[21] Single crystals of silicon were used as the standard of the reflectivity.[22]

The photocurrent of the single crystals was measured at room temperature with a Keithley 602 electrometer or a Cary 401 vibrating-reed electrometer by a two-probe method with an arrangement of the so-called surface type. Electrical contacts onto the crystals were made with colloidal silver. Typical conditions of the electric field and the cross section of the crystal were 100 V across an electrode gap of 1 mm and 0.2 mm^2. Measurements were carried out in a nitrogen atmosphere. Spectral response of the photocurrent was measured with a monochromatized light source equipped with a 150 W tungsten-iodine lamp and a neutral filter with a variable density. It gave a constant flux of photons at any wavelength in the visible and near-infrared regions. The spectral width of the monochromator was about 6 nm (240 cm^{-1}) at 500 nm.

Results and Discussion

Reflection Spectra. Figures 2 and 3 show the reflection spectra of the $(01\bar{1})$ face of the 1:1 modification and of the (100) face of the 3:1 modification, respectively. Each figure shows the spectra measured respectively for the light polarizations parallel and perpendicular to the stacking axis (a-axis of the 1:1 modification and c-axis of the 3:1 modification). Recently, Bandrauk and his coworkers[23] reported the reflection spectra of the two modifications of the perylene-TCNQ complex. Their results are different in some respects from ours. In their c-polarized spectrum of the bc-plane of the 3:1 modification, the peak reflectances of the CT-band as well as those of the local-excitation bands are much smaller than our results. In addition, there appears a small dispersion around 500 nm in their spectrum obtained for another light polarization on the same crystal plane. We could not observe such a dispersion for any light polarization on the (100) face (bc-plane) of the 3:1 modification, but observed a similar dispersion in the spectra taken on another crystal face which is considered to be the (001) face (ab-plane).

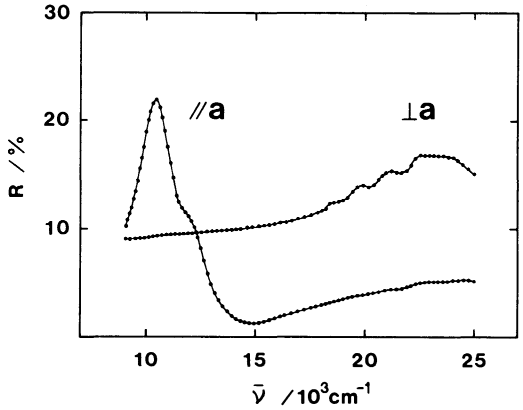

Fig. 2. Reflection spectra of the $(01\bar{1})$ face of the 1 : 1 modification with the polarizations along and perpendicular to the stacking axis (a-axis).

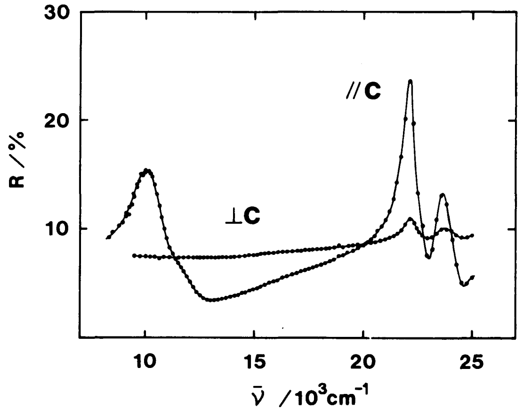

Fig. 3. Reflection spectra of the (100) face of the 3 : 1 modification with the polarizations along and perpendicular to the stacking axis (c-axis).

From the observed reflectivity data, we calculated the optical constants by the Kramers-Kronig transformation, assuming simple dispersions of the optical constants outside of the energy region where the measurement was carried out.[21] Optical constants near the upper limit of the experiment (25×10^3 cm^{-1}), therefore, naturally contain some ambiguity on account of this assumption. Absorption spectra thus calculated of the $(01\bar{1})$ face of the 1:1 modification are shown in Fig. 4. The lowest-energy band is almost completely polarized along the stacking axis (a-axis). It has the peak at 10.6×10^3 cm^{-1} and a shoulder around 12×10^3 cm^{-1}. The peak molar extinction coefficient is 2.4×10^4 dm^3 mol^{-1} cm^{-1}. According to the polarization, this band must arise from the CT-transition between the perylene and TCNQ stacking in a column.

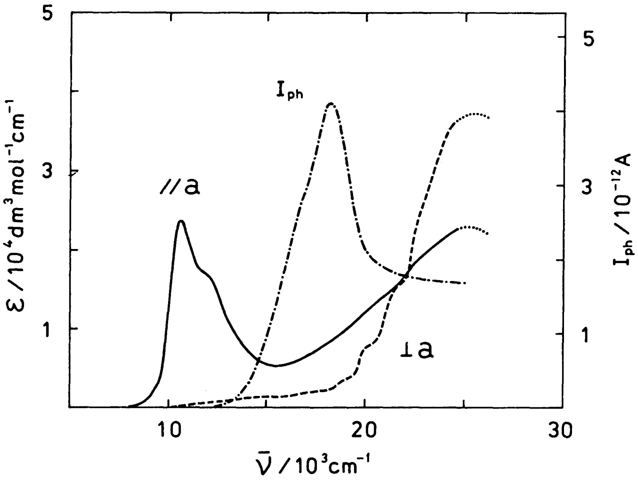

Fig. 4. Absorption spectra on the $(01\bar{1})$ face of the 1 : 1 modification with the polarization along (——) and perpendicular (----) to the stacking axis (a-axis), and photoelectric response (—·—) of the same modification.

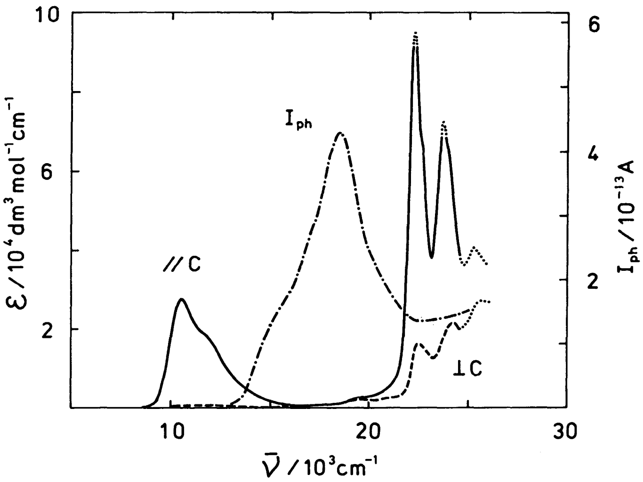

Fig. 5. Absorption spectra on the (100) face of the 3 : 1 modification with the polarizations along (——) and perpendicular (----) to the stacking axis (c-axis), and photoelectric response (—·—) of the same modification.

The energy difference between the peak and the shoulder suggests that this shoulder may be a vibrational structure, but there remains a possibility that it is related to a higher CT-state. The nature of this shoulder will be discussed later in connection with the spectrum of the 3:1 modification. As is seen in the ⊥a spectrum, local-excitation transitions of the perylene and TCNQ arise above 19×10^3 cm^{-1}. Note that the absorption at the higher-energy side of the CT-band in the //a spectrum does not completely decay but is followed by an absorption which gradually increases its intensity until the local-excitation region above 19×10^3 cm^{-1}. This implies that, in the above-mentioned region, there are some more electronic transitions polarized along the stacking axis. They may be mixed states between higher CT-states and the local-excitation states.

Absorption spectra on the (100) face of the 3:1 modification were similarly calculated from the reflection spectra (Fig. 5). The lowest-energy band of this modification, polarized along the c-axis, has a strong resemblance to the corresponding band of the 1:1 modification, and can be assigned to the CT-transition between perylene and TCNQ stacking in a column. It has the peak at 10.5×10^3 cm^{-1} and a shoulder around 12×10^3 cm^{-1}. The peak molar extinction coefficient is 2.8×10^4 dm^3 mol^{-1} cm^{-1}. The higher-energy side of the above shoulder decays clearly, and does not show any absorption which continues to the local-excitation region.

The similarity and the differences between the CT-bands of these two modifications may be understood by comparing their crystal structures[19,20] which have already been described. Electronic overlaps between the donor and acceptor of the nearest neighbor are similar in the two modifications. However, the interactions with the molecules in the second nearest unit and the farther units are by no means the same. It is therefore inferred that the lowest CT-states in the two modifications are similar, but that some differences may be seen for the higher CT-states. These are the features seen in the observed spectra if we consider that the shoulders around 12×10^3 cm^{-1} are the vibrational structures of the lowest CT-bands and that the absorption in the region of 15×10^3—20×10^3 cm^{-1} in the //a spectrum of the 1:1 modification is associated with the higher CT-states. Very weak absorption in the same region in the spectra of the 3:1 modification suggests the small transition probabilities to the higher CT-states in this modification.

Pronounced peaks are seen in the local-excitation region in the //c spectrum of the 3:1 modification. The peak wave numbers, 22.2 and 23.7×10^3 cm^{-1}, fall between the corresponding wave numbers[24] of the absorption peaks of perylene in the solution and the α-perylene crystal which is composed of perylene molecules with a dimer-type conformation. Taking account of the polarization of the above peaks and the crystal structure, those peaks are assigned to the transitions in the interstitial perylenes. Molar extinction coefficients at the peaks of these bands could not be estimated accurately because the interval of the experimental points of the reflection spectrum was not small enough compared with the band width. However, they seem to be almost three times as large as the extinction coefficients of the corresponding peaks in the solution spectrum,[24] which is in harmony with a simple expectation based on the oriented-gas model. These observations indicate the weakness of the interaction of the interstitial perylenes with other molecules in the stacks.

Photoconduction of the 1:1 Modification. The spectral response of the photocurrent of the 1:1 modification obtained by the recrystallization from tetrahydrofuran is shown in Fig. 4. A crystal obtained by the sublimation method gave an almost similar result. These spectral-response curves qualitatively agree with those of needle crystals reported by Vincent and Wright.[7,25] The curve shows a peak around 18×10^3

cm^{-1} with a long tail in the small wave-number side. Note that excitation in the lowest CT-band region seemingly does not give rise to a photocurrent efficiently. The photocurrent, I_{ph}, changed nonlinearly against the intensity of the excitation light, L, as follows:

$$I_{\mathrm{ph}} = aL^n, \tag{1}$$

where a is a constant and n was 0.4—0.6 depending on the crystal. This result indicates that the steady-state photocurrent in our crystals was affected by the presence of charge-carrier traps.[26] However the dominant mechanism of the carrier generation may not be the detrapping of the carriers by the excitons, because no large photoelectric response was observed around the lowest CT-band region.

Energy for the charge-carrier generation in molecular crystals has been estimated by Lyons' scheme.[27,28] This scheme also seems applicable to weak molecular complexes.[29,30] Figure 6 illustrates this idea for the perylene-TCNQ complexes, where I_c=5.7 eV[31] is the adiabatic photoelectron-emission threshold and E_A=2.8 eV[32] is the electron affinity of TCNQ. Since the direct measurement of P^-, the polarization energy of the TCNQ anion in the complex, is practically difficult,[30] we roughly estimated it by assuming that P^- is the same as P^+, the polarization energy of the perylene cation in the complex. The latter was estimated to be 1.2 eV from the difference between I_c and the ionization potential of perylene molecule.[33–35] Thus the energy for generating a pair of thermally relaxed charge carriers, $I_c - E_A - P^-$, is estimated to be 1.7 eV (14×10^3 cm^{-1}). The photocurrent in Fig. 4 does not show efficient response at this energy. One must, however, examine the threshold region of the spectral response more precisely.

It has been empirically found[27] that the quantum yield, Y, of the photocarrier generation in some molecular crystals around the threshold is given by

$$Y = b(E-E_{\mathrm{th}})^{2.5}, \tag{2}$$

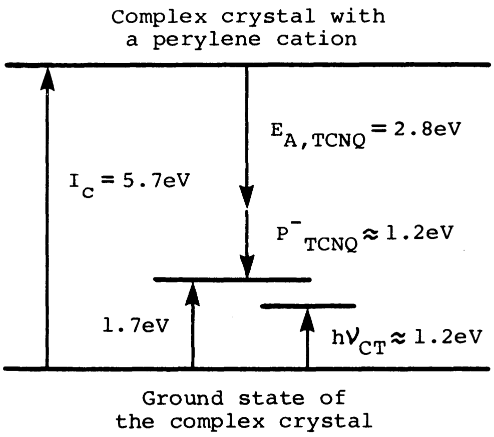

Fig. 6. Energy diagram for estimating the threshold energy of the carrier generation in the 1 : 1 modification, where I_c is the ionization potential of the 1 : 1 complex, $E_{A,\mathrm{TCNQ}}$ is the electron affinity of TCNQ, and P^-_{TCNQ} is the assumed polarization energy for TCNQ$^-$ in the complex crystal (see the text). Threshold energy is estimated to be 1.7 eV. $h\nu_{\mathrm{CT}}$ shows the approximate level of the lowest CT-state.

where E is the photon energy, E_{th} is the threshold energy of the carrier generation, and b is a constant. In our experiment, we utilized a light source by which a constant photon flux, L_0, was obtained at each wavelength studied. The photocurrent spectrum reflects, then, the quantum yield of the carrier generation, as follows:

$$I_{\mathrm{ph}}(E) = c\{L_0Y(E)\}^n, \tag{3}$$

where n is the number appeared in Eq. (1), and c is a constant. We therefore plotted $I_{\mathrm{ph}}^{1/2.5n}$ against the photon energy. Curve A in Fig. 7 shows the result thus plotted in the threshold region for the 1 : 1 modification. A straight line can been seen in the region above 14×10^3 cm^{-1}. Extrapolation of this line gives the value of E_{th} to be 13.8×10^3 cm^{-1} (1.71 eV). Deviation from the line in the smaller-energy region may arise from some extrinsic carrier generations which involve the carrier traps at the impurity sites. The E_{th} value obtained above agrees well with the energy for the carrier generation estimated from the photoemission data and is a little larger than the peak energy of the lowest CT-band.

CT-Excitons have the character of a Wannier exciton. If one took a one-electron scheme,[27] the threshold of the carrier generation might be found at an energy where the series of the higher CT-states (larger Wannier excitons) converges. A simple consideration indicates that the lowest CT-state is more stable by approximately $e^2/2\varepsilon R$ than this energy, where R is the distance between the nearest donor-acceptor couple and ε is the dielectric constant of the crystal along the stacking axis. This difference may be as large as 1 eV. The threshold of the photoconduction, then, would be expected at an energy much higher than the lowest CT-band. This does not agree with the experimental observation. This discrepancy may be understood if one thinks about the relaxation from higher CT-states to the pair of the thermally relaxed charge carriers. In CT-complexes, CT-excitations contribute an non-negligible amount to the total polarizability of the crystal.[21] The polarization energy gained by localizing a unit charge in a molecular crystal is as large as 1 eV.[34]

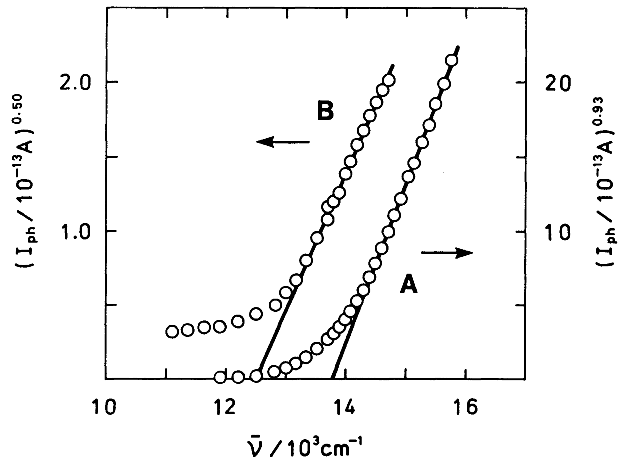

Fig. 7. (A) Plot of $I_{\mathrm{ph}}^{1/2.5n}$ for the 1 : 1 modification. The number n (see the text) was 0.43 for this crystal. (B) $I_{\mathrm{ph}}^{1/2.5n}$ for the 3 : 1 modification. n was 0.80 for this crystal.

Then the energy gain by relaxing the higher CT-states to a pair of charge carriers may be as large as several tenths of 1 eV. This energy may compensate a considerable part of the energy difference between the higher CT-states and the lowest CT-state. This may be the reason why we observed the threshold of the photocarrier generation only a little above the lowest CT-band.

Photoconduction of the 3:1 Modification. The spectral response of the photoconduction of the 3:1 modification is shown in Fig. 5. Although this spectrum is similar to that of the 1:1 modification, the photocurrent is smaller by one or two orders of magnitude, though the experimental conditions were similar. $I_{\mathrm{ph}}^{1/2.5n}$ plotted for the threshold region is shown in Fig. 7 (curve B). There seems a threshold of the carrier generation at 12.5×10^3 cm^{-1} (1.55 eV). Small shoulders of photocurrent are seen around 15 and 17×10^3 cm^{-1} in Fig. 5. They suggest that some density of states related to the initial step of carrier generation are located around those energies. These may be mixed states of the higher CT-states and the local-excitation states. The threshold energy is smaller than that of the 1:1 modification, but the difference is not large. This is reasonable because the stabilization of the valence electrons in the crystal and also the polarization energies of the charge carriers are inferred to be almost the same in the two modifications.

The spectral response shows that the efficiency of the photocarrier generation is small around the threshold region and larger in the region of the higher CT-states. This may be easily understood if one considers a competition between the carrier generation through the CT-states and the deactivation of these states. The molar extinction coefficient of the lowest CT-band is very large although it is an intermolecular transition. Then, the radiative deactivation may be fast and the probability of the carrier generation from this state may be small, even if the thermal energy required to activate the carrier generation from this state were very small. For the higher CT-states, the transition dipoles to the ground state are small, and the thermal relaxation easily causes the localization of the electron and generates the charge carriers.

The small photoelectric response of the 3:1 modification compared with the 1:1 modification may be explained in terms both of the carrier generation and of the mobility. The weak absorption in the intermediate region between the lowest CT-band and the local excitation region in the absorption spectra of the 3:1 modification (Fig. 5) seems to indicate the small transition probabilities to the higher CT-states and then the smaller probability of the photocarrier generation. The crystal structure of the 3:1 modification obviously does not favor the carrier transport either.

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