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Optical Properties and Thermochromism of the Crystals of Chloranil-Hexamethyl Benzene and Fluoranil-Perylene Charge-Transfer Complexes[#]

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The reflection spectra of the crystal of chloranil-hexamethyl benzene and fluoranil-perylene charge-transfer complexes were measured, and the charge-transfer degrees in these complexes were estimated. Furthermore, the polarized IR absorption spectra of these crystals were measured and compared with those of the powders of the complexes and the component compounds in the KBr disks. The thermochromism of these CT complex crystals was studied by differential scanning calorimetry and the IR spectra.

It is well known that *p*-benzoquinone and its derivatives form a charge-transfer complex with aromatic hydrocarbons. Some of them exhibit thermochromism. For example, benzo[*c*]cinnoline (Bc) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) give a charge transfer (CT) complex having the formula Bc_2DDQ. This CT crystal exhibits thermochromism at 138 °C.[1] The thermochromism at the solid phase of the CT complex has possible applications to molecular devices, such as a compact disk-write once-read many memory (CD-WORM). In the present paper, we report on the optical properties and the thermochromism of the chloranil (CHL)-hexamethylbenzene (HMB) and fluoranil (FLU)-perylene (PERY) CT crystalline complexes.

Experimental

The crystals were obtained as purple-red (CHL-HMB)[2] or bluish black (FLU-PERY)[3] needles by mixing equimolecular proportions of hot concentrated solutions of the two components in benzene, and allowing the mixture to slowly cool with a gradual evaporation of the solvent. The thermal treatment of the complexes was made by heating at 110 °C or 130 °C for a few minutes in air. Thermal analyses were carried out using a Shimadzu DSC-50 (a TGA-50) at a heating rate of 10 $°C\,min^{-1}$ under N_2 gas. The IR spectra were recorded using a JASCO FTIR VALOR-III as the single crystal and the KBr disk. The reflection spectra of the CHL-HMB and FLU-PERY crystals were taken using a polarized reflection spectrophotometer made in our laboratory.[4]

Results and Discussion

Optical Properties of the CHL-HMB Crystal. The crystal of the CHL-HMB complex has one donor (HMB) and one acceptor (CHL) in the unit cell, as shown in Fig. 1.[2] The donor and the acceptor form mixed stacked columns along the *a*-axis. The absorption spectra of the crystal of the CHL-HMB complex were recorded for light polarized both parallel and perpendicular to the *a*-axis, as is shown in Fig. 2. The depth of the crystal was estimated by measuring the peak interval of the interference pattern. The $\|a$-axis spectrum has a very broad absorption band at about 20000 cm^{-1} (ε=270 $dm^3\,mol^{-1}\,cm^{-1}$). The absorption spectrum for light polarized perpendicular to the *a*-axis has a maximum peak at 25000 cm^{-1}, which may be assigned to the n→π* band of chloranil. The reflection spectra are depicted in Fig. 3. The spectra do not show any apparent dispersion between 10000 and 30000 cm^{-1}. The reflectivity (R=0.05) of the crystal corresponds to a refractive index of n=1.57 for light polarized parallel to the *a*-axis. The oscillator strength can thus be defined as

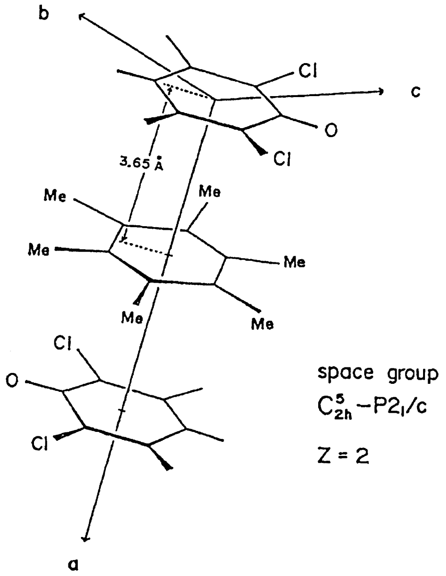

Fig. 1. View of the CHL-HMB crystal.[2]

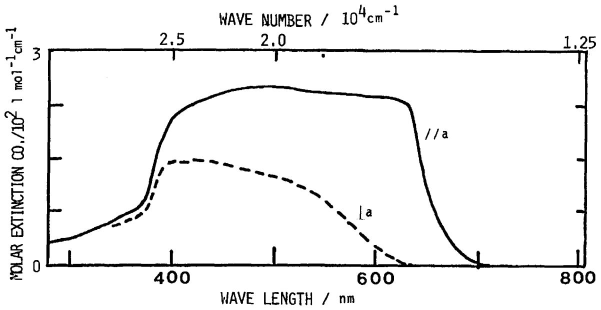

Fig. 2. Polarized absorption spectra of the CHL-HMB crystal.

[#] In memory of Professor Hiroshi Kato.

Table 1. IR Bands (cm^{-1}) of CHL, HMB, CHL-HMB Compounds in KBr Disks and CHL-HMB Crystal

KBr disk				Crystal		Assignement
$\tilde{\nu}/\mathrm{cm}^{-1}$	$\tilde{\nu}_0/\mathrm{cm}^{-1}$		$\Delta\tilde{\nu}=\tilde{\nu}-\tilde{\nu}_0$	$\tilde{\nu}/\mathrm{cm}^{-1}$		
Complex	CHL	HMB	cm^{-1}	$\parallel a$	$\perp a$	
3341 w	3359 m		−18		3393 s	CHL
	2924 m					CHL
2926 s		2907 vs	19	2955 vs	3009 vs	HMB C–H stretch.
		2853 vs			2924 s	HMB
2361 w	2361 w		0	2361 w	2361 w	CHL
1686 vs	1692 vs		−6	1686 w	1686 w	CHL C=O stretch.
1561 vs	1570 vs		−9	1561 s	1566 s	CHL C=C stretch.
1456 s		1464 s	−8	1443 s	1466 s	HMB $\mathrm{CH_3}$ deform.
1383 s		1377 s	6		1387 s	HMB
1248 m	1260 s		−12	1248 s	1248 s	CHL C–C stretch.
1225 m	1237 s		−12	1225 s	1227 s	CHL C–C stretch.
1206 w	1211 w		−5			CHL
1111 vs	1119 vs		−8	1115 m	1115 s	CHL C–Cl stretch.
		1059 w			1061 w	HMB $\mathrm{CH_3}$ deform.
990 w				992 m		HMB
903 w	907 m		−4	899 w	903 w	CHL
739 s	754 s		−15	737 s	745 s	CHL C–Cl stretch.
708 s	712 s		−4	702 m	695 w	CHL

† Doublet peak.

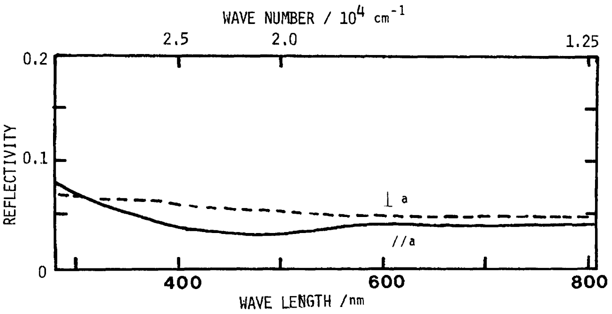

Fig. 3. Polarized reflection spectra of the CHL-HMB crystal.

$$f = 4.32 \times 10^{-9} \int n(\tilde{\nu})\varepsilon(\tilde{\nu})\mathrm{d}\tilde{\nu}. \qquad (1)$$

On the other hand, the oscillator strength for the CT transition of the donor–acceptor alternative stacking system can be expressed by the following equation:[5]

$$f = 3 \times 1.085 \times 10^{11} \times \tilde{\nu}_{\mathrm{CT}} b^2 |R_{\mathrm{AD}}|^2. \qquad (2)$$

Here, R_{AD} is the distance between the acceptor and the donor molecules in units of cm; $\tilde{\nu}_{\mathrm{AD}}$ is the excitation energy in units of cm^{-1}.

The observed oscillator strength of the CT band leads to $f=0.02$ by using Eq. 1 and a constant refractive index of $n=1.57$. The distance between CHL and HMB is $R_{\mathrm{AD}}=3.65\times10^{-8}$ cm and the excitation energy is $\tilde{\nu}_{\mathrm{CT}}=20000$ cm^{-1}. The charge-transfer degree was estimated to be $b^2=0.002$ by using Eq. 2.

Table 1 shows the IR vibrational bands of the complex and those of the component compounds in the KBr disks and in the single crystal. The bands assigned to chloranil are shifted to lower energy, while two bands at 2907 and 1377 cm^{-1} of HMB are shifted to higher energy, 2926 and 1383 cm^{-1}. The behavior of the spectra is in good agreement with those observed by Yamada and Kawamori.[6] The bands at about 3000 cm^{-1}, attributed to HMB, appears as a strong doublet at 3009 and 2924 cm^{-1} for light polarized perpendicular to the *a*-axis.

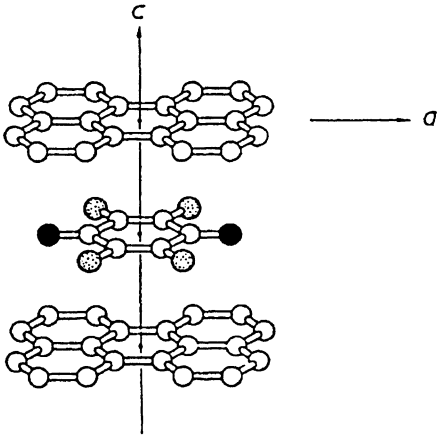

Fig. 4. View of the FLU-PERY crystal.[3]

Optical Properties of the FLU-PERY Crystal. The Crystal of the FLU-PERY complex has one donor (PERY) and one acceptor (FLU) in the unit cell, as shown in Fig. 4.[7] The donor and acceptor form mixed-stacked columns along the *c*-axis. The reflection spectra of the crystal of the FLU-HMB complex were recorded for light polarized parallel and perpendicular to the *c*-axis, as is shown in Fig. 5 (A). The $\parallel c$-axis absorption spectra shown in Fig. 5 (B) were obtained by

Table 2. IR Bands (cm^{-1}) of FLU, PERY, FLU-PERY Compounds in KBr Disks and FLU-PERY Crystal

KBr disk				Crystal		
$\tilde{\nu}/\mathrm{cm}^{-1}$	$\tilde{\nu}_0/\mathrm{cm}^{-1}$		$\Delta\tilde{\nu}=\tilde{\nu}-\tilde{\nu}_0$	$\tilde{\nu}/\mathrm{cm}^{-1}$		Assignement
Complex	FLU	PERY	cm^{-1}	$\parallel c$	$\perp c$	
	3384 m					FLU
3050 w		3050 s	0		3087 m	PERY
	3050 w					FLU
	2921 w					FLU
	2708 vw					FLU
2361 m		2361 m	0			PERY
	2463 vw					FLU
	2363 w					FLU
		1923 m			1958 m	PERY
		1867 w			1811 m	PERY
		1786 w			1721 m	PERY
	1709 vs		−23			
1686 vs	1692 vs		−6	1690 s	1690 s	FLU C=O stretch.
1657 vs	1678 vs		−21	1657 vs	1661 vs	FLU C=C stretch.
		1605 m			1640 s	PERY
1590 m		1592 s	−2	1603 s	1603 s	PERY
	1518 w					FLU
1493 w		1493 s	0	1495 s	1493 s	PERY
	1401 m			1480 m		FLU
1381 m		1379 s	3			PERY
1316 s	1331 vs		−16	1331 s	1329 vs	FLU C–C stretch.
	1223 m			1285 w	1285 s	FLU C–C stretch.
1213 w		1213 s	0			PERY
		1127 m				PERY
1186 w		1186 s	0	1186 w	1186 s	PERY
1150 w		1150 w	0		1130 s	PERY
	1087 m					FLU
	1046 s				1069 m	FLU
1040 vw		1042 w	−2	1044 s	1044 m	PERY
978 vs	1013 vs		−35	980 vs	986 vs	FLU C–F stretch.
		967 w			972 s	PERY
		889 w			903 m	PERY
816 vs		810 s	6	820 s	822 vs	PERY
768 vs		768 s	0	764 s	777 vs	PERY
721 vw	737 s		−14	723 s		FLU C–F stretch.

† Multiplet peak.

a Kramers–Kronig analysis of the reflection spectra.[4)] The maximum peak appears at about 13500 cm^{-1} ($\varepsilon = 1.5\times10^4$ $\mathrm{dm}^3\,\mathrm{mol}^{-1}\,\mathrm{cm}^{-1}$), which is assigned to be the CT band. The observed oscillator strength of the CT band was calculated to be $f=0.44$ by using Eq. 1. The distance between FLU and PERY is $R_{\mathrm{AD}}=3.5\times10^{-8}$ cm, and the excitation energy is $\tilde{\nu}_{\mathrm{CT}}=13500$ cm^{-1}. The charge-transfer degree was estimated to be $b^2=0.08$ by using Eq. 2.

Table 2 shows the IR vibrational bands of the complex and those of the component compounds in the KBr disks and in the single crystal. The effect of the large charge-transfer degree in the FLU-PERY system is also observed in the energy shift. For example, the shift energy of the band at 1709 cm^{-1} assigned to the C=O stretching of fluoranil is −23 cm^{-1}, and those of the bands at 1678 cm^{-1} (C=C stretching), 1331 cm^{-1} (C–C stretching) and 1013 cm^{-1} (C–F stretching) are −21, −16, and −35 cm^{-1}, respectively. These values are larger than those observed in the C=O, C=C, C–C, and C–Cl stretching bands of the CHL-HMB system. The bands assigned to fluoranil are shifted to a lower energy, while the bands at 1379 and 810 cm^{-1} of perylene are shifted to a higher energy, 1381 and 816 cm^{-1}. With complex formation, the bands of fluoranil at 3050, 2921, 2708, 2463, 2363, 1518, and 1087 cm^{-1} do not appear in the crystal and in the KBr disk, while the bands due to perylene have considerable intensity. A few peaks of perylene are observed only for the $\perp c$ spectrum.

Thermochromism of the CHL-HMB and FLU-PERY Complexes. In the CHL-HMB system, two endothermic peaks (46.7 and 206.4 °C) were observed for the differential scanning calorimetry (DSC) curve. The red needle-like crystal of the CHL-HMB complex changed to a yellow powder upon being heated at temperatures higher than 47 °C. The IR spectrum in the

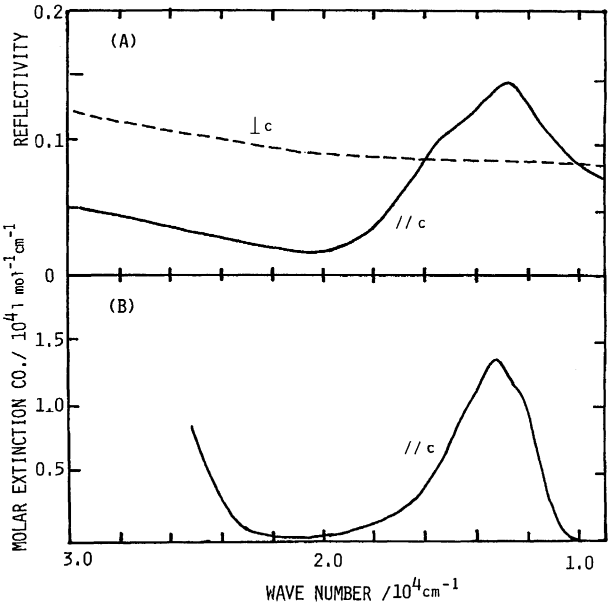

Fig. 5. (A) Polarized reflection spectra of the FLU-PERY crystal and (B) polarized absorption spectra obtained by the K–K analysis of the reflection spectra.

KBr disk of the pyroproduct heated at 110 °C for 10 min corresponds to that of CHL. That is, the crystal of the CHL-HMB complex changes to a powder of chloranil upon being heated at temperatures higher than 47 °C, while the melting points of CHL and HMB are 289 and 167 °C, respectively. In the FLU-PERY system, two endothermic peaks (51.4 and 163 °C) were observed for the DSC curve. The bluish-black needle crystal changed to a green residue and a yellow residue at temperatures higher than 51 °C. The IR spectrum of a crystal of the pyroproduct heated at 130 °C for 10 min is similar to that of perylene. That is, the crystal of the FLU-PERY complex changes to that of perylene upon being heated at temperatures higher than 51 °C, while the melting points of FLU and PERY are 183 and 277 °C, respectively.

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