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Strikingly different electronic spectra of structurally similar perylene imide compounds

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Abstract

Perylene imide derivatives are well known organic pigments and have also attracted attention as photoconductors for electrophotographic photoreceptors as well as materials for optical disks. *N*,*N*′-di-bis(2-(4-phenyl)ethyl)perylene-3,4:9,10-bis(dicarboximide) (i.e. 4-phenylethyl derivative: EPH) is a commercial black pigment. However, 4-pyridylethyl derivative (EPY) is found to exhibit a vivid red as well as black color, depending on the solvent used for recrystallization. Furthermore, the color changes from black to vivid red around 100 °C. In order to study the correlation between color and constitution, structure analysis was carried out on both materials of EPY. Then, we found two kinds of molecular conformation in EPY: *cis* and *trans* forms. The red color arises from a solid with the *cis* form while the black one is characteristic of the *trans* form. The mechanism of the two different colors has then been interpreted as arising from a different fashion of molecular arrangement and its characteristic excitonic interactions. In addition, the transformation from the black phase to the red one is found to be applicable to DVD-recordable disks that operate with a laser diode of 635 nm.

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Keywords: Perylene pigment; Crystal structure; Electronic structure

1. 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 [1]. Among these, Pigment Black 31 (EPH: Fig. 1(a)) has also attracted attention as a material for electrophotographic photoreceptors [2], photovoltaic elements [3] as well as for optical disks [4]. We have previously investigated the electronic structure of EPH on the basis of the crystal structure [5] in an attempt to develop an optical disk system for DVD (Digital Versatile Disk) that operates at 635 nm [4]. The black color is characterized by two absorption bands: one is attributed to individual molecules (530 nm) and the other is due to excitonic interactions along the stacking axis (610 nm). As typical of the excitonic interaction, the latter band appears or disappears when the molecules are ordered or disturbed, respectively. Based upon this effect, we have developed an optical disk system for DVD [4]. In EPH, the molecule is of the *trans* form and two molecules are stacked as shown in Fig. 2(a) [5], where the transition dipole lies along the long-molecular axis. Since the slip angle is 48° and below the critical angle of 54.7°, an additional bathochromic band will result due to excitonic interactions [4].

However, to our surprise, replacement of the phenyl rings in EPH by pyridyl rings (EPY: Fig. 1(b)) is found to bring about a vivid red color in the solid state when

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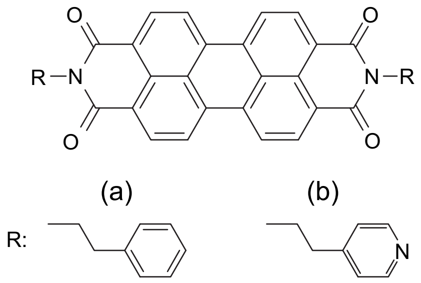

Fig. 1. Molecular structure of perylene imide derivatives: (a) EPH and (b) EPY.

recrystallized from solution in nitrobenzene, i.e. an aprotic solvent. Structure analysis revealed that the molecule is not of the *trans* form but of the *cis* one, and the two molecules are stacked in a "parallel" fashion (Fig. 2(b)) [6]. This is the first finding of the *cis* form in perylene imide pigments, although a number of crystal structures have been published so far [7,8]. In spite of the formation of the *cis* form, we believed that black EPY might still be available if we could prepare a *trans* form as found in EPH (Fig. 2(a)). For this reason, an attempt was made in the present investigation to grow single crystals from solution in protic solvents such as phenol and *m*-cresol. In fact, two kinds of solvated single crystals of the *trans* form have successfully been isolated: EPY/(phenol)$_2$ and EPY/(*m*-cresol)$_2$. The colors are black and reddish black, respectively.

This paper deals with crystal and electronic structure of red and black EPYs and discusses their use for a potential application to DVD-recordables.

2. Experiment

2.1. Synthesis and preparation of single crystals

EPY was synthesized by heating perylene-3,4:9,10-tetracarboxylic dianhydride and 4-(2-aminoethyl)-pyridine at 130 °C in water for 5 h. The dark and viscous cake was isolated. However, to our surprise, the black color became immediately vivid red when washed with dimethylformamide (DMF). It is also to be noted that the black powders were obtained when the viscous cake was directly dried under vacuum at room temperature. However, the color changes again from black to vivid red when heated above 100 °C.

Single crystals of the red color were grown by recrystallization from solution in nitrobenzene. A number of rod-like crystals were obtained. On the other hand, single crystals of the black color were grown by recrystallization from a 1:1 solution of phenol and ethanol, using an autoclave. The crystal shape was platelet. These crystals were found to include two solvent molecules in the form of EPY/(phenol)$_2$. Likewise, single crystals of the reddish black color were recrystallized from solution in *m*-cresol. A number of needle-like crystals were isolated with a composition of EPY/(*m*-cresol)$_2$.

It is also important to note that single crystals were successfully grown from the vapor phase of EPY. However, it turned out that the single crystals obtained were not EPY, but *N*,*N*′-di-bis(2-(4-pyridyl)ethyl)perylene-3,4;9,10-bis(dicarboximide): i.e. R = H in the perylene imide compound in Fig. 1 known as Pigment Violet 29 (hereafter abbreviated to PV29) [1,9]. This implies that two pyridyl rings of EPY were thermally eliminated during the crystal growth to give PV29 [9].

2.2. MO calculations

Geometry optimization was carried out for EPH as well as for the *cis* and *trans* forms of EPY by means of the AM1 Hamiltonian in Quantum CAChe Ver.3.2 from Fujitsu [10]. Spectroscopic calculations were then made on the basis of the optimized geometry, using the INDO/S Hamiltonian in ZINDO program package [11].

2.3. Equipment

UV–Vis spectra were recorded on a UV-2400PC spectrophotometer (Shimadzu). Measurements for polarized reflection spectra were made on single crystals by means of a UMSP80 microscope-spectrophotometer (Carl Zeiss). An Epiplan Pol (×8) objective was used together with a Nicol-type polarizer. Reflectivities were corrected relative to the reflection standard of silicon carbide.

Reflection data were collected by means of an R-AXIS RAPID F diffractometer from Rigaku, using Cu$K\alpha$. All measurements were carried out at −180 °C in order to suppress the solvent evaporation. The programs to solve the structure were SHELXS-86 [12] for EPY, EPY/(phenol)$_2$ and EPY/(*m*-cresol)$_2$. Refinement

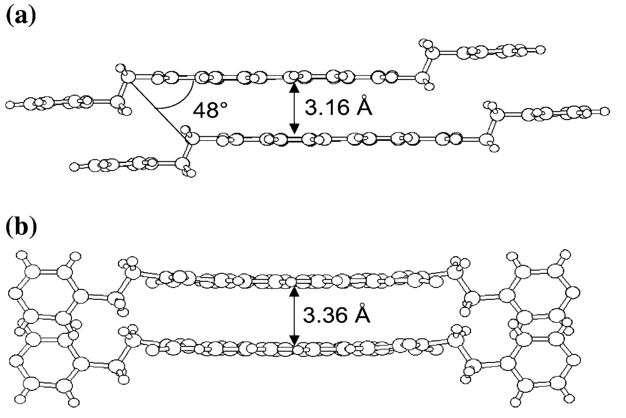

Fig. 2. Overlap of two molecules: (a) EPH (*trans* form) and (b) EPY (*cis* form).

was then made on F^2 by full-matrix least-squares calculations using the teXsan program package [13].

TGA/DTA (thermogravimetric analysis and differential thermal analysis) measurements were made on powdered EPY of the red and black colors by means of a Rigaku Thermo Plus 8230 at a heating rate of 10 °C/min.

3. Results and discussion

3.1. MO calculations

The heat of formation, calculated absorption band and its oscillator strength for EPH are 18.5 kcal/mol, 433.6 nm and 1.36, respectively. The molecule has C_i symmetry and the torsion angle between the perylene imide skeleton and the phenyl ring amounts to 17°.

The heat of formation for the *cis* form of EPY is 40.8 kcal/mol and is slightly larger than that of the *trans* form (38.3 kcal/mol). The *cis* form has C_2 symmetry. The torsion angle is 70.5°, showing that the pyridyl rings are almost vertically attached to the perylene imide skeleton. On the other hand, the pyridyl rings are parallel to each other due to the C_i symmetry in the *trans* form and the torsion angles are 33.2°. The calculated absorption band and oscillator strength are: 440.3 nm and 1.35 for the *cis* form, and 432.8 nm and 1.35 for the *trans* form. No significant difference is recognized in the absorption wavelength between the *cis* and *trans* forms.

3.2. Solution spectra

Fig. 3 shows the solution spectra for EPH and EPY in dimethylsulfoxide. The absorption maxima of EPH are slightly displaced toward longer wavelengths as compared with those of EPY. This is consistent with the MO calculations. In both spectra, there observed a progression of the absorption bands. Since the longest-wavelength band is quite steep and the absorption bands are equally spaced (about 1400 cm^{-1}), the longest-wavelength band is assigned to the pure electronic transition as denoted by the 0–0 transition and the second longest-wavelength band is attributed to the 0–1 vibronic band where the electronic transition is coupled with one vibrational transition. Likewise, the 0–2 and 0–3 transitions are assigned as shown.

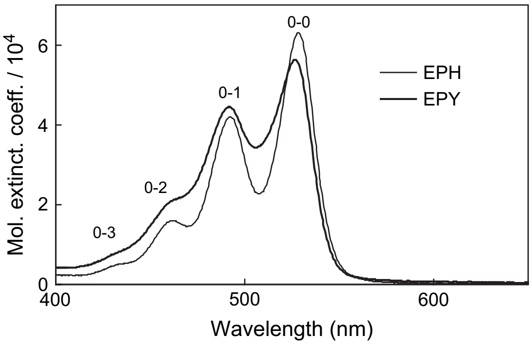

Fig. 3. Solution spectra for EPH and EPY in dimethylsulfoxide.

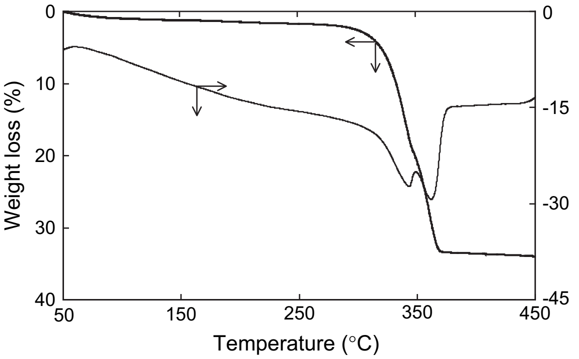

Fig. 4. TGA/DTA curves for red EPY.

3.3. TGA/DTA measurements

Fig. 4 shows the TGA/DTA curves for EPY of the red color. The onset of the weight loss begins at about 100 °C and is completed at 370 °C. The total weight loss amounts to about 35% which corresponds exactly to the transformation from EPY to another perylene compound with R = H in Fig. 1 registered as PV29. This transformation is also borne out by the formation of single crystals of PV29 when grown from the vapor phase as stated previously [9]. As evident from the two endothermic peaks around 340 and 360 °C in the DTA curve, elimination of two pyridyl rings in EPY proceeds in two steps (i.e. one by one).

Fig. 5 shows the TGA/DTA curves for EPY of the black color. A significant difference is recognized between red and black EPYs in the range between 50 and 110 °C. At higher temperatures above 100 °C, however, the thermal process is exactly the same in both compounds. The weight loss in the range between 50

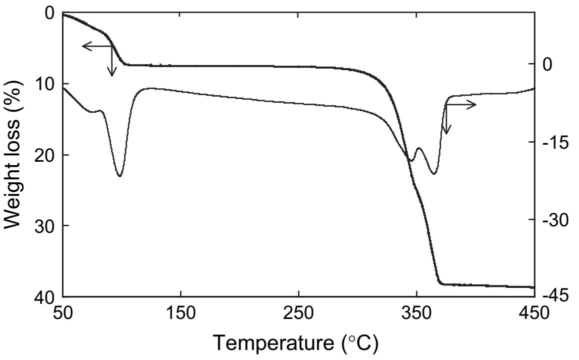

Fig. 5. TGA/DTA curves for black EPY.

and 100 °C is accompanied by a large endothermic peak at about 100 °C. This corresponds to the desorption of two water molecules, indicating an original composition of EPY/$(H_2O)_2$. Upon desorption of water, the color changes immediately from black to vivid red.

3.4. IR spectra measured on powders

IR spectra were measured on three different black powders of EPY as synthesized (i.e. EPY/$(H_2O)_2$, EPY/(phenol)$_2$ and EPY/(*m*-cresol)$_2$) in order to study the intermolecular N···HO hydrogen bond between the N atom of the pyridyl ring and the H atom of water molecule, as well as the one between the N atom of the pyridyl ring and the H atom of phenol or *m*-cresol. In these compounds, a broad band of the OH stretching was observed around 3200 cm^{-1}. The present band is considerably displaced toward lower wavenumbers as compared with the free OH stretching band (about 3500 cm^{-1}). This indicates the formation of N···HO intermolecular hydrogen bonds.

3.5. Crystal structure of EPY, EPY/(phenol)$_2$ and EPY/(m-cresol)$_2$

Table 1 details the crystallographic parameters for EPY [6] as well as the two kinds of solvated crystals: (phenol)$_2$ [14] and EPY/(*m*-cresol)$_2$ [15]. The space groups are *Pccn*, $P\bar{1}$ and $P2_1/c$, respectively. The molecular symmetry is C_2 for the *cis* form while C_i for EPY/(phenol)$_2$ and EPY/(*m*-cresol)$_2$.

Fig. 6(a) and (b) shows the ORTEP plot of EPY and molecular arrangement, respectively. The overlap of two molecules is given in Fig. 2(b). The perylene skeleton is entirely planar. However, two pyridyl rings are twisted in opposite directions by about 72°, just as in the case of Pigment Red 149 (i.e. R = 3,5-xylyl group in Fig. 1) where the 3,5-xylyl groups are nearly vertically connected to the skeleton [16]. In addition, the two ethylpyridyl groups are located on the one side of the perylene skeleton, i.e. in a "*cis*" fashion, showing a molecular symmetry of C_2. Therefore, the molecule possesses a slight dipole moment of about 0.13 D. All molecules are arranged on the (*a*,*b*) plane and stacked along the *c*-axis.

Fig. 7(a)–(c) shows the ORTEP plot, molecular arrangement as well as overlap of two molecules for EPY/(phenol)$_2$, respectively. Likewise, the same illustrations are given for EPY/(*m*-cresol)$_2$ in Fig. 8(a)–(c), respectively. As seen from Figs. 7(a) and 8(a), the molecular conformation of EPY/(phenol)$_2$ and EPY/(*m*-cresol)$_2$ is of the *trans* form and there are N···HO intermolecular hydrogen bonds between the N atom of the pyridyl ring and the hydroxyl group of phenol or *m*-cresol. In EPY/(phenol)$_2$, the pyridyl rings are twisted by 31.2° in the same direction because of the C_i symmetry (Fig. 7(a)); whereas the torsion angle is only 4.8° in EPY/(*m*-cresol)$_2$ (Fig. 8(a)). The angle (∠NHO) and N/O distance of the N···HO hydrogen bond are 170.3° and 2.72 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, the N/O distance of the N···HO hydrogen bond in EPY/(*m*-cresol)$_2$ is 2.76 Å.

We focus now on the overlap of two molecules along the stacking axis. In EPY (Fig. 2(b)), the interplanar distance amounts to 3.36 Å and the molecules are stacked with "zero" slip angle. In EPY/(phenol)$_2$ (Fig. 7(c)), 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)$_2$ (Fig. 8(c)): 3.53 Å and 47°, respectively. The present molecular arrangement has

Table 1
Crystallographic parameters for EPY, EPY/(phenol)$_2$ and EPY/(*m*-cresol)$_2$

	EPY (*cis* form) [6]	EPY/(phenol)$_2$ (*trans* form) [14]	EPY/(*m*-cresol)$_2$ (*trans* form) [15]
Formula	$C_{38}H_{24}O_4N_4$	$C_{38}H_{24}O_4N_4 \cdot C_{12}H_{10}O_2H_2$	$C_{38}H_{24}O_4N_4 \cdot C_{14}H_{14}O_2H_2$
Crystal system	orthorhombic	triclinic	monoclinic
Space group	*Pccn*	$P\bar{1}$	$P2_1/c$
Molecular symmetry	C_2	C_i	C_i
Z	4	1	2
a (Å)	25.957(2)	6.513(2)	4.903(6)
b (Å)	15.199(1)	12.182(2)	29.26(4)
c (Å)	6.7114(6)	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)	1.51	1.41	1.37
*R*1	0.058	0.048	0.100

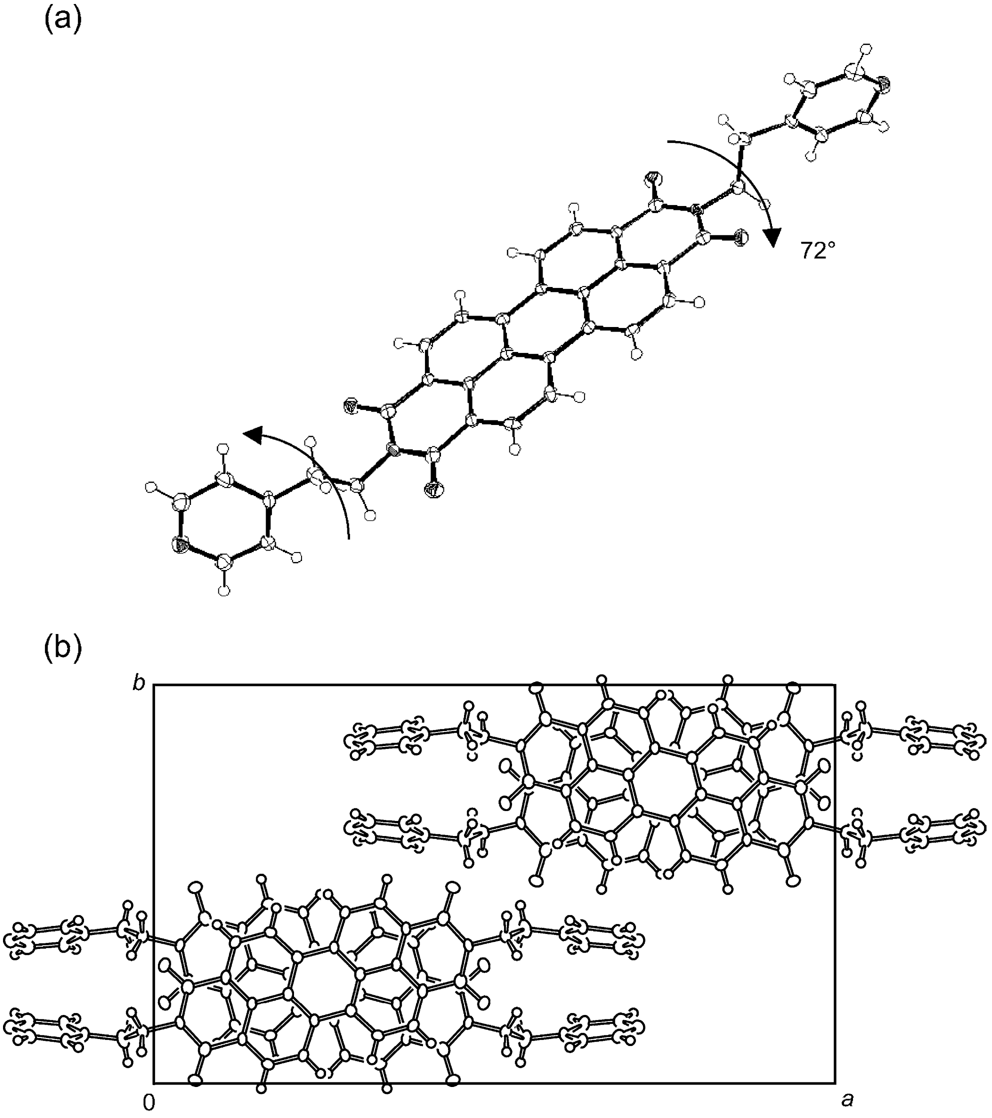

Fig. 6. (a) Molecular conformation and (b) molecular arrangement for EPY (red).

a profound influence on the excitonic interactions, as discussed later.

3.6. Polarized reflection spectra measured on single crystals of EPY, EPY/(phenol)$_2$ and EPY/(m-cresol)$_2$

Fig. 9 shows the polarized reflection spectra measured on the (010) plane of EPY single crystals together with the projection onto the (*a*,*c*) plane. Two prominent reflection bands appear around 470–500 nm together with a small band around 550 nm for polarization parallel to the *a*-axis. This is the direction of the transition dipole as deduced from MO calculations. However, these bands are quenched for polarization perpendicular to the *a*-axis, i.e. parallel to the *c*-axis. This clearly indicates that three bands in the visible region arise from one single electronic transition (i.e. HOMO/LUMO $\pi-\pi*$ transition) and that the direction of the transition dipole points along the long molecular axis.

Similarly, Fig. 10 shows the polarized reflection spectra of EPY/(phenol)$_2$ measured on the (001) plane together with the projection of the crystal structure onto the (*a*,*b*) plane. Polarized light was induced parallel and perpendicular to the long-molecular axis. Two broad reflection bands appear around 470 nm and 600 nm for polarization parallel to the long-molecular axis. Because of the two visible bands, the crystal bears a black color. On the other hand, these intense bands completely disappear by polarized light perpendicular to the long-molecular axis. This indicates again that the transition dipole points along the long-molecular axis and that all reflection bands in the visible region are attributed to the one single electronic transition: HOMO/LUMO $\pi-\pi*$ transition.

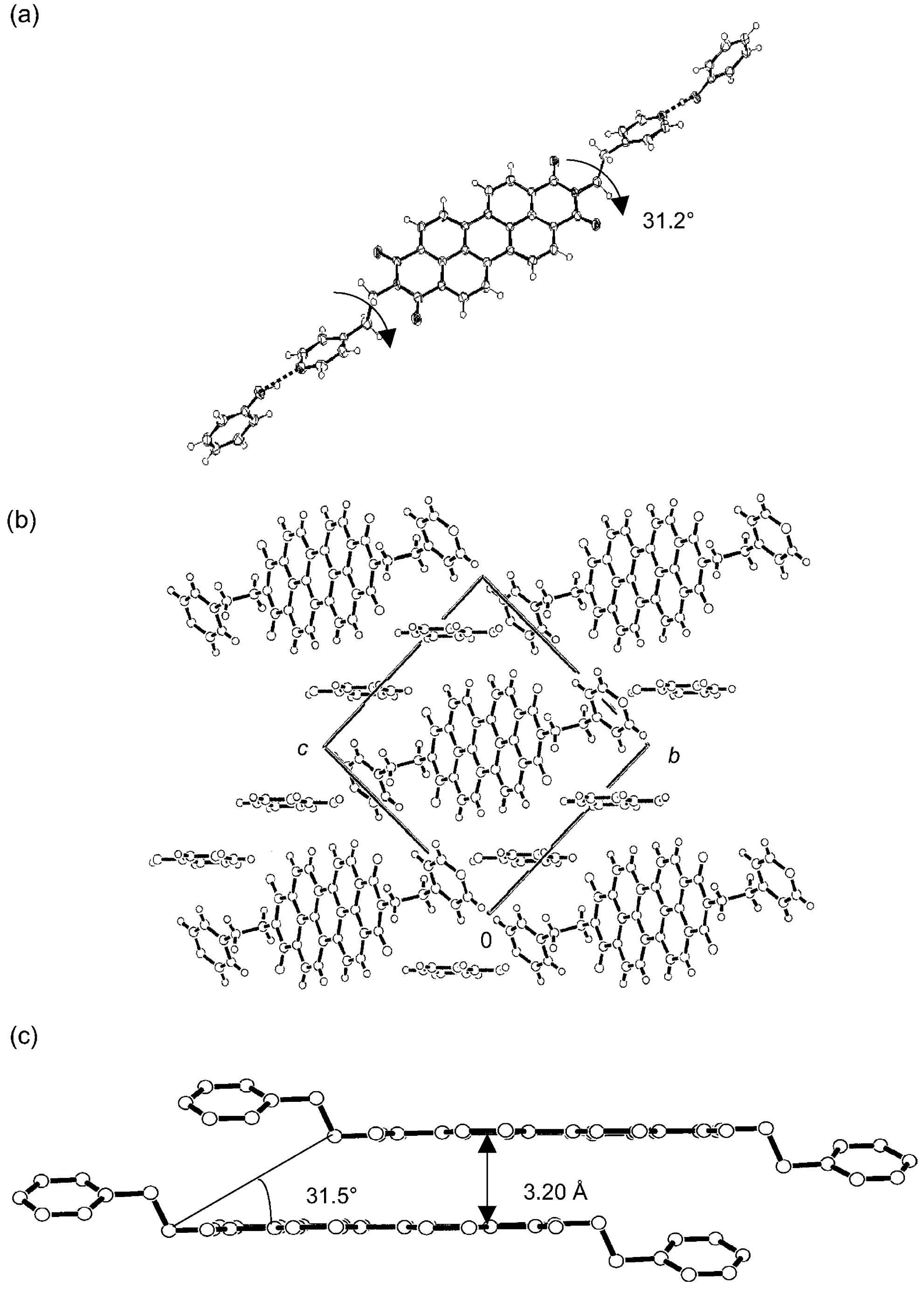

Fig. 7. (a) Molecular conformation, (b) molecular arrangement and (c) molecular stack for EPY/(phenol)$_2$.

A similar result is also obtained in EPY/(m-cresol)$_2$. Fig. 11 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 parallel to the long-molecular axis. Since the longer-wavelength band is present around 570 nm, the color is reddish black. On the other hand, these bands are completely quenched for polarization perpendicular to the long-molecular axis.

3.7. Excitonic interaction and appearance of the longer-wavelength band

The excitonic interactions [17] play an important role in dyestuffs and pigments, where the component molecule has a large absorption coefficient; i.e. proportional to the square of the transition dipole. The interaction energy ($\Delta E_{\mathrm{exciton}}$) is given by the dipole–dipole equation: $\Delta E_{\mathrm{exciton}} = |\mu_{\mathrm{T}}|^2(1 - 3\cos^2\theta)/r^3$, where

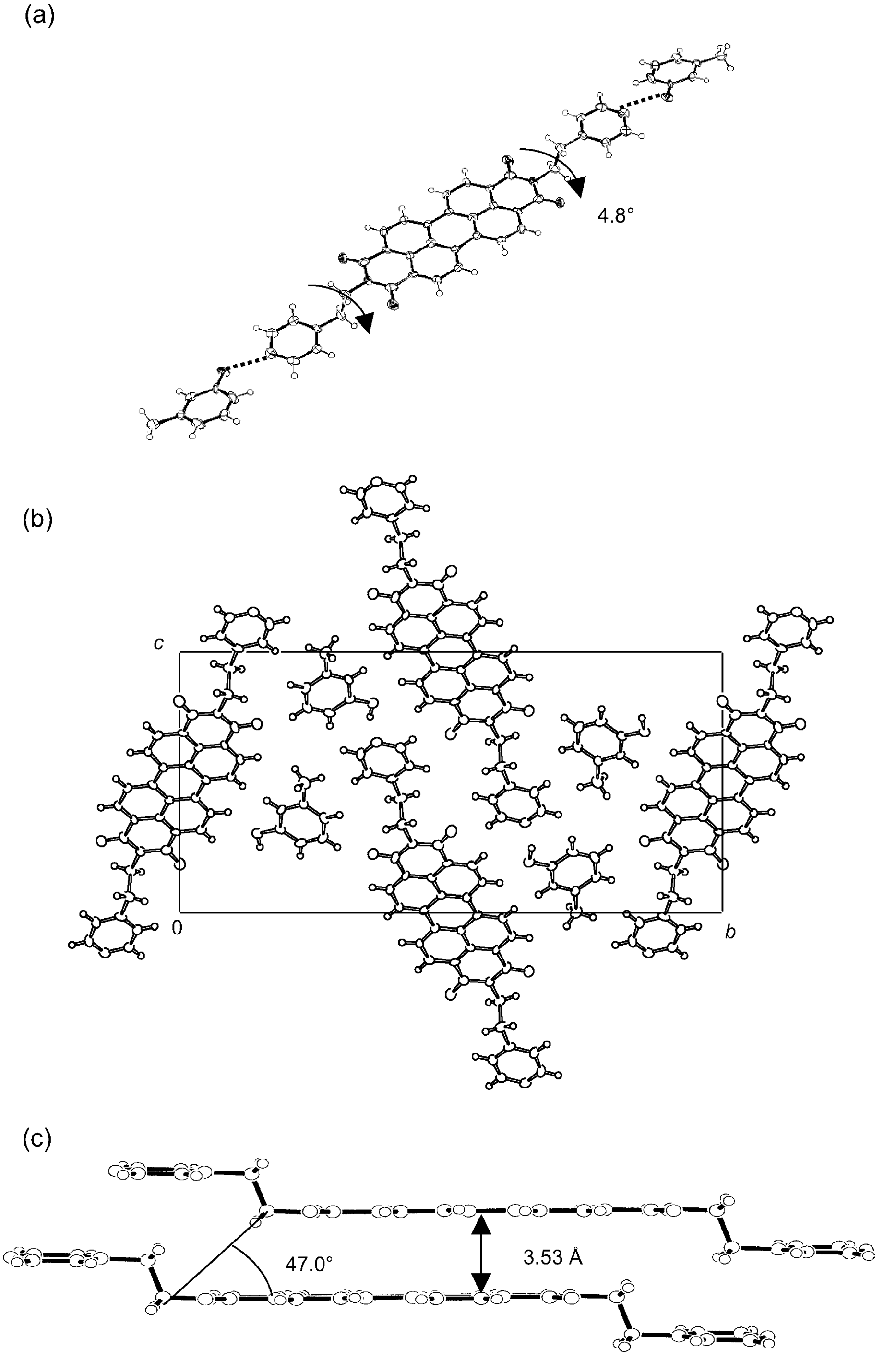

Fig. 8. (a) Molecular conformation, (b) molecular arrangement and (c) molecular stack for EPY/(*m*-cresol)$_2$. The H atoms of hydroxyl groups of *m*-cresol could not be localized on the Fourier map.

the transition dipole is denoted by μ_T, 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 ($|\mu_T|^2$) as well as by 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 $\theta = 54.7°$, below which the former will result and above which the latter will be the case.

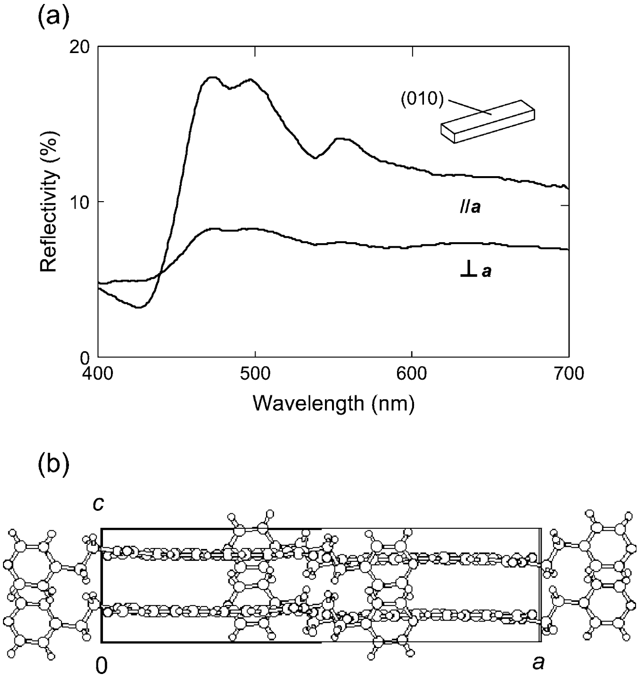

Fig. 9. (a) Polarized reflection spectra measured on the (010) plane of EPY and (b) projection onto the (*a*,*c*) plane. The direction of the transition dipole as deduced from MO calculations points along the long molecular axis.

Judging from the inverse cube dependence of the distance on the interaction energy, it is obvious in EPY, EPY/(phenol)$_2$ and EPY/(*m*-cresol)$_2$ that the stack pair makes a marked contribution to the spectral shift as compared with that of the molecular plane. In EPH (Fig. 2(a)), the slip angle and interplanar distance are 48° and 3.16 Å, respectively. Since the present angle is below the critical angle of $\theta = 54.7°$, an additional band is expected to appear at a longer wavelength. This corresponds to the band around 610 nm in experiment [4]. On the contrary, the situation of EPY is totally different because the slip angle is almost 90° which is larger than the critical angle. Therefore, the excitonic band is displaced toward shorter wavelength relative to the solution spectrum (Fig. 3). The reflection spectrum shown in Fig. 9(a) represents a superimposed picture composed of the molecular band and hypsochromically-displaced excitonic band, giving rise to a vivid red color. In EPY/(phenol)$_2$ and EPY/(*m*-cresol)$_2$, the excitonic interactions are quite similar to that of EPH. As seen from Figs. 7(c) and 8(c), it is apparent that the interaction energy of the stack pair in EPY/(phenol)$_2$ (slip angle: 31.5°; interplanar distance: 3.20 Å) is larger than that in EPY/(*m*-cresol)$_2$ (slip angle: 47°; interplanar distance: 3.53 Å). It follows that the former longer-wavelength band is supposed to appear at longer wavelengths than the latter. In fact, the former is present around 600 nm (Fig. 10(a)) while the latter around 570 nm (Fig. 11(a)).

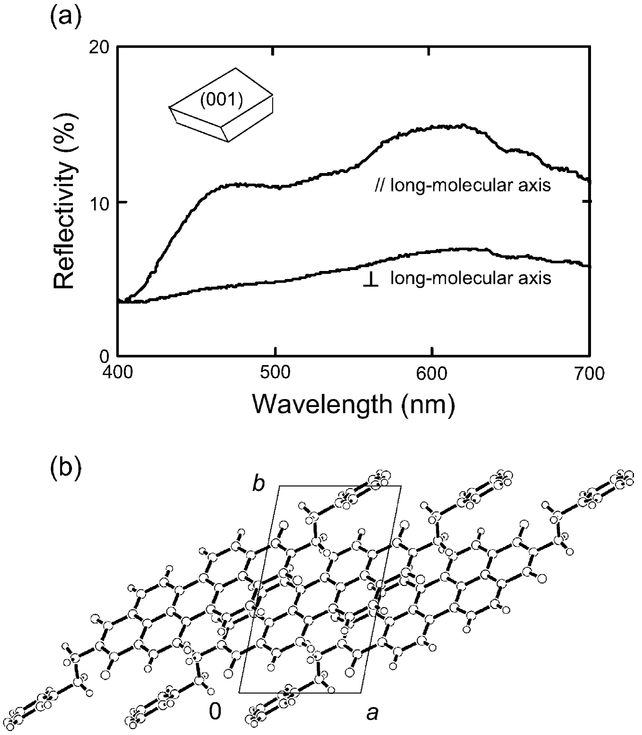

Fig. 10. (a) Polarized reflection spectra measured on the (001) plane of EPY/(phenol)$_2$ and (b) projection onto the (*a*,*b*) plane. The direction of the transition dipole points along the long molecular axis.

As described above, a variety of shades appear in the solid state through excitonic interactions which depend largely on the molecular arrangement.

3.8. Characterization of the black phase as synthesized and its application to DVD-recordable disks

The molecular conformation of the black product as synthesized is not yet fully understood. However, it is highly probable that the molecule is of the *trans* form in consideration of the structure analysis as well as electronic characterization of EPH, EPY, EPY/(phenol)$_2$ and EPY/(*m*-cresol)$_2$. In addition, it is likely that two water molecules are hydrogen-bonded, in a *trans* fashion, to the N atom of pyridyl ring, just as in the case of phenol- or *m*-cresol-solvated EPY. Then, desorption of water molecules around 100 °C may induce a conformational change from the *trans* form to the *cis* one even in the solid state, accompanied by subsequent molecular arrangement. The present assumption is also supported by the coincidence of the TGA/DTA curves of EPY and EPY/(phenol)$_2$ in the temperature range between 100 and 450 °C (Figs. 4 and 5).

Fig. 12 shows the diffuse reflectance spectra of powdered EPY of the red and black colors. As discussed in the preceding section, the black spectrum is composed

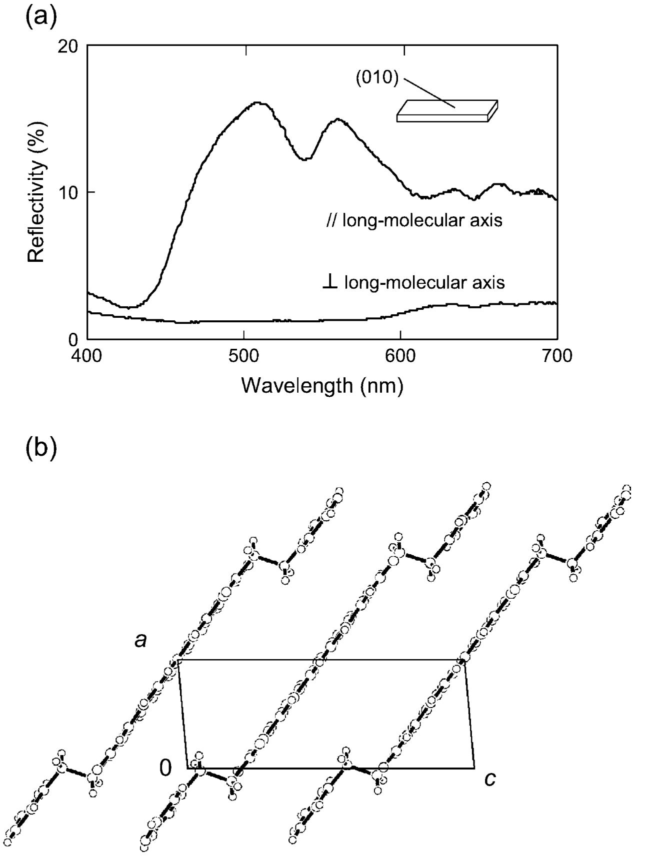

Fig. 11. (a) Polarized reflection spectra measured on the (010) plane of EPY/(*m*-cresol)$_2$ and (b) projection onto the (*a*,*c*) plane. The direction of the transition dipole points along the long molecular axis.

of two absorption bands: one is due to individual molecules (500 nm) and the other is caused by excitonic interactions (635 nm). The latter band disappears when the black phase is heated above 100 °C. The present transformation from the black to the red phase can be applied to DVD-recordable disks. The system starts from the state with an absorption of 635 nm ("black") and ends up with quenching of this absorption ("red") by laser irradiation. The disk structure of the write once is: substrate/EPY/Al-reflection layer/protection layer. Information is written and read out by a laser diode of 635 nm. Upon irradiation, the optical energy is absorbed in the black EPY layer due to an intense absorption and converted into thermal energy to cause a color change from black to red. This leads to the disappearance of the band around 635 nm. At this moment, the reflectivity changes from low to high.

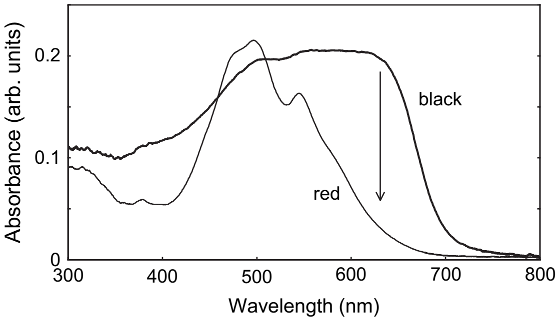

Fig. 12. Diffuse reflectance spectra of powdered EPY of the red and black colors. Laser irradiation disturbs the molecular arrangement of the black phase to cause the band around 635 nm to disappear (i.e. "laser writing").

4. Conclusions

The mechanism of two shades (red and black) 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 follows.

1. Two kinds of solvated crystals are isolated from protic solvents: EPY/(phenol)$_2$ (black) and EPY/(*m*-cresol)$_2$ (reddish black). In each crystal, the molecule has a conformation of the *trans* form.
2. N···HO intermolecular hydrogen bonds are present between the N atom of the pyridyl ring and the hydroxyl group of the solvent molecule (i.e. phenol or *m*-cresol).
3. A distinct difference is found in stack pairs between EPY (*cis* form: vivid red), EPY/(phenol)$_2$ (*trans* form: black) and EPY/(*m*-cresol)$_2$ (*trans* form: reddish black). The molecules of the *cis* form in EPY are stacked with a slip angle of 90° while the angles are 31.5° and 47° for EPY/(phenol)$_2$ and EPY/(*m*-cresol)$_2$, respectively. The present difference in molecular stack determines mainly the direction of the spectral shift as well as the extent of excitonic interactions, leading to the two distinct colors of vivid red (*cis* form) and black (*trans* form).
4. The black phase as synthesized is characterized as EPY/(H_2O)$_2$. The transition from the black phase to the red one due to thermal energy can be applied to DVD-recordable disks operating with a laser diode of 635 nm.

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