Correlation between Electronic and Crystal Structures in Diketopyrrolopyrrole Pigments

Ayae ENDO, Shinya Matsumoto and Jin Mizuguchi
Department of Applied Physics, Faculty of Engineering,
Yokohama National University
Yokohama, Japan

Abstract

Correlation between electronic and crystal structures of some diketopyrropyrrole (DPP) pigments has been investigated on the basis of the exciton coupling effects. The color changes variously from vivid red to yellowish red on going from *p*-Cl DPP via DPP to *m*-CN DPP. Polarized reflection spectra on these single crystals revealed that the reflection maximum is hypsochromically shifted in the above order as the number of atomic contacts between stacking molecules is increased. We assumed the present color change as arising from exciton coupling effects and calculated the spectral shifts for the nearest-neighbor molecules. The hydrogen-bond pair ("head-to-tail" arrangement) is found to displace the absorption maximum towards longer wavelengths, while the stack pair ("parallel" arrangement) significantly contributes to the hypsochromic shift. The present result is qualitatively in good agreement with the experiment.

Introduction

One of the appealing features of the hydrogen-bonded pigments such as diketopyrrolopyrrole (DPP)[1], quinacridone and indigo is to exhibit vivid red or blue colors in the solid state, although the molecular weight is quite small (DPP=288, indigo=262 and quinacridone=292). These pigments are composed of a π-conjugated chromophore and two pairs of NH (donor) and C=O (acceptor) as auxochromes.

DPP derivatives (Fig. 1) exhibit a variety of shades in the solid state, although no significant difference is recognized in solution spectra of these compounds[2,3]. For example, *p*-Cl DPP shows a vivid red; whereas *m*-CN DPP bears yellowish red. Roughly speaking, the yellow component increases from *p*-Cl DPP (left) to *m*-CN DPP (right). The purpose of the present investigation is to interpret the difference in shade in terms of exciton coupling effects on the basis of the crystal structure.

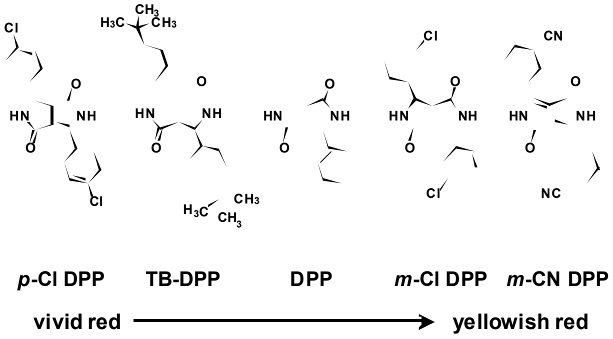


Figure 1. Molecular structure of DPP derivatives.

Crystal Structure of DPP Pigments

All DPP pigments except for *p*-Cl DPP (monoclinic) belong to the triclinic crystal system and the molecules are arranged in a fashion *quasi* "bricks in a brick wall" [4-7]. The structure of *m*-CN DPP[7] is isomorphous with that of *m*-Cl DPP.

Fig. 2 shows the projection of the crystal structure of DPP onto the (*b*,*c*) and (*a*,*c*) planes.[4] There are four intermolecular hydrogen bonds per molecule between the NH group of one molecule and the O atom of the neighboring along the *b*-axis. The hydrogen-bond network is common in all DPP pigments, but the molecular overlap along the stacking axis is quite different for each DPP derivative. Fig. 3 illustrates the typical overlap of two molecules, for example, for *p*-Cl DPP and *m*-Cl DPP. The number of directly-overlapping atoms is 2, 9, 12 for *p*-Cl DPP, DPP and *m*-Cl DPP, respectively,[4,5] while 6 and 14 for TB-DPP[6] and m-CN DPP,[7] respectively. The extent of the overlap increases from *p*-Cl DPP to *m*-CN DPP in Fig. 1 in agreement with the increasing order of yellow component.

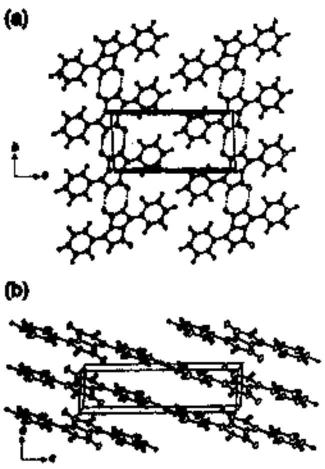


*Figure 2 Projection of the crystal structure of DPP: onto (*b,c*) plane and (b) (*a,c*) plane.*

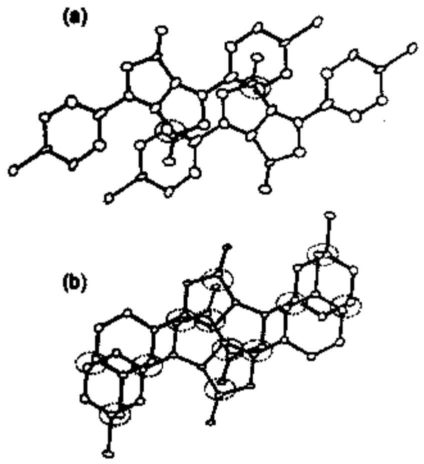


Figure 3 Overlap of two molecules for (a) p-*Cl DPP and (b)* m-*Cl DPP.*

Observed Correlation Between Spectral Shape and Molecular Overlap in the Solid

Fig. 4 shows the three characteristic spectra of evaporated DPP. Spectrum (a) is obtained as evaporated and its spectral shape is quite similar to that in solution (λ_{max}=507 nm).[3] Spectrum (a) then changes via (b) to (c) when exposed to the vapor of certain organic solvents such as acetone.[4] Spectra (a), (b) and (c) represent the spectral shape of the polarized reflection spectra of single crystals for the DPP pigments: spectrum (a) corresponds to those of p-Cl DPP (λ_{max}=550 nm) and TB-DPP (λ_{max}=531 nm), spectrum (b) to DPP (λ_{max}=459 nm) and spectrum (c) to m-Cl DPP (λ_{max}=450 nm) and m-CN DPP (λ_{max}=444 nm).

The solid-phase as evaporated has already been characterized as a crystallized state by means of X-ray diffraction analysis shown in Fig.5. Molecular ordering is clearly recognized along the (001) direction (van der Waals interactions) but there is little order along the (1-11) (stacking axis). This phase is also characterized by intermolecular hydrogen bonds as observed by IR spectra. The above results indicate that the spectral displacement on going from solution to the solid state arises from the intermolecular hydrogen bonds. On the other hand, the X-ray diagram after vapor treatment (Fig. 5) indicates that the molecular ordering along the stacking (1-11) axis is brought about by vapor treatment. The present result suggests that the absorption maximum is displaced towards shorter wavelengths as the molecules are ordered along the stacking axis.

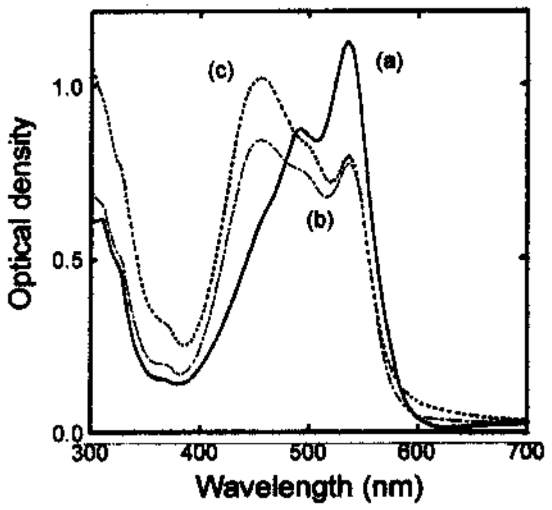


Figure 4 Spectral change of evaporated DPP due to vapor treatment.

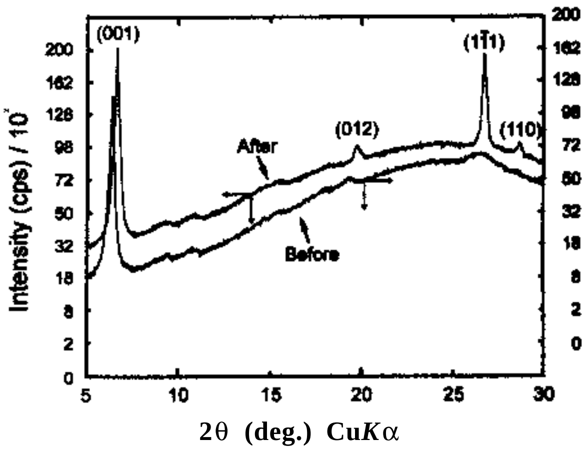
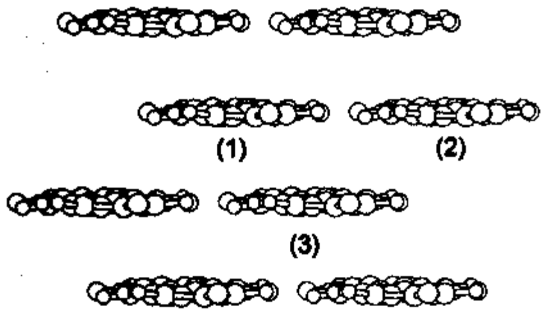


Figure 5 X-ray diffraction diagrams of evaporated DPP:before and after vapor treatment.

Exciton Coupling Effects and Spectral Shifts

Outline of the Calculation

In molecular systems, transition dipoles will appear on the molecules as soon as the molecules are excited. The resonance interaction is then induced by two transition dipoles to displace the excited energy level downwards (red shift) or upwards (blue shift), depending on the relative orientation of the transition dipoles: "parallel"or "head-to-tail". The exciton displacement energy ($\Delta E_{\text{exciton}}$; spectral shift) is given by the following equation[8]: $\Delta E_{\text{exciton}}=|\mu|^2(1-3\cos^2\theta)/r^3$, where the transition moment is denoted by μ, the distance and angle between two transition dipoles by r and θ, respectively. The term $(1-3\cos^2\theta)$ determines the geometrical relationship of transition moments which is correlated with the crystal structure. In the present investigation, the exciton displacement energies have been calculated only for the nearest molecule-pairs of DPP derivatives.



No.		Energy shift (cm^{-1})
(1), (2)	H-bond pair	-2116
(1), (3)	Stack pair	-731

Figure 6 Molecular arrangement of p-Cl DPP.

Results and Discussion

Fig. 6 shows the molecular stack of *p*-Cl DPP as viewed from the long molecular axis. The intermolecular hydrogen bonds are present on the horizontal plane between the NH group of molecule (1) and the O atom of molecule (2). The energy calculation has been made for the nearest-neighbor molecules around molecule (1). The combination of molecules (1) and (2) is a hydrogen bond pair (H-bond pair). There are two kinds of stack pairs: one is a less-overlapped pair composed of molecules (a) and (3) and the other is a more-overlapped pair consisting of molecules (2) and (3). The calculated results are shown in Table 1.

The largest contribution to the bathochromic shift is made by the H-bond pair (-2116 cm^{-1}), since the angle is very small and the distance is relatively short. The additional contribution is found in stack pairs I and II by amounts of 731 and 809 cm^{-1}, respectively, where the angles are slightly smaller than 54.7°. On the other hand, the hypsochromic component is given by stack pair III and the cross pair whose angles are larger than 54.7°. The bathochromic shift amounts to -5252 cm^{-1}. The present result indicates that the bathochromic shift prevails due to the H-bond pair and the hypsochromic component is quite small because of the lack of the atomic contacts along the stacking axis. The present hypsochromic component significantly increases from *p*-Cl DPP via DPP to *m*-CN DPP due to the increased number of the atomic contacts.

Table 1. 12 Nearest neighbors around the molecule at (1/2, 1/2, 0) and their displacement energies.

Type of molecule pairs	Number of molecules	Site	r (Å)	θ (°)	ΔE*
		Homochiral pair			
H-bond pair	**2**	**(3/2,1/2,1)**	**7.297**	**3.460**	**-2116**
Stack pair I (more overlap)	2	(1/2,1/2,1)	5.585	49.047	-731
Stack pair II (less overlap)	2	(3/2,1/2,0)	5.658	48.208	-809
Stack pair III (semi-full overlap)	2	(3/2,1/2,-1)	8.425	89.252	734
Cross pair	4	(1,0,1/2)	12.135	68.330	148
Total	12				**-5252**

* μ (Å)=1.9462

**The minus and plus sign correspond to the bathochromic and hypsochromic shift, respectively.

Table 2. Calculated and experimental results of the spectral shift for all DPP pigments.

	Calculated (cm^{-1})	Experimental (cm^{-1})
p-Cl DPP	-5252	-1182
TB-DPP	-3214	-719
DPP	195	2086
m-Cl DPP	1123	2336
m-CN DPP	2801	3067

Table 2 summarizes the calculated results for all DPP pigments. The extent of the hypsochromic displacement is clearly in line with the increased number of the atomic contacts along the stacking axis. The tendency of the spectral shift is in fairly good agreement with the experimental results, although we need discussions for further details.

Conclusions

The spectral shifts for five kinds of DPP pigments have been calculated in consideration of the exciton coupling effects. The conclusions can be summarized in the following.

1. The H-bond pair shifts the absorption maximum towards longer wavelengths by about 2000 cm^{-1}. On the contrary, the stack pair contributes to the hypsochromic displacement by about 3000-4500 cm^{-1}.
2. In *p*-Cl DPP and TB-DPP, the bathochromic contribution due to the H-bond exceeds the hypso-

chromic contribution due to the stack pair. On the other hand, in DPP, *m*-Cl DPP and *m*-CN DPP, the stack-pair contribution is larger than the H-bond contribution, leading to the hypsochromic shift.

3. The exciton coupling model allows us to qualitatively interpret the correlation between the crystal and electronic structures in DPP pigments.

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Biography

Ayae Endo received her B. of Ed. from Yokohama National University in 1998. She is currently in the graduate course for materials science at Yokohama National University. Her research interest includes electronic characterization of organic pigments together with their electronic applications. She is a member of Chemical Society and the Electrochemical Society of Japan.