Crystal and Electronic Structure of 2,9-Dichlorodithioketoquinacridone

- Polymorph of Dimethylacetamide-Solvated Crystals -

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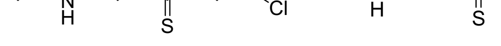
Abstract

2,9-Dichlorodithioketoquinacridone (DTQ-Cl: Fig.1(a)) is a thionated derivative of industrially important 2,9-dichloroquinacridone used as colorants in painting and imaging industries. Crystallographic and electronic characterization has been carried out on dimethylacetamide-solvated single crystals: DTQ-Cl/(DMA)$_2$. There are two crystal Modifications I and II which crystallize in the space group of *P*2$_1$/*c* and *P*-1, respectively. In both crystals, two DMA molecules are hydrogen-bonded to one DTQ-Cl molecule. A larger bathochromic is observed on going from solution to the solid state in Modification II than in Modification I (730 and 520 cm^{-1}). This is presumably due to larger excitonic interactions between transition dipoles in modification II than in modification I.

1. Introduction

2,9-Dichlorodithioketoquinacridone (DTQ-Cl: Fig.1(a)) is a thionated derivative of industrially important 2,9-dichloroquinacridone used as colorants in painting and imaging areas.[1] We have so far studied the crystal and electronic structure of unsubstituted dithioketoquinacridone (DTQ: Fig. 1(b)) which exhibits an intense near-IR absorption used for laser printers and optical disks based on GaAsAl laser diodes.[2,3] In DTQ as well as other quinacridone pigments,[4] intermolecular hydrogen bonds based on NH···S or NH···O play an important role to bridge molecules firmly together and also to displace the absorption band toward longer wavelengths upon crystallization due to interactions between transition dipoles.[3-6]



(a) DTQ-Cl **(b) DTQ**

Figure 1. Molecular structure of DTQ-Cl and DTQ.

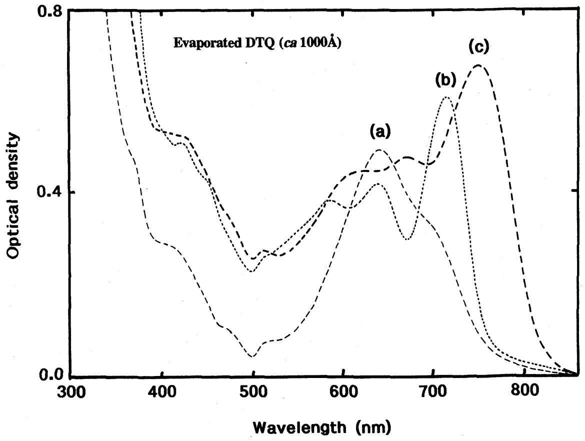


Figure 2. Absorption spectra of evaporated DTQ: (a) as evaporated, (b) vapor-treated for 5 min (phase I) and (c) vapor-treated for 15 min (phase II).

In the course of our studies on the crystal structure of DTQ-Cl, we found that DTQ-Cl includes solvent molecules upon crystallization in such a way as to block intermolecular NH···S hydrogen bonds. Two kinds of dimethylacetamide (DMA)-solvated DTQ-Cl (modifications I and II) are isolated in which two DMA molecules are hydrogen bonded to one DTQ-Cl molecule. There are intermolecular hydrogen bonds between the NH group of DTQ-Cl and the O atom of DMA. In this relation, we have attempted to characterize the NH···O hydrogen bonds between DTQ-Cl and DMA in order to eventually elucidate the electronic structure of both complexes.

Our previous studies on the electronic structure of DTQ[2,3] can be summarized as follows. There are three characteristic absorption spectra in evaporated films as shown in Fig. 2 [(a) as evaporated, (b) phase I and (c) phase II], among which only spectrum (c) is near-IR-active. A prominent absorption band appears around 720 nm in phase I and 756 nm in phase II, respectively. These absorption maxima are present at longer wavelengths by about 72 nm (*ca* 1550 cm^{-1}) and 108 nm (*ca* 2200 cm^{-1}), respectively as compared with that of DTQ in 1,4-dioxane. The crystal structure which corresponds to spectrum (b) has been analyzed and the structure is shown in Fig. 3.[3] There are intermolecular hydrogen bonds between the NH group of one molecule and the S atom of the neighboring one. One molecule is hydrogen-bonded to four neighboring molecules. Thus the molecules are arranged in a fashion "hunter's fence".

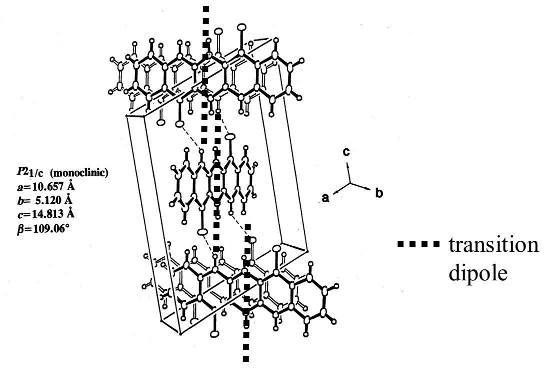


Figure 3. Molecular arrangement of DTQ (phase I).

2. Experiment

2.1 Preparation of DTQ-Cl and its Solvated Single Crystals

DTQ-Cl was prepared by thionation of commercially available 2,9-dichloroquinacridone with a Lawesson's regent.[1] Single crystals of DTQ-Cl were grown by recrystallization from solution in dimethylacetamide (DMA). Two kinds of DMA-solvated single crystals (modifications I and II) were isolated while no solvent-free crystals were recrystallized. Single crystals of modification I were formed in needles while platelet in modification II. The crystal growth from the vapor phase failed because the decomposition occurs around 350°C.

2.2 Structure Analysis

X-ray diffraction data were collected at –180°C on a R-AXIS RAPID-F diffractometer from Rigaku using Cu$K\alpha$ radiation (λ = 1.5418 Å). The structure was solved by direct methods using Shelxs-97 and refined by full-matrix least squares on F^2 using Shelxl-97[7].

2.3 Molecular Orbital (MO) Calculations

MO calculations were made using Quantum CAChe Ver.3.2. from Fujitsu, Ltd. The geometry was first optimized for DTQ-Cl and DTQ-Cl/(DMA)$_2$, using the AM1 Hamiltonian. Then, the absorption bands were calculated for the optimized DTQ-Cl using the INDO/S Hamiltonian. The same spectroscopic calculations were also carried out on two kinds of DMA-solvated complexes extracted from the crystal lattice on the basis of the X-ray coordinates.

2.4 Equipment

UV-vis spectra in solution were recorded on a Shimadzu UV-2400PC spectrophotometer. Polarized reflection spectra were measured on single crystals by means of a microscope-spectrophotometer (UMSP 80 from Carl Zeiss).

3. Results and Discussion

3.1 Crystal Structure of Modifications I and II

Table 1 details the crystallographic parameters for DMA-solvated complexes: modifications I and II. In both crystals, two DMA molecules are hydrogen-bonded to one DTQ-Cl molecule. However, these complexes are arranged in a different way as characterized by the space group, $P2_1/c$ and P-1, respectively.

Figures 4(a) and 4(b) show the ORTEP plots of modifications I and II. In both complexes, there are NH···O intermolecular hydrogen bonds between the NH group of DTQ-Cl molecule and the O atom of DMA. The N/O distance and the NH/O angle are 1.894 Å and 176° for Modification I, respectively: the N/O distance and the NH/O angle are 1.868 Å and 173° for modification II, respectively. These hydrogen bonds are considered relatively strong, since the distance is short and the angle is close to 180° in both crystals. Furthermore, no significant difference in conformation is recognized between these complexes, although their arrangement is different in the crystal lattice as shown below.

Figures 5(a) and 5(b) show the projection of the crystal structure of modification I onto the (*a*,*c*) plane as well as the molecular stack. On the other hand, the molecular arrangement of modification II on the (*b*,*c*) plane and along the *a*-axis are shown in Fig. 6(a) and 6(b). It is apparent in both crystals that there are two kinds of molecular columns along the *b*- and *a*-axes in modifications I and II, respectively: one is composed of DMA molecules and the other comprises the molecules of DTQ-Cl. Therefore, the DTQ-Cl molecules work as the spacer to separate DTQ-Cl molecules. It is also of great interest to note that the complexes (DTQ-Cl/(DMA)$_2$) are arranged in a different way, leading to a different in color in the solid state as discussed later. In modification I ($P2_1/c$), the DTQ-Cl molecules cross each other at angles of about 60° as shown in Fig. 5(b). On the other hand, in modification II (P-1), the DTQ-Cl molecules are almost on the molecular plane as seen in Fig. 6(b).

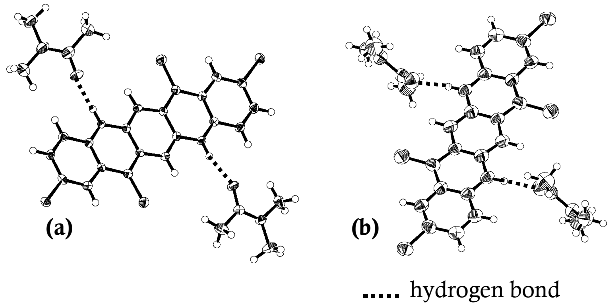


Figure 4. ORTEP plots for (a) modification I and (b) modification II.

Table 1. Crystallographic Parameters for DMA-Solvated DTQ-Cl: Modifications I and II.

	Modification I	Modification II
Molecular formula	DTQ-CI/(DMA)2	DTQ-CI/(DMA)2
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	P-1
Molecular symmetry	C_1	C_1
Z	4	1
a	14.0592 (9)	7.140 (6)
b	7.7443 (5)	8.966 (8)
c	25.092 (2)	11.379 (8)
α	90	103.97 (4)
β	90.462 (5)	96.78 (4)
γ	90	107.43 (4)

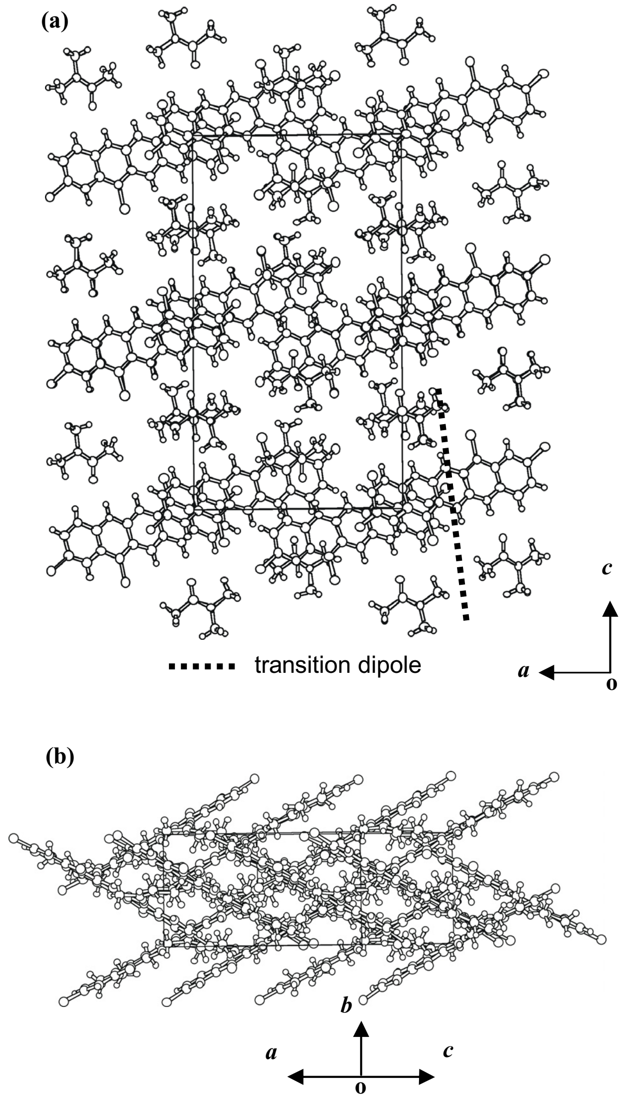


Figure 5. Molecular arrangement of modification I: (a) projection onto the (a,c) plane and (b) molecular stack along the b-axis.

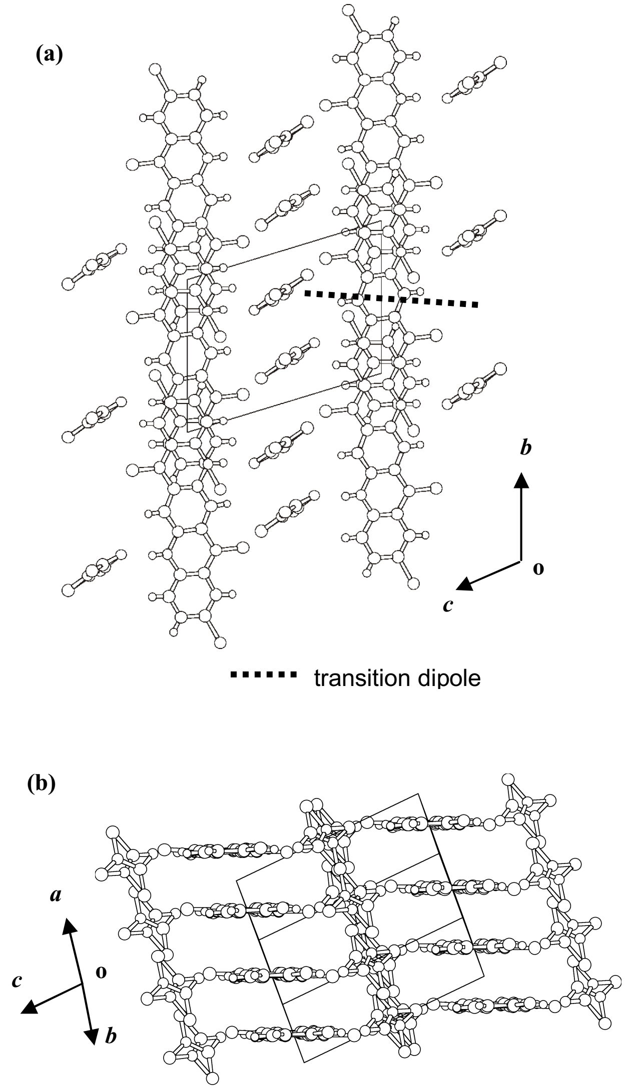


Figure 6. Molecular arrangement of modification II: (a) projection onto the (b,c) plane and (b) molecular stack along the a-axis.

3.2 Solution Spectra and the Effect of H-bond on the Spectral Shift

Figure 7 shows the solution spectra of DTQ-Cl measured in 1,4-dioxane, DMA and DMSO (dimethylsulfoxide). In all spectra, there observed a progression of absorption bands starting from 640 nm (for example, in DMA) toward shorter wavelengths. Since the absorption edge of the longest-wavelength band is quite steep and the subsequent bands are equally spaced (about 1400 cm^{-1}), the longest-wavelength band is assigned to the 0-0 transition and the second longest wavelength band to the 0-1 transition and so on. This assignment is also borne out by MO calculations as described below.

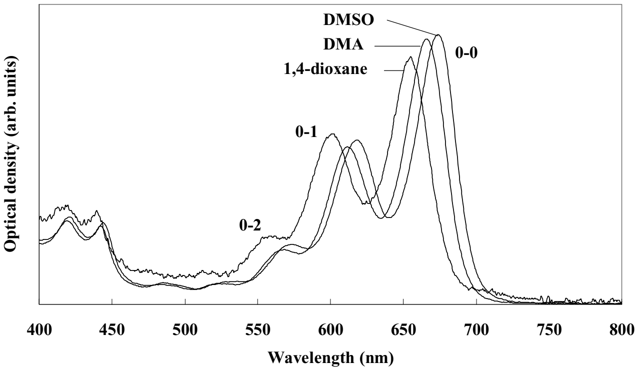


Figure 7. Solution spectra in three different solvents: 1,4-dioxane, DMA and DMSO.

It is also to be noted that the absorption maximum is slightly displaced toward longer wavelengths in sequence of 1,4-dioxane, DMA and DMSO. This is the increasing order of the polarity of the solvent. The present bathochromic shift is closely linked with the hydrogen band formation between the NH group of DTQ-Cl and the O atom of solvents as supported by ^{1}H-NMR experiments (not shown here). The proton signal is shifted towered higher magnetic fields as the temperature of the solution is increased from RT to 100ºC. At the same time, the extent of the bathochromic shift is remarkably reduced due to the weakening of the hydrogen bond caused by enhanced kinetic motion of molecules at high temperatures.

3.3 MO Calculations

Table 2 details the results of the spectroscopic calculations for DTQ-Cl and DTQ-Cl/(DMA)$_2$ in modifications I and II together with the experimental values in solution and in the solid state. The optimized geometry of DTQ-Cl gives an absorption band around 426 nm. This is in agreement with the calculated band using the X-ray coordinates of modifications I and II. This corresponds to the experimental value of 666 nm, although the calculated result is significantly underestimated. On the other hand, the absorption maximum appears around 435 nm for the geometry-optimized DTQ-Cl/(DMA)$_2$ as well as for the one based on the X-ray coordinates of modification II while the complex in modification I yields a value of 448 nm. This indicates that the absorption maximum is supposed to occur in the solid state at longer wavelengths in modification I than in modification II. However, the opposite is the case as revealed from the polarized reflection measurements as described below: 690 nm in modification I and 700 nm in modification II. The present result suggests that intermolecular interactions are involved in the solid state to displace the absorption band toward more longer wavelengths in modification II than in modification I.

3.4 Polarized Reflection Spectra Measured on Single Crystals

Figure 8 shows the polarized reflection spectra measured on the (*a,c*) plane of modification I together with the corresponding projection. In modification I, a prominent reflection band appears around 690 nm, accompanied by two small bands around 632 and 586 nm for polarization parallel to the transition dipole deduced from MO calculations. On the other hand, these reflection bands are completely quenched for polarization perpendicular to the transition dipole. This result indicates that the direction of the transition dipole experimentally determined here is in accord with the calculated one. The same spectroscopic behavior is observed for modification II as shown in Fig. 9. However, the reflection maximum appears around 700 nm. This band is present at longer wavelengths by about 10 nm (~207 cm^{-1}) as compared with that of modification II.

Table 2. Calculated and Observed Absorption Bands for DTQ-Cl and DTQ-Cl/(DMA)$_2$.

	molecule or complex	calculated		observed	
		λ	f	λ	f
geometry optimization	DTQ-Cl	426.1	0.528	666	5.20
	DTQ-Cl/(DMA)$_2$	435.2	0.550	-	-
modification I	DTQ-Cl	440.4	0.528	-	-
	DTQ-Cl/(DMA)$_2$	448.1*	0.639	690**	-
modification II	DTQ-Cl	426.2	0.593	-	-
	DTQ-Cl/(DMA)$_2$	435.2*	0.593	700**	-

* On the basis of the X-ray coordinates

** Polarized reflection measurement (Figs. 8 and 9)

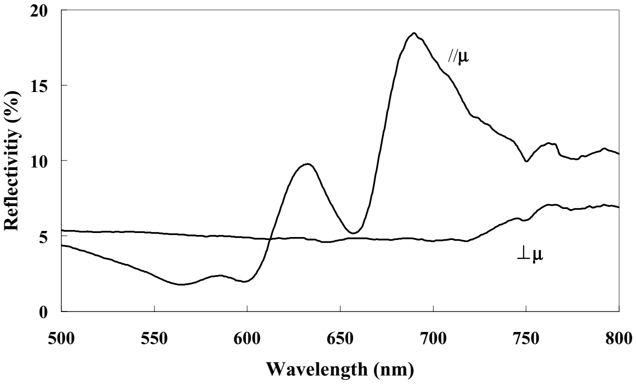


Figure 8. Polarized reflection spectra measured on the (a,c) plane of modification I. The projection onto the (a,c) plane is shown in Fig. 5(a).

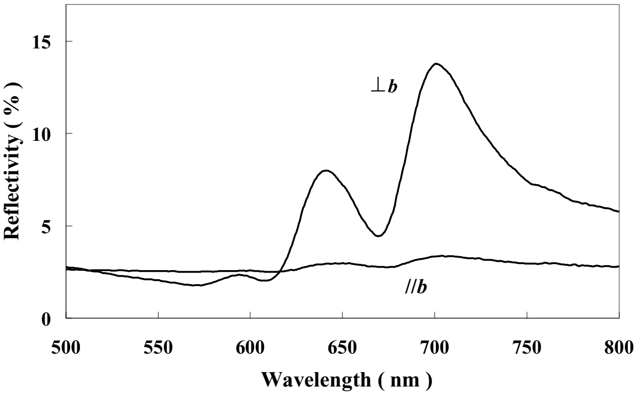


Figure 9. Polarized reflection spectra measured on the (b,c) plane of modification II. The projection onto the (b,c) plane is shown in Fig. 6(a).

3.5 Bathochromic Shift Due to NH···O Hydrogen Bonds in DTQ-Cl/(DMA)$_2$

As stated in section 3.2, the absorption band is red-shifted when the NH···O intermolecular hydrogen bonds are formed between the NH group of DTQ-Cl and the O atom of solvents. This spectral shift can be explained in terms of partial electron transfer from the proton to the nitrogen atom, therefore increasing the electron density on the nitrogen atom.

In addition to its primarily electrostatic character, the hydrogen bond has some covalent nature correspond to the scheme: $N^- - H^+ \cdots O = C \Leftrightarrow N^- - H - O^+ = C$. This second charge transfer form involves electron donation from the oxygen into the N – H bond increasing the electron density on the nitrogen atom. This increased electron density can then be more delocalized into the chromophore in the excited state, contributing to the bathochromic shift. An alternative way of explaining the spectral shift is as follows. In both the electrostatic model and the partial charge transfer one, more negative charge appears on the N atom due to the formation of NH···O hydrogen bond. It is also likely that the electron density is more increased with the polarity of the solvent (Fig. 7). Then, the electron-donating power of the N atom is enhanced so that the electron transfer, upon light absorption, from the donor part (NH group) to the acceptor part (C = O) in the DTC-Cl is facilitated by the hydrogen bonding effect. This leads to a bathochromic shift.

3.6 Difference in Color in Modifications I and II

In MO calculations described in section 3.3, the absorption bands based on the X-ray coordinates for DTQ-Cl/(DMA)$_2$ in modifications I and II have been estimated to be 448 and 435 nm, respectively (Table 2). However, in polarization experiments on single crystals (Figs. 8 and 9), the opposite is the case. That is, the reflection maxima appear around 690 and 700 nm for modifications I and II, respectively. The difference in wavelength amounts to 10 nm (about 207 cm^{-1}). This is obviously attributed to intermolecular interactions.

In pigment systems in which the absorption coefficient (that is proportional to the square of transition dipole) of the component molecule is large, the interaction between transition dipoles plays the major role in intermolecular interactions in the solid state.[3-6] In fact, in DTQ, large bathochromic shifts of about 1550 cm^{-1} and 2200 cm^{-1} appear upon crystallization as a result of interactions between transition dipoles (Fig. 3). The NH···S intermolecular hydrogen bond aligns the transition dipoles in a fashion “head-to-tail”, leading to the bathochromic shift.[8] However, in DMA-solvated DTQ-Cl systems, the DMA molecules are hydrogen-bonded to DTQ-Cl molecules to block the formation of NH···S hydrogen bonds. Therefore, the excitonic interactions between transition dipoles are considered to be small. Nevertheless, the two values of bathochromic shift of about 520 cm^{-1} and 730 cm^{-1} are observed in modifications I and II, respectively, and the difference in spectral shift between them is quite small (about 207 cm^{-1}). Furthermore, semi-quantitative calculations of the excitonic interactions have been carried out on the basis of the X-ray coordinates, and the results indicate that the extent of bathochromic shift is slightly larger in modification II than in modification I. This is consistent with the tendency of the experimental result.

4. Conclusions

Crystallographic and electronic characterization has been carried out on the modifications I and II of DTQ/(DMA)$_2$. The conclusions can be summarized as follows.

1. Modifications I and II crystallize in two different space groups: *P*21/*c* and *P*-1, respectively. In both crystals, two DMA molecules are hydrogen bonded to one DTQ-Cl molecule. The DTQ-Cl molecules are arranged in a fashion “hunter’s fence” in modification I; whereas all DTQ-Cl molecules are nearly on the molecular plane and stacked in a layered structure along the *a*-axis in modification II.
2. Intermolecular NH···O hydrogen bonds between the

NH group of DTQ-Cl and O atom of DMA in solution bring about bathochromic shifts of 11 nm (252 cm^{-1}). MO calculations revealed that the DTQ-Cl/(DMA)$_2$ complex in modification I induces a larger bathochromic shift than in modification II. However, in experiment, a larger bathochromic shift is observed in modification II than in modification I (730 and 520 cm^{-1}). This is presumably due to larger excitonic interactions between transition dipoles in modification II than in modification I.

References

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Biography

Tomonori Hoki received his Bachelor of Engineering from Yokohama National University in 2003. He is currently in the graduate course of the Department of Applied Physics at Yokohama National University. His research interest includes crystal and electronic structure of organic pigments together with their applications.

Appendix

Crystal Structure of DTQ-Cl/(DMF)$_2$

Single crystals of DTQ-Cl/(DMF)$_2$ were grown by recrystallization from solution in dimethylformamide. The crystallographic parameters are: monoclinic, $C2/c$, $Z = 4$, $a = 33.254(4)$ Å, $b = 4.2677(6)$ Å, $c = 21.586(3)$ Å, $\beta = 123.876(9)°$. The ORTEP plot as well as the molecular arrangement is shown below.

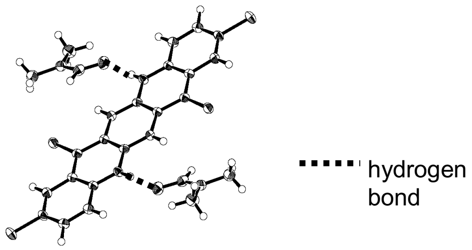

Figure 10(a). ORTEP plot of DTQ-Cl/(DMF)$_2$.

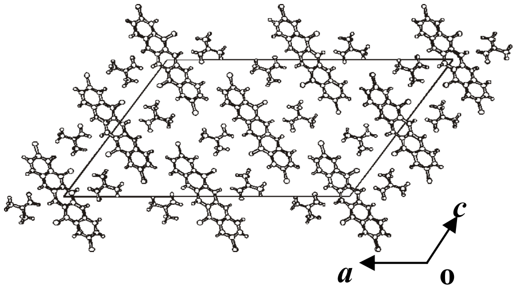

Figure 10(b). Molecular arrangement of DTQ-Cl/(DMF)$_2$: projection onto the (b,c) plane.