Polymorph of Perylene Imide Derivatives

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Abstract

Perylene imide derivatives are well known organic pigments that exhibit a variety of shades in the solid state from red via maroon to black. These materials have attracted attention as photoconductors for photoreceptors as well as materials for optical disks. 4-Phenylethyl derivative (EPH) is a commercial black pigment. However, 4-pyridylethyl derivative (EPY) is found to exhibit both red and black colors, depending on the solvent used for recrystallization. The colors are differentiated by molecular conformation in the crystal lattice, and the red color corresponds to the *cis* form while the black one is characterized by the *trans* form. Additionally, the excitonic interaction along the molecular stack is found to play an important role in the determination of the shade in the solid state.

Introduction

Perylene imide derivatives are well known organic pigments that exhibit a variety of shades in the solid state from red via maroon to black. These materials have attracted attention as photoconductors for electrophotographic photoreceptors as well as materials for optical disks.[1] We have previously investigated the color generation mechanism of Pigment Black 31 (EPH: Fig. 1) on the basis of the crystal structure and intermolecular interactions[1] The black color is characterized by two absorption bands which cover the whole visible region. The shorter-wavelength band is attributable to individual molecules while the longer-wavelength-band is caused by interactions between transition dipoles as shown in Fig. 2(a), where the transition dipole lies along the long-molecular axis. The molecules of the *trans* form are stacked with a slip angle of about 48°. Therefore, a bathochromic shift will result because the slip angle is below the critical angle of 54.7°.[1]

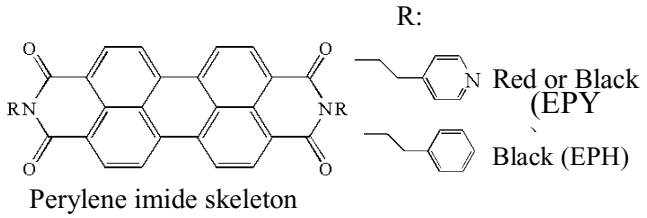

Figure 1. Molecular structure of perylene imide derivatives.

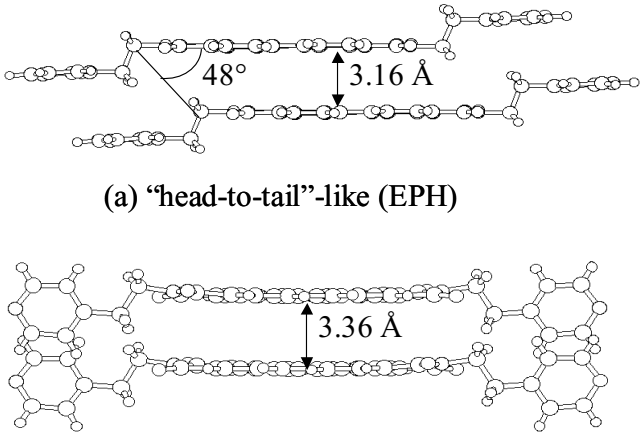

Figure 2. Molecular arrangement of the molecular stack (a) EPH and (b) EPY (cis isomerl).

Replacement of the phenyl rings in EPH by pyridyl rings (EPY: Fig. 1) brings about a vivid red color in solid when recrystallized from nitrobenzene(aprotic solvent), quite contrary to our expectation. Structure analysis revealed that the molecule is of the *cis* form and the two molecules are stacked in a fashion "parallel"(Fig. 2(b)).[2] We believed, however, that black EPY might still be available if we could realize a conformation of the *trans* form as found in EPH. For this reason, an attempt was made to grow single crystals from solution in protic solvents such as phenol and *m*-cresol. In fact, two kinds of single crystals of the *trans* form have successfully been isolated: EPY/$(phenol)_2$ and EPY/$(m\text{-cresol})_2$. The colors are black and dark red, respectively. This paper deals with these structures and discusses their electronic structure.

Experiment

EPY was synthesized by heating Perylene-3,4,9,10-tetracarboxylic dianhydride and 4-(2-aminoethyl)-pyridine at 400 K in water for 5 hours. Single crystals of the black color [EPY/$(phenol)_2$] were grown by recrystallization from a 1:1 solution of phenol and ethanol, using an autoclave. The crystal shape was platelet. Likewise, single crystals of the dark red color [EPY/$(m\text{-cresol})_2$] were recrystallized from

solution in *m*-cresol. A number of needle-like crystals were isolated.

Results and Discussion

1. Collection of Reflection Data and X-ray Structure Analysis

Reflection data were collected on a R-AXIS RAPID-F diffractometer from Rigaku using Cu$K\alpha$ radiation (λ = 1.5418 Å) at a temperature of –180 ± 1°C in order to suppress the solvent evaporation. The structures were solved by direct methods (Shelxs-86) and refined full-matrix least-squares on F^2 (teXsan program package).

Table 1 details the crystallographic parameters for two kinds of solvated crystals: EPY/(phenol)$_2$ and EPY/(*m*-cresol)$_2$. The space groups are P-1 and $P2_1/c$, respectively. The molecular symmetry is C_i in both crystals.

Table 1 Crystallographic Parameters

	EPY/(phenol)$_2$	EPY/(*m* -cresol)$_2$
Formula	$C_{38}H_{24}O_4N_4 \cdot C_{12}H_{10}O_2H_2$	$C_{38}H_{24}O_4N_4 \cdot C_{14}H_{14}O_2H_2$
Crystal system	triclinic	monoclinic
Space group	P-1	$P2_1/c$
Molecular symmetry	C_i	C_i
Z	1	2
a (Å)	6.513(2)	4.903(6)
b (Å)	12.182(2)	29.26(4)
c (Å)	12.200(2)	13.96(2)
α (°)	89.36(1)	-
β (°)	81.11(1)	97.65(6)
γ (°)	76.81(2)	-
Density (g/cm^3)	1.41	1.37

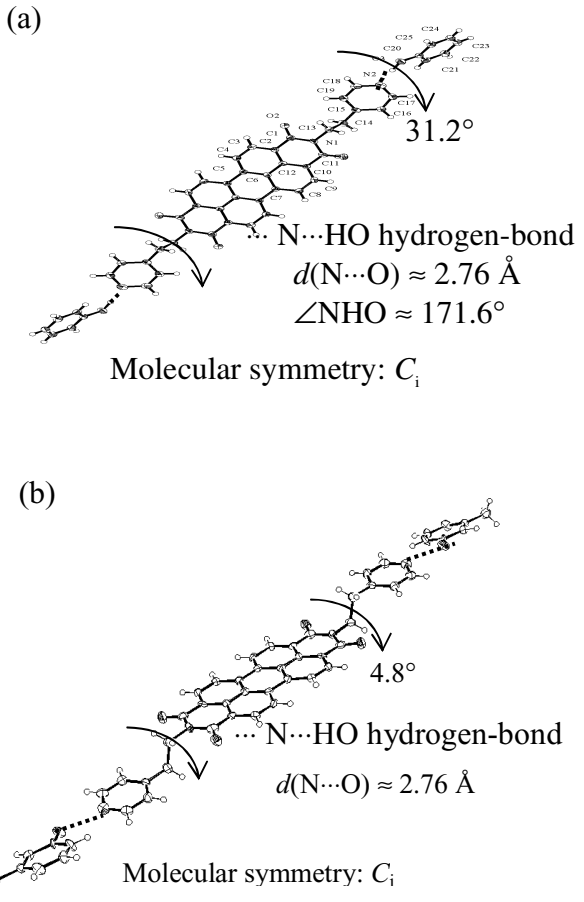

Figure 3. Molecular conformations of (a) EPY/(phenol)$_2$ and (b) EPY/(m-cresol)$_2$.

In both solvated crystals, each molecule has a conformation of the *trans* form as shown in Figs. 3(a) and 3(b), and the solvent molecules are hydrogen-bonded to the N atom of the pyridyl ring. That is, there is an intermolecular hydrogen bond between the hydroxyl group of phenol or *m*-cresol and the N atom of the pyridyl ring.

The deviation angle of the pyridyl ring from the perylene skeleton is also different in each crystal. In EPY/(phenol)$_2$, the pyridyl rings are twisted by 31.2° in the same direction because of the C_i symmetry (Fig. 3(a)); only 4.8° in EPY/(*m*-cresol)$_2$ (Fig. 3 (b)). The angle (∠NHO) and N/O distance of the N···HO hydrogen bond are 171.6° and 2.70 Å, respectively, for EPY/(phenol)$_2$. The three atoms (N, H and O) are well aligned and the N/O distance is short. This indicates that the N···HO bond in both crystals is quite strong. On the other hand, N/O distance of the N···OH hydrogen bond is 2.76 Å. However, the H atoms of hydroxyl groups of *m*-cresol could not be localized on the Fourier map.

The overlap of two molecules are shown in Figs.4 (a) and 4 (b) for EPY/(phenol)$_2$ and EPY/(*m*-cresol)$_2$, respectively. In EPY/(phenol)$_2$, the molecules are stacked with a distance of about 3.20 Å and a slip angle of 31.5°. In contrast, the interplanar distance is longer and the slip angle is larger in EPY/(*m*-cresol)$_2$: 3.53 Å and 47°. The present difference in geometry has a profound influence on the excitonic interactions, as discussed later.

2. Polarized Reflection Spectra

Figure 5 shows the polarized reflection spectra of EPY/(phenol)$_2$ measured on the (001) plane together with the projection of the crystal structure onto the (001) plane. The direction of the transition dipole (μ) as deduced from MO calculations[3] is shown by dotted lines. This is assigned to the HOMO/LUMO π-π^* transition.

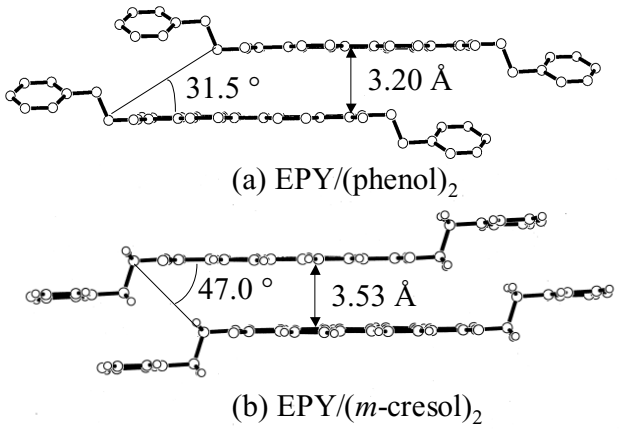

Figure 4. Molecular arrangement of the molecular stack (a) EPY/(phenol)$_2$ and (b) EPY/(m-cresol)$_2$.

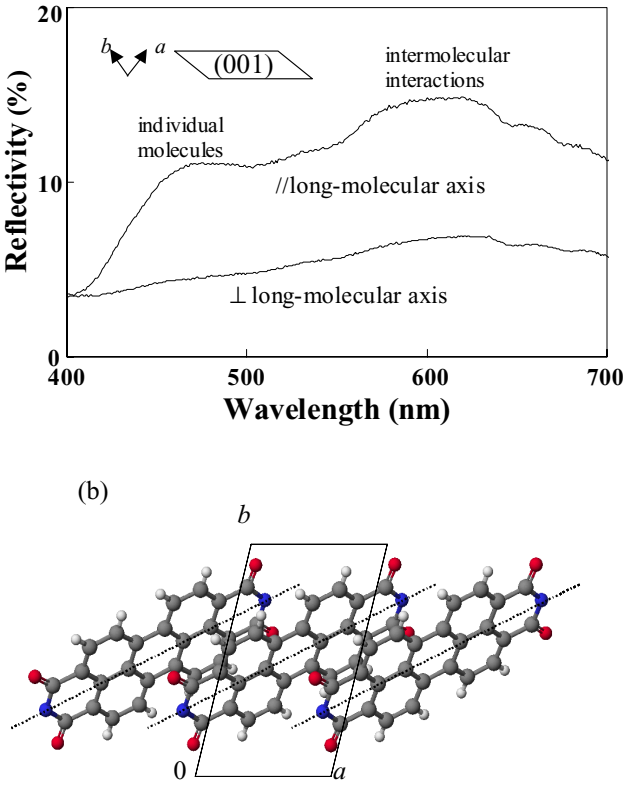

Figure 5. (a) Polarized reflection spectra of EPY/(phenol)$_2$ measured on the (001) plane and (b) projection onto (a,b) plane.

Polarized light was induced parallel and perpendicular to the long-crystal axis. Two prominent, broad reflection bands appear around 470 nm and 600 nm for polarization perpendicular to the long-crystal axis. This makes the color black. On the other hand, these intense bands completely disappear by polarized light parallel to the long-crystal axis. This clearly indicates that the transition dipole points along the long-molecular axis as predicted by MO calculations and that all reflection bands in the visible region are attributed to the same electronic transition due to the HOMO/LUMO π-π^* transition.

A similar result is also obtained in EPY/(*m*-cresol)$_2$. Fig. 6 shows the polarized reflection spectra together with the projection onto the (*a*,*c*) plane. Here again, two intense bands appear around 510 nm and 570 nm for polarization perpendicular to the long-crystal axis. This yields a color of dark red. On the other hand, these bands are completely quenched for polarization parallel to the long-crystal axis.

3. Excitonic Interaction and Spectral Shifts

The excitonic interactions[4] play an important role in dyestuffs and pigments, where the component molecule has a large absorption coefficient: proportional to the square of the transition dipole. The interaction energy ($\Delta E_{exciton}$) is given by the dipole-dipole equation: $\Delta E_{exciton} = |\mu|^2(1-3\cos^2\theta)/r^3$, where the transition dipole is denoted by μ, the distance and angle between two transition dipoles by r and θ, respectively. As evident from the present equation, the overall shift energy is determined by the strength of the interneighbor coupling ($|\mu|^2$) as well as on the mutual relative orientation of the transition dipoles in molecular assemblies. That is, the term $(1-3\cos^2\theta)/r^3$ determines the geometrical relationship of transition dipoles correlated with the crystal structure. Since this term falls off as the inverse cube of distance, most of the interaction would come from the nearest neighbors. The bathochromic or hypsochromic shift depends on the critical angle of θ=54.7°, below which the former will result and above which the latter will be the case.

Judging from the geometrical term $(1-3\cos^2\theta)/r^3$ on the basis of the crystal structure of EPY/(phenol)$_2$ and EPY/(*m*-cresol)$_2$, it is obvious that the stack pair makes, by far, larger contribution to the bathchromic shift as compared with that of other nearest pairs. If we look at the stack pairs shown in Figs. 4(a) and 4(b), it is apparent that the interaction energy of the stack pair in EPY/(phenol)$_2$ is larger than that in EPY/(*m*-cresol)$_2$. It follow that the former longer-wavelength band appears at longer wavelengths (about 600 nm shown in Fig. 5 (a)) than the latter (about 570 nm shown in Fig. 6 (a)).

In summary, the difference in molecular arrangement and its resulting excitonic interactions determine mainly the position and intensity of the absorption band, leading to different shades in the solid state.

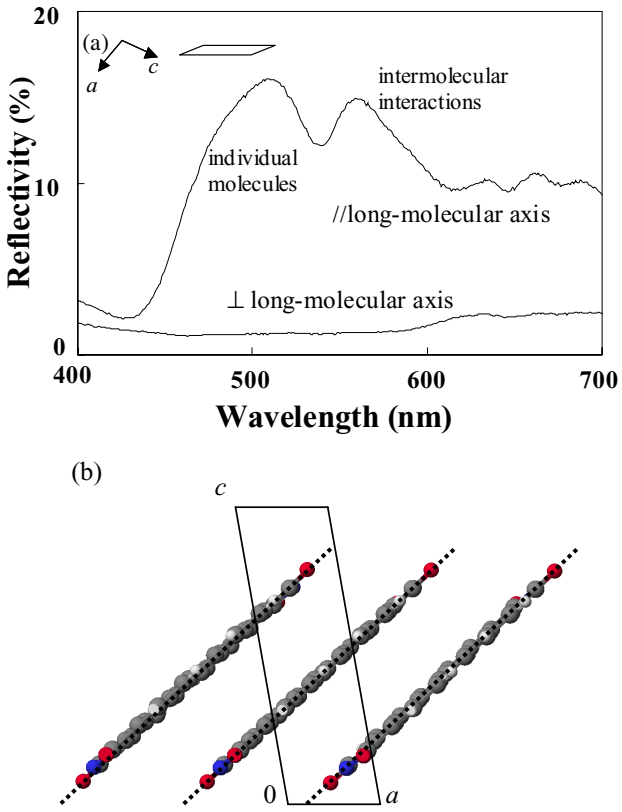

Figure 6. (a) Polarized reflection spectra of EPY/(m-cresol)$_2$ measured on the (a,c) plane and (b) projection onto (a,c) plane.

Conclusions

The mechanism of two shades (black & dark red) in EPY has been investigated from the standpoint of the crystal structure and intermolecular interactions. The conclusions drawn from the present investigation can be summarized as follow:

1. Two kinds of solvated crystals of protic solvents have been isolated: EPY/(phenol)$_2$ and EPY/(*m*-cresol)$_2$. In each crystal, the molecule has a conformation of the *trans* form. The colors are black and dark red, respectively.
2. There are intermolecular N···HO hydrogen bonds between the hydroxyl group of the solvent (phenol or *m*-cresol) and the N atom of the pyridyl ring.
3. A distinct difference is found in stack pairs between EPY/(phenol)$_2$ and EPY/(*m*-cresol)$_2$. The difference in geometrical arrangement determines the extent of excitonic interactions and is responsible for the two colors of black and dark red.

References

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Biography

Kazuyuki Hino 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.