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THE OPTICAL STUDY OF THE THERMOCHROMISM OF THE CT CRYSTAL BETWEEN BI(ANTHRACENE-9,10-DIMETHYLENE) AND TCNQ

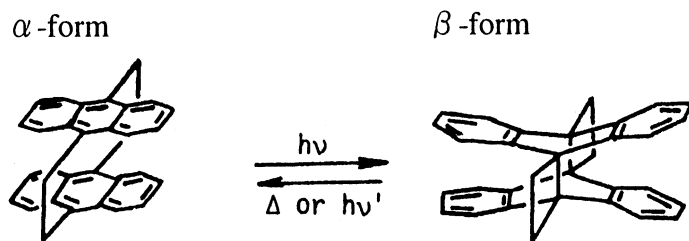
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The thermochromism and photochromism of the bi(anthracene-9,10-dimethylene) (BADM) crystal were studied by the measurement of the temperature-variable and time-variable IR and the thermochromism of the charge transfer(CT) complex crystal between BADM and tetracyanoquinodimethane(TCNQ) was studied by the temperature variable IR measurement.

Keywords: thermochromism; photochromism; CT crystal; IR spectra

INTRODUCTION

Golden obtained an orange solid of BADM [1]. This orange crystal (α -form) shows the photochromism and gives rise to a colorless solid isomer (β -form). Furthermore, the β -form shows the thermochromism and reacts to the α -form as is shown in the scheme. We made the black crystal of the CT complexes of BADM with TCNQ and discovered the thermochromism of the black crystal. We measured the IR spectral change and the DSC and



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TGA curves of the α -form of BADM on lighting and the β -form on heating. Furthermore, we report the DSC and TGA curves and the temperature-variable IR spectra of the CT complex on the thermochromism.

RESULTS AND DISCUSSIONS

1. The DSC and TGA Measurement of the α and β -forms of BADM

The DSC and TGA curves of the α -form of BADM and the β -form photo-reacted from the α -forms of BADM are shown in Figure 1.

The α -form of BADM has a exothermic peak at 262.8°C with the melting energy of $\Delta H = 22.2$ kJ/mol. The β -form photoreacted from the α -form of BADM has two exothermic peaks at 113.7°C and 263.0°C. The first peak at 113.7°C means the $\beta \rightarrow \alpha$ transition of BADM crystal with the transition energy of 21.5 kJ/mol and the second peak at 263.0°C corresponds to the melting point of α -forms of BADM. The figure shows that the β -form transforms to the α -form at 113.7°C and the α -form does not change to the β -form by heating.

2. The IR Spectra of the α - and β -forms of BADM

The α - and β -forms of BADM are shown in Figures 2 and 3. The α -forms has the characteristic bands of three aliphatic stretching bands (νCH_2) at 2866, 2928, and 2970 cm^{-1} and one aromatic stretching band ($\nu\text{C-H}$) at 3063 cm^{-1} . The in-plane bending (scissoring) band ($\delta_s\text{CH}_2$) can be

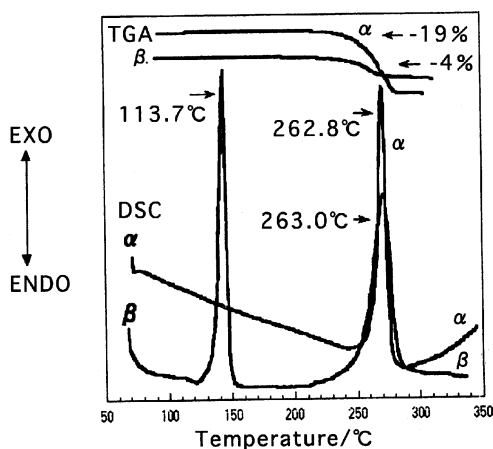


FIGURE 1 The DSC and TGA curves of the BADM crystals.

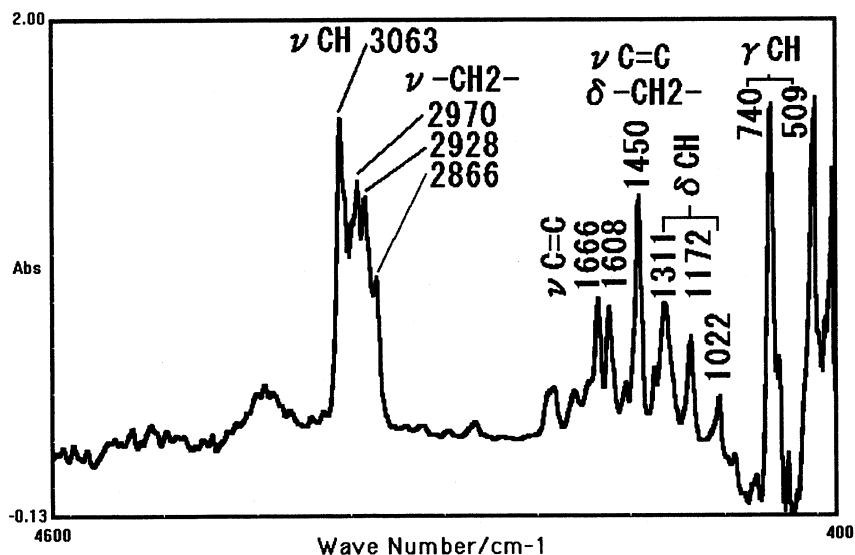


FIGURE 2 The IR spectrum of the α -form of BADM.

observed at 1450 cm^{-1} and the wagging bands $(\omega\text{CH})_2$ at 1311 and 1172 cm^{-1} . Furthermore, the out of plane bending (twisting) band (γCH_2) are at 740 cm^{-1} . These all IR spectra are taken by the micro IR photometer made by JASCO.

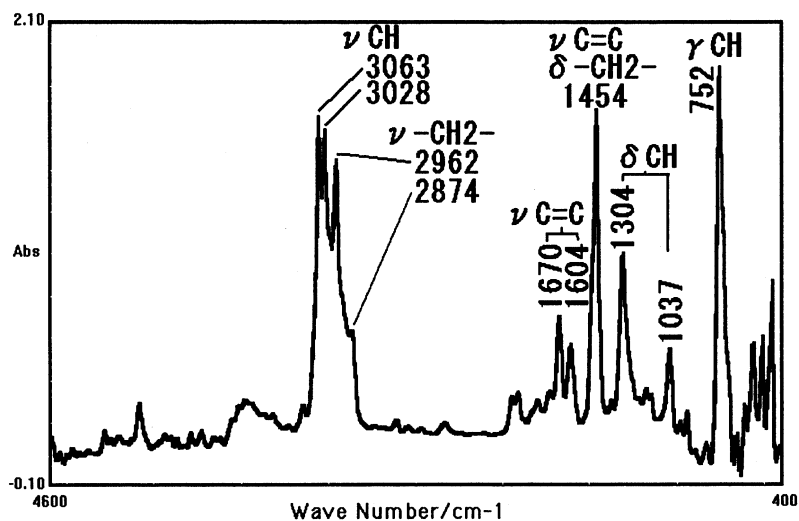


FIGURE 3 The IR spectrum of the β -form of BADM.

The β -forms has the characteristic bands of two aliphatic stretching bands (νCH_2) at 2874, and 2962 cm^{-1} and two aromatic bands ($\nu\text{C-H}$) at 3028 and 3063 cm^{-1} . The in-plane bending (scissoring) band ($\delta_s\text{CH}_2$) can be observed at 1454 cm^{-1} and the wagging bands (ωCH_2) at 1304 and 1037 cm^{-1} . The out of plane bending (twisting) band (γCH_2) are located at 752 cm^{-1} . Many peaks of the anthracene and 9,10-bi-anthracene molecules can not be observed in region of 1000 to 800 cm^{-1} . The comparison between the IR spectra of the α - and β -forms of BADM shows that the big differences are observed at the aromatic stretching band and the aliphatic twisting band. That is, the β -forms has the new aromatic bands ($\nu\text{C-H}$) at 3028 cm^{-1} and the α -forms has the aliphatic stretching bands (νCH_2) at 2866 cm^{-1} . The α -forms decreases the intensity of the aliphatic scissoring band (δCH_2) at 1450 cm^{-1} .

3. The IR Spectral Measurement of the Photochromism of BADM Crystal

The IR spectra of the α -form of BADM were taken on each exposure time by the halogen light. The orange crystal transformed to the colorless crystal after about one hour. The time-variable behavior of the IR spectra on the light exposure is shown in Figure 4a. The C=C stretching band is observed intensely at 1615 cm^{-1} for the α -form but this band splits into two peaks at 1622 and 1601 cm^{-1} for the β -form by the photoreaction. The scissoring band ($\delta_s\text{CH}_2$) at 1464 cm^{-1} dose not change the peak intensities and the

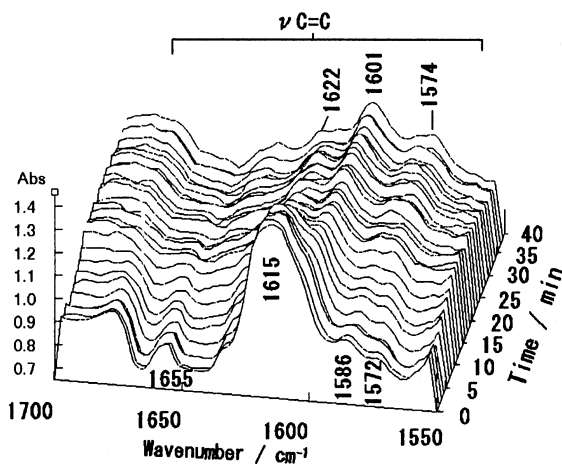


FIGURE 4a The IR spectral change of the photochromism of α -form (1700–1550 cm^{-1}).

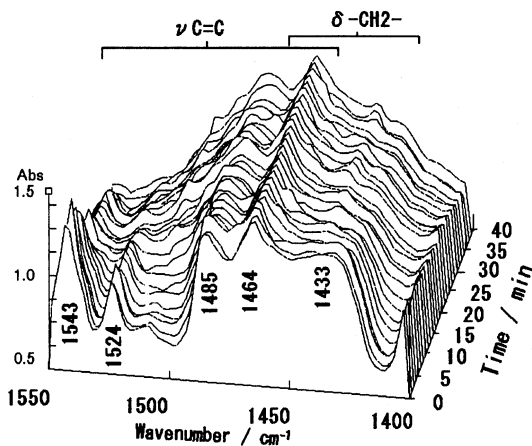


FIGURE 4b The IR spectral change of the photochromism of α -form (1550-1400 cm^{-1}).

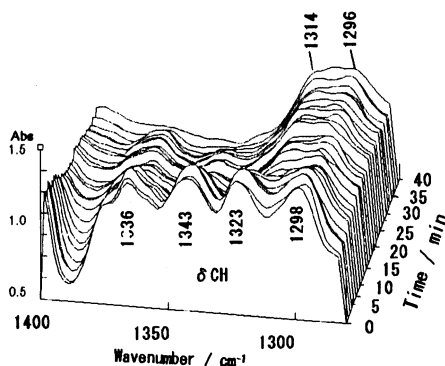


FIGURE 4c The IR spectral change of the photochromism of α -form (1400-1250 cm^{-1}).

peak location as is shown in Figure 4b. The in-plane aromatic bending bands ($\delta\text{C-H}$) are observed in the region of 1250-1300 cm^{-1} as is shown in Figure 4c. Two separated C-H band at 1336 and 1343 cm^{-1} disappears on light exposure and the bands at 1323 and 1294 cm^{-1} does not changes. The separated C-H bands at 1336, 1343, and 1323 cm^{-1} become one peaks at 1314 cm^{-1} as is shown in Figure 4d.

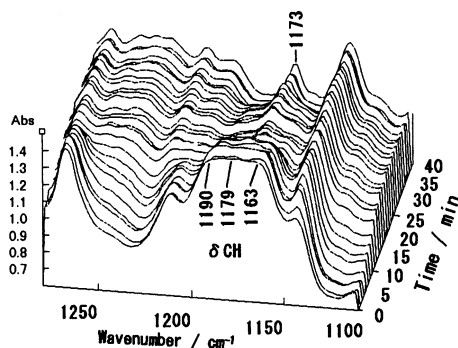


FIGURE 4d The IR spectral change of the photochromism of α -form (1300-1100 cm^{-1}).

4. The IR Spectral Measurement of the Thermochromism of the β BADM Crystal Obtained by the Photoreaction of the Halogen Lamp

The spectral behavior of the thermochromism of the β -form of BADM crystal has the relationship between the real image and the mirror image with the spectral behavior of the photochromism of the α -form. The examples are shown in Figures 5a and b.

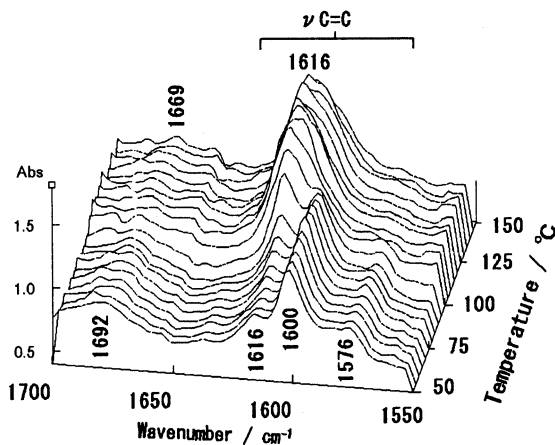


FIGURE 5a The IR spectral change of the thermochromism of β -form (1700-1550 cm^{-1}).

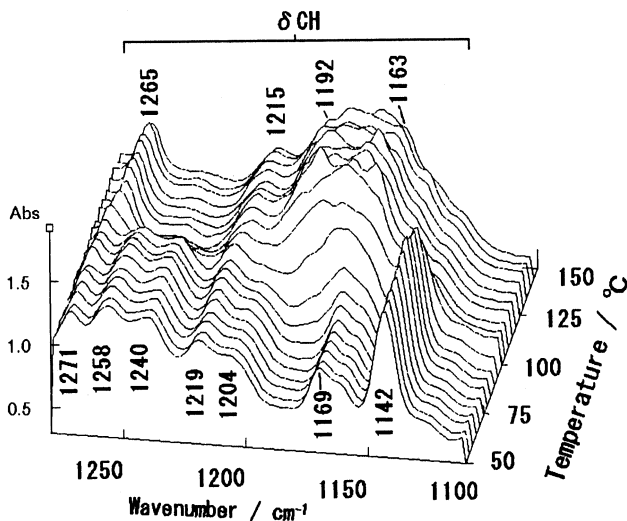


FIGURE 5b The IR spectral change of the thermochromism of β -form (1300–1100 cm^{-1}).

5. The DSC and TGA Measurement of the CT Complex of BADM with TCNQ

The thermochromism of the black crystal of the CT complex between BADM and TCNQ was studied by measuring the DSC and TGA curves. The DSC curve of the CT crystal has two peaks at 199 and 278°C as is shown in Figure 6. The black crystal change to the orange crystal at 199°C and the second peak is the melting point.

6. The IR Spectral Measurement of the Thermochromism of the CT Complex Crystal

The IR spectra of the α -form and β -form of BADM, and the CT complex crystal of BADM with TCNQ and the TCNQ molecule are shown in Figure 7. The IR spectra of CT complex has the aliphatic stretching bands (νCH_2) at 2908 and 2857 cm^{-1} and the aromatic C-H stretching band at 3063 cm^{-1} are similar to the band of the α -forms of the BADM. That is, the CT complex seems to have the stacking structure between one anthracene molecular plane of the α -form of BADM and one TCNQ molecule. The IR temperature-variable spectra (3300–2500 cm^{-1}) of the thermochromism of the CT complex crystal are shown in Figure 8a. The aliphatic stretching band (νCH_2) at 2857 cm^{-1} disappears over 200°C although another aliphatic stretching peaks (νCH_2) and the aromatic stretching peaks ($\nu\text{C-H}$) do not

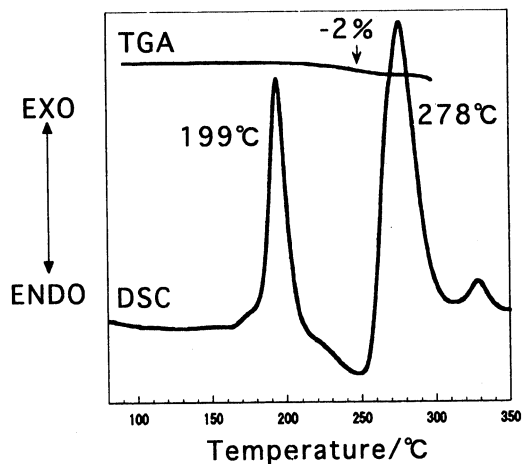


FIGURE 6 The DSC and TGA curves of the CT crystal.

change on heating. However, the $\text{C}=\text{C}$ stretching band at 1615 cm^{-1} shifts to the higher wave-number region over the transition point (about 200°C) as is shown in Figure 8b. Such shifts of the IR bands can be explained by the thermal behavior of the $\text{C}\equiv\text{N}$ stretching band of the TCNQ as is shown

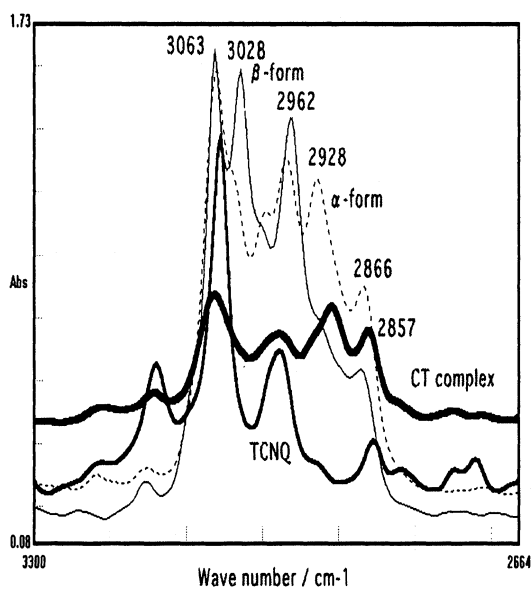


FIGURE 7 The IR spectra of the α - and β -forms and CT complex and TCNQ.

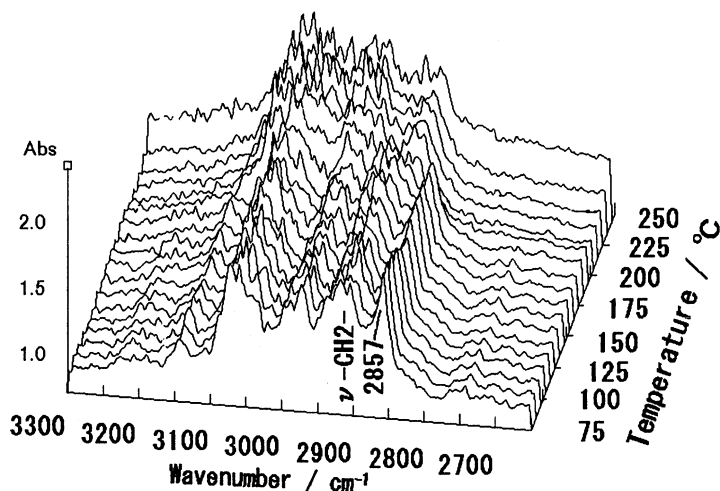


FIGURE 8a The IR temperature-variable spectra of the CT complex crystal ($3300\text{--}2500\text{ cm}^{-1}$).

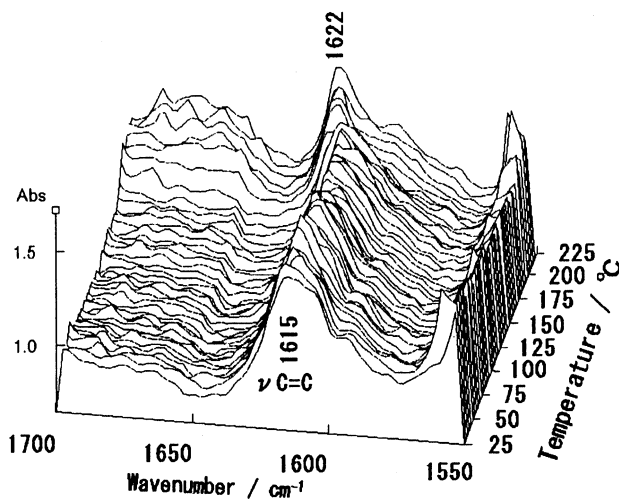


FIGURE 8b The IR spectral change of the thermochromism of the CT crystal ($1700\text{--}1550\text{ cm}^{-1}$).

in Figure 8c. Many CT complex of TCNQ were studied by measuring the IR spectra and the linear dependence of the $\text{C}\equiv\text{N}$ stretching wave-number on the formal charge was observed [2–3]. That is, the neutral TCNQ molecule (TCNQ^0) has the $\text{C}\equiv\text{N}$ stretching band at 2240 cm^{-1} and the

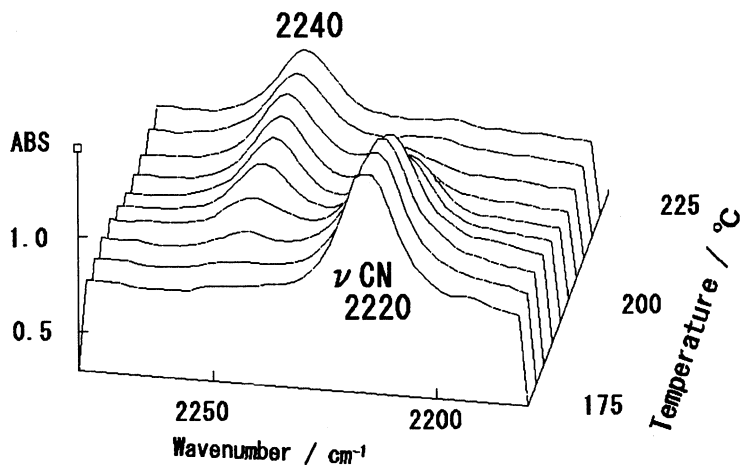


FIGURE 8c The thermal behavior of the $\text{C}\equiv\text{N}$ stretching band of the CT crystals ($2500\text{--}2000\text{ cm}^{-1}$).

ionized TCNQ(TCNQ^{-1}) has the $\text{C}\equiv\text{N}$ stretching band at 2220 cm^{-1} . This fact means that the TCNQ molecule in the CT complex is the anion (TCNQ^{-1}) at room temperature and becomes neutral after the transition point by heating. The CN stretching band of TCNQ shifts from 2220 cm^{-1} to 2240 cm^{-1} upon heating the CT crystal. This means the TCNQ^{-1} anion changes to the TCNQ^0 neutral molecule.

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