Crystal and Electronic Structures of Perylene Derivatives

K. Tojo and J. Mizuguchi
Graduate School of Engineering, Yokohama National University
Yokohama, Japan

Abstract

Perylene pigments are known to exhibit a variety of shades in the solid state from vivid red, via maroon to black, although their solution spectra are quite similar. The color generation mechanism has therefore been investigated in three typical perylene derivatives on the basis of the crystal structure and intermolecular interactions. The color is found to be mostly determined by two absorption bands in the visible region: one is due to individual molecules and the other is caused by interactions between transition dipoles (“exciton coupling effects”). The red color appears as a result of insignificant exciton coupling while the colors of maroon and black are characterized by medium and strong exciton coupling, respectively.

Introduction

Perylene derivatives are well-known organic pigments which exhibit a variety of shades in the solid state from vivid red, via maroon to black (Fig. 1),[1] although no significant difference is recognized in their solution spectra. These compounds have attracted attention as colorants as well as photoconductors for copiers in the imaging area.

We have previously investigated the color generation mechanism of perylene black (PB31)[2] together with its application to optical disks. The solution spectrum and solid-state spectra in evaporated films are shown in Fig. 2. In solution, there is only one electronic transition coupled with vibrational transitions, giving a progression of absorption bands as designated by 0-0, 0-1 , 0-2 and 0-3 (Fig.2(a)). In the solid state, the color is vivid red as evaporated. However, the color changes from red to black when the evaporated film is heated at 100 °C for several seconds to minutes (Fig.2 (b)). In the red phase, absorption band is quite similar to the one in solution, and one-to-one correspondence in absorption bands is possible. On the other hand, there observed an additional small band around 610 nm in 30-60 seconds and grows up to a big absorption band to give a black color. This additional band is clearly attributed to the band due to intermolecular interactions, since the band is not explicable by the absorption bands in solution (Fig.2(a)). Based on the crystal structure and intermolecular interactions, we have elucidated the black color as arising from two absorption bands: the shorter-wavelength band is due to individual molecules and the longer-wavelength-band is caused by interactions between transition dipoles (“exciton coupling effects”).[3]

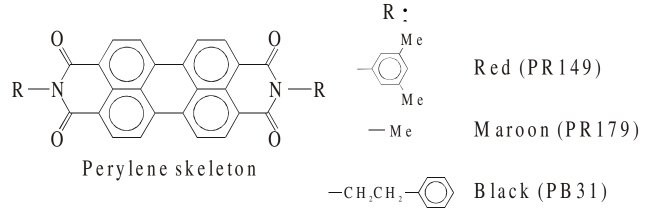

Figure 1. Molecular structure of perylene derivatives.

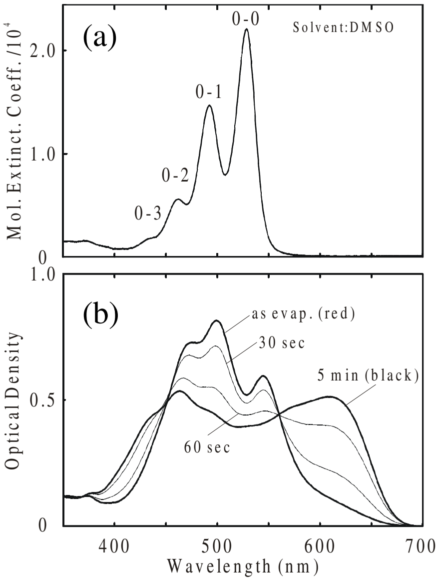

Figure 2. UV-Vis absorption spectra of PB31: (a) solution spectra and (b) spectral changes in an evaporated film as a function of heat-treatment at100 ℃.

The present investigation based on red, maroon and black pigments (PR149, PR179, and PB31 respectively) aims at generalizing the above color generation mechanism on the basis of the crystal structure and intermolecular interactions.

Table 1 Crystallographic Parameters

Sample	PR149	PR179
Formula	$C_{40}H_{26}N_2O_4$	$C_{26}H_{14}N_2O_4$
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
Z	2	2
Molecular weight	598.66	418.39
Molecular symmetry	C_i	C_i
a (Å)	17.0313(5)	3.8648(4)
b (Å)	4.869(3)	15.5654(17)
c (Å)	17.096(5)	14.6603(16)
β(°)	93.40(2)	97.414(2)

Results and Discussion

1. X-ray Structure Analysis

The single crystals of PR149 and PR179 were grown from the vapor phase using a two-zone furnace.[4] Structure has newly been analyzed for PR149[5] while the structure of PR179 was identified as the same as reported by Graser and Hädicke.[6]

Table 1 details the crystallographic parameters for PR149 and PR179. The molecule of PR179 is entirely planar while the two 3,5-xylyl groups of PR149 are symmetrically twisted by 95.76° with respect to the perylene skeleton. The molecules are stacked in a fashion "herringbone" along the *b* axis in PR149 and along the *a*-axis in PR179.

2. Solution and Solid-State Spectra

Figs. 3 (a) and 3 (b) show the solution spectrum as well as the solid-state spectra in evaporated films for PR149, PR179 and PB31, respectively. No noticeable difference is recognized in solution spectra, indicating that the substituents in these compounds are not directly involved in the chromophore (Fig.3(a)).

On the other hand, the absorption spectra in the solid state are strikingly different as characterized by red, maroon and black colors for PR149, PR179 and PB31, respectively (Fig.3(b)). The present difference in shades is obviously attributed to the molecular arrangement that has a profound influence on the exciton coupling. In order to elucidate the different colors in the solid state, we focused our attention on the similarity in spectral changes of band B (as designated by arrow) in Fig.3(b) to the gradual growth of the longer-wavelength band in PB31 in the heat-treatment process (Fig.2(b)). It is also to be noted that the shorter-wavelength band around 450-500 nm (band A) in Fig.3(b) remains relatively unchanged. On the other hand, the shoulder around 570 nm in PR149 grows up to an absorption band in PR179 and the present band is further displaced towards longer wavelengths in PB31, accompanied by intensity enhancement. These facts prompted us to assume that the exciton coupling of the present band is intensified in the order of PR149 (red), PR179 (maroon) and PB31 (black). This assumption will be experimentally borne out as shown below.

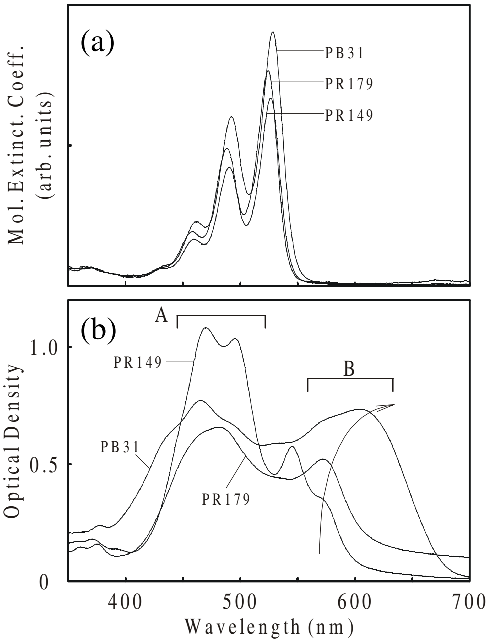

Figure 3. (a) Solution spectra and (b) solid state spectra in evaporated films.

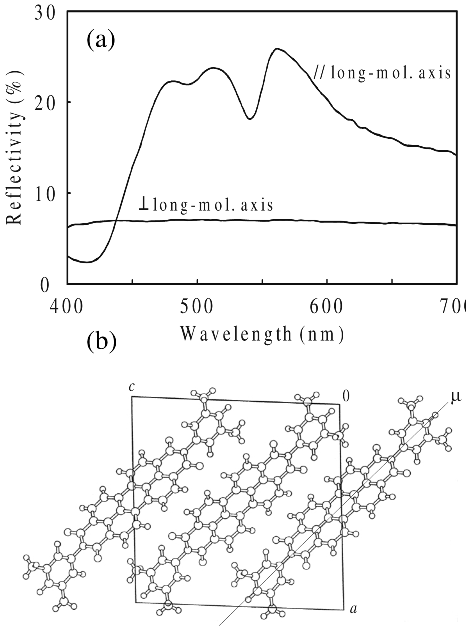

*Figure 4. (a) Polarized reflection spectra of PR149 measured on the (012) plane and (b) projection onto the (*a,c*) plane.*

3. Polarized Reflection Spectra

Figure 4 shows the polarized reflection spectra of PR149 measured on the (012) plane together with the projection of the crystal structure onto the (*a*,*c*) plane.

Likewise, Fig.5 shows the polarized reflection spectra measured on the (102) plane together with the projection onto the (*b*,*c*) plane for PR179. On both projections, the direction of the transition dipole (μ) is also shown by dotted lines. This is due to the HOMO/LUMO π-π^* transition as determined by MO calculations.

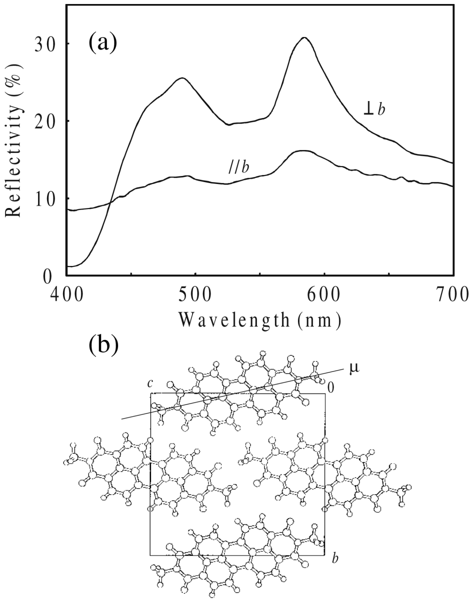

*Figure 5. (a) Polarized reflection spectra of PR179 measured on the (102) plane and (b) projection onto the (*b,c*) plane.*

In PR149, polarized light was introduced parallel and perpendicular to the long-molecular axis of the molecule. Two prominent reflection bands appear around 475-525 and 575 nm for polarization parallel to the long-molecular axis. On the other hand, these intense bands completely disappear by polarized light perpendicular to the molecular axis. The present results clearly indicate that the transition dipole points the long-molecular axis as predicted by MO calculations and that all reflection bands in the visible region are assigned to the same electronic transition due to the HOMO/LUMO π-π^* transition. It is also to be noted that the longer-wavelength band around 580 nm is significantly more intensified as compared with the corresponding band in evaporated films (Fig.3(b)). This can occur because the polarized reflection spectra with polarized light using single crystals are quite different, depending on the measuring conditions such as crystal planes and polarization directions. On the other hand, the absorption spectrum in evaporated films yields, more or less, averaged information.

PR179 exhibits similar spectroscopic behavior to that of PR149. As shown in the projection (Fig.5(b)), the molecules are arranged in a zig-zag fashion, quite in contract to the arrangement in PR149. Therefore, polarization perpendicular to the *b*-axis is more favored for excitation of the molecules than that parallel to the *b*-axis.

4. Temperature Dependence of Absorption Spectra and Lattice Contraction

Based on the preceding polarization experiments, band B in Fig.38b) can be interpreted as being due to interactions between transition dipoles that depend on the molecular arrangement. If this is the case, band B is highly expected to exhibit considerable temperature dependence because of enhanced intermolecular interactions due to lattice contraction at low temperatures.

Figs.6(a-c) show the temperature dependence of absorption spectra in evaporated films for PR149, PR179 and PB31, respectively, measured in the temperature range between 20 and 300 K.

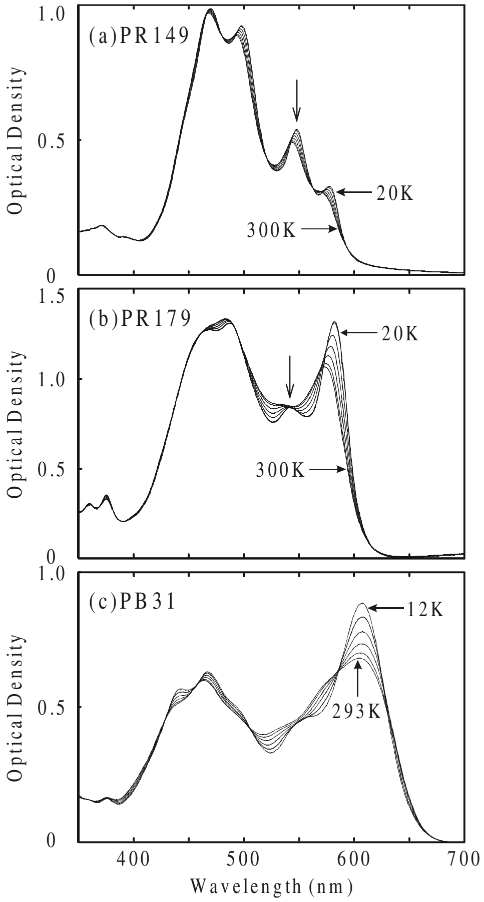

Figure 6. Temperature dependence of absorption spectra: (a) PR149, (b) PR179 and (c) PB31.

Significant temperature dependence is clearly recognized in band B in PR179 and PB31 while the shorter-wavelength band exhibits no noticeable temperature effect. On the contrary, PR149 shows quite insignificant temperature dependence in the whole visible region. The present results indicate that band B is due to exciton coupling effects and that the exciton coupling is small in PR 149 while it is appreciably intensified in the order of PR179 and PB31. On the other hand, the shorter-wavelength bands (band A) in PR149, PR179 and PB31 are quite insensitive to temperature variations because the present band is due to individual molecules.

It should also be noted that the second longest-wavelength band in PR179 around 550 nm, as denoted by arrow, was not observed at room temperature (Fig.6(b)). However, it appears as a small band at 20 K, and one-to-one correspondence in absorption bands can clearly be recognized between PR149 and PR179.

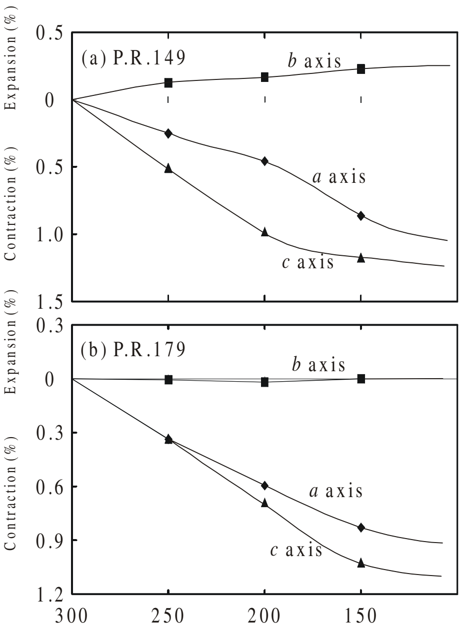

Figure 7. Temperature dependence of lattice parameters: (a) PR149 and (b)PR179.

Figure 7 shows the temperature dependence of lattice parameters in single crystals for PR149 and PR179 measured in the temperature range between 150 and 300 K. In both cases, crystal lattice is predominantly contracted on the (*a,c*) plane. The present lattice contraction induces a significant temperature dependence of absorption spectra as shown in Fig. 6.

Conclusions

The mechanism of various shades in perylene pigments has been investigated from the standpoint of the crystal structure and intermolecular interactions. The solid-state color of perylene pigments is mainly determined by two characteristic absorption bands in the visible region. The shorter-wavelength band is due to individual molecules that appear in common in all perylene derivatives. On the other hand, the longer-wavelength band is caused by interactions between transition dipoles. Therefore, the color in the solid state can variously change, depending on the extent of exciton coupling on the basis of the molecular arrangement. The red color appears when the coupling is quite small; whereas the maroon and black colors are characterized by medium and strong exciton coupling, respectively.

References

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Biography

K. Tojo received his Bachelor of Education from Yokohama National University in 2000. He is currently in the graduate course of engineering at Yokohama National University. His research interest includes electronic characterization of organic pigments together with their electronic applications.