Electronic characterization of *N,N'*-bis(2-phenylethyl)perylene-3,4:9,10-bis(dicarboximide) and its application to optical disks

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The title compound is a commercial black pigment based on the perylene skeleton. As evaporated, it exhibits a brilliant red color (absorption maximum: 500 nm). However, it undergoes a color change from red to black (absorption maxima: 473 and 610 nm) when exposed to acetone vapor or heated above 100 °C for several seconds. The electronic spectra have been characterized on the basis of the crystal structure and intermolecular interactions. The red color (500 nm) is due to randomly oriented, individual molecules in the amorphous phase; whereas the black phase is characterized by a quasiordered system which gives two absorption bands: one is due to individual molecules (473 nm) and the other is due to exciton coupling effects (610 nm). The color change is attributed to the appearance ("on" state) or disappearance ("off" state) of the absorption band around 610 nm and is applicable to optical disk systems based on an AlGaInP diode laser of 635 nm. An information storage system has been developed in which the absorption at 635 nm is switched on (red–black) or switched off (black–red) on irradiation with laser in the presence of a hydrazone compound that induces a phase change. © 1998 American Institute of Physics. [S0021-8979(98)04220-0]

I. INTRODUCTION

N,N'-bis(2-phenylethyl)perylene-3,4:9,10-bis (dicarboximide) (abbreviated to PDC; shown in the inset of Fig. 1) is a commercial black pigment manufactured by BASF AG.¹ Besides its use as a pigment, PDC has also attracted attention as a material for electrophotographic photoreceptors² as well as photovoltaic elements.³ Perylene pigments cover a variety of colors starting from red, bordeaux, violet, brown, to black. Black perylene pigments are derived through slight changes in the substitution on the moiety which is not part of the conjugated system.¹ The difference in shade has been attributed to a structurally controlled special arrangement of the pigment molecules within the crystal lattice.¹ Graser and Hädicke and their co-workers pointed out that the degree of "area overlap" of successive perylenes determines simply the shift of the absorption maximum.^{4–8} On the contrary, Kazmaier and Hoffmann proposed a new concept of the quantum interference effect in order to explain the spectral shift.⁹ However, details are not yet fully understood at the moment.

Our initial interest was to clarify the electronic structure of PDC on the basis of the crystal structure and intermolecular interactions. We started reproducing the previous results reported in the literature^{10–12} and confirmed that the color as evaporated is not black, but brilliant red (Fig. 1). Then, it undergoes a color change from red (amorphous phase) to black (crystalline phase) when exposed to acetone vapor. In the course of our studies on electronic characterization, we observed that the color change also occurs thermally when heated above about 100 °C for several seconds. Furthermore,

we found a new crystalline phase¹³ different from the one reported by Hädicke and Graser.⁴ The moment we saw the appearance of the absorption band at 610 nm due to vapor or heat treatment, we immediately thought of an application to optical disks operating at 635 nm based on an AlGaInP diode laser.

This article is composed of two parts. The first part deals with electronic characterization of PDC on the basis of crystal structure and intermolecular interactions. The second part describes an application to optical disks utilizing the appearance or disappearance of the absorption band around 610 nm.

II. ELECTRONIC CHARACTERIZATION OF PDC

A. Crystal structure and reflection spectra

The crystal structure of PDC has already been analyzed by Hädicke and Graser⁴ who grew single crystals from cresol. On the contrary, we prepared them from the vapor phase and found a new crystal phase.¹³ The phase of BASF will hereafter be designated by phase I while ours is called phase II. The crystal data are listed in Table I. The structure is mostly similar, but some differences can be recognized in deviation angle of the phenyl ring from the perylene skeleton as well as in density.

Figures 2(a) and 2(b) show the side view of the molecule of modifications I and II as well as the projection of the crystal structure onto the (*a*,*c*) and (*b*,*c*) planes, respectively. All molecules are oriented in the same direction in

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FIG. 1. Absorption spectra of evaporated PDC before and after vapor treatment (film thickness: about 1000 Å).

phase I; whereas the molecules are arranged in a zigzag fashion along the *b* axis in phase II.

Figures 3(a) and 3(b) show the polarized reflection spectra for phases I and II, respectively, measured on the (001) plane of the single crystals of each modification by means of a microscope-spectrophotometer (UMSP80; Carl Zeiss). A prominent reflection band appears around 650 nm in phase I for polarization parallel to the *b* axis [Fig. 3(a)]. A rather broad band peaking at 470 nm is also recognized. These two bands approximately correspond to those in evaporated films (Fig. 1), although the band at longer wavelengths is more intensified than that at shorter wavelengths. The reflection bands shown in Fig. 3(b) for phase II roughly correspond to those in phase I. It should be, however, noted that the reflection bands for polarization perpendicular to the *a* axis is slightly shifted towards longer wavelengths as compared with those for polarization parallel to the *a* axis. The present effect that the band position depends on the crystal axis is called the factor-group (or Davydov) splitting as caused by interactions between transition moments in the excited state.^{14–16} Another remarkable point is that the longest-wavelength band in modification I always appears at longer wavelengths than in modification II by about 17 nm (about 413 cm^{-1}). The difference in absorption maximum as well as

FIG. 2. Molecular conformation and projection of the structure: (a) phase I onto the (*a*,*c*) plane and (b) phase II onto the (*b*,*c*) plane.

the nature of the absorption band will be discussed in Sec. II D.

B. Phase change from an amorphous to the crystalline state

Figure 4 shows the x-ray diffraction diagrams in evaporated films before and after vapor treatment. The broad band around 25° is due to the glass substrate used. The halo diffraction pattern before vapor treatment is indicative of an amorphous state; whereas the crystallization due to vapor treatment is distinctly recognized by diffraction peaks assigned as shown. The symbols I and II beside the parentheses in Fig. 4 denote modifications I and II, respectively. This indicates that the black phase is, for the most part, characterized by phase II.

It is of interest to note that the same color change also occurs thermally as shown in Fig. 5, displaying the gradual spectral changes as a function of heat treatment time at 100°C . The spectral change proceeds with time, accompanied by two isosbestic points at 350 and 560 nm. The phase change can be demonstrated by measurements differential scanning calorimetry (DSC) as shown in Fig. 6. A broad exothermic peak of 23.0 J/g is clearly observed around $75\text{--}100^\circ\text{C}$ which corresponds to the phase transition from

TABLE I. Crystallographic data for phases I and II.

	Modification I	Modification II
Space group	$C2/c$	$P2_1/c$
<i>Z</i>	4	2
Molecular symmetry	C_i	C_i
Torsion angle ($^\circ$) ^a	19	3
<i>a</i> (Å)	20.131	4.737
<i>b</i> (Å)	4.741	32.450
<i>c</i> (Å)	29.953	9.507
β ($^\circ$)	103.35	100.27
Density (g/cm^3)	1.43	1.38
<i>R</i> -factor (%)	6.1	7.6

^aThe torsion angle implies the deviation of the phenyl ring from the perylene skeleton.

FIG. 3. Polarized reflection spectra measured on the (001) plane in each modification: (a) phase I and (b) phase II.

an amorphous state ($\lambda_{\max}=500$ nm) to the crystalline state ($\lambda_{\max}=610$ nm). Further crystallization is also recognized in the range between 220 and 320 °C in the form of a flat plateau. During this exothermic process of 21.2 J/g, the absorption maximum is further displaced to 631 nm, accompanied by an increase in absorption intensity; whereas the intensity of the band at 473 nm is greatly diminished. The final spectrum ends up nearly with the reflection spectra shown in

FIG. 4. X-ray diffraction diagrams of evaporated PDC before and after vapor treatment.

FIG. 5. Spectral changes as a function of heat-treatment time at 100 °C.

Fig. 3. The nature of the absorption bands in Fig. 5 is characterized below on the basis of the solution spectrum.

Figure 7 shows the solution spectrum of PDC in dimethylsulfoxide (DMSO), in which the solid-state spectrum of an evaporated film is superimposed. The solution spectrum exhibits a progression of absorption bands starting from 527 nm with a spacing about 1370 cm^{-1} . So, the longest-wavelength band at 527 nm is attributed to the 0–0 transition and the second-longest band at 492 nm to the 0–1 transition, etc. In the solid state, the absorption bands are slightly displaced, due to polarization effect, towards longer wavelengths and the 0–1 transition at 500 nm becomes the strongest band. On the basis of the present assignment, we will characterize the absorption bands in Fig. 5. As the heat treatment proceeds, the 0–1 band is slightly displaced towards shorter wavelengths, accompanied by reduction in absorption intensity. In 60 s, the 0–2 band becomes the strongest. On the other hand, an absorption shoulder begins to appear in 30 s and grows up to an absorption peak at 610 nm. The present result evidently indicates that all absorption bands in solution are well preserved in the solid state and that the absorption band at 610 nm is assigned to a new band due to intermolecular interactions as caused by molecular rearrangements.

FIG. 6. DSC measurements of PDC showing the heat flow as a function of temperature.

FIG. 7. Solution spectrum of PDC in DMSO together with the solid-state spectrum in an evaporated film.

C. Temperature dependence of absorption spectra and lattice contraction

In order to study the influence of intermolecular interactions on the optical absorption, the temperature dependence of absorption spectra as well as lattice contraction has been studied on the following assumption: (1) lattice contraction enhances intermolecular interactions because of the lattice shrinkage and (2) the enhanced interaction then induces some change in absorption bands.

Figures 8(a) and 8(b) show the temperature dependence of absorption spectra of evaporated PDC before and after vapor treatment measured in the temperature range between 12 and 293 K. No significant temperature dependence is recognized in the sample before vapor treatment. This is typical of isolated, randomly oriented molecules in the amorphous phase. Vapor treatment, then, brings about a remarkable temperature dependence, particularly around 610 nm as shown in Fig. 8(b). This clearly indicates that the present absorption band is very structure sensitive and is due to intermolecular interactions. In other words, the absorption band is correlated with molecular arrangement.

Figures 9(a) and 9(b) show the temperature dependence of lattice parameters of modifications I and II, respectively, measured on single crystals in the temperature range between 100 and 300 K. The contraction along the c axis is remarkably temperature dependent in phase I. There is a marked difference in lattice contraction between the c axis and the a and b axes by about one order of magnitude. The lattice is namely contracted along the c axis on the (a, c) plane [Fig. 2(a)]. This indicates that the increased intermolecular interaction along the c axis is responsible for the temperature dependence of absorption spectra. The lattice in phase II is again predominantly contracted along the b axis together with angle β . However, the single crystal shattered under 123 K. Nevertheless, it is safe to say that the enhanced intermolecular interaction along the b axis on the (b, c) molecular plane [Fig. 2(b)] is responsible for the temperature dependence of absorption spectra.

D. Exciton coupling effects

The results presented in the preceding section (that the intermolecular interaction is appreciably associated with the absorption band around 610 nm) strongly suggest that exci-

FIG. 8. Temperature dependence of absorption spectra: (a) before vapor treatment and (b) after vapor treatment.

ton coupling occurs in the present optical process. For this reason, the exciton displacement energy has been calculated for the nearest neighbor molecules for modifications I and II.

When an excitation induces a single transition moment in the molecule, the excited state in crystals involves wave functions with significant probabilities on nearest neighbors.¹⁴⁻¹⁶ Thus, the exciton coupling may well involve energy contributions from interactions with all of these nearest neighbor molecules acting in concert in the lattice. This may lead to the band splitting of the excited state or spectral displacement towards longer wavelengths (redshift) or shorter wavelengths (blueshift). The overall spread or shift energy is determined by the strength of the interneighbor coupling which directly depends on the absorption coefficient of the molecule as well as the mutual relative orientation of the transition moments in molecular assemblies. Since PDC is a system of high absorption intensity, a large exciton coupling can be expected. This allows us to keep only the dipole-dipole potential term in the multipole expansion of the intermolecular Coulomb potential, neglecting higher terms. This approximation, in turn, permits us to treat the intermolecular interaction in terms of a quasiclassical vector model for transition dipoles. That is, the lattice interaction is formally identical with the potential problem of a set of permanent dipoles located at lattice points. The exciton

FIG. 9. Temperature dependence of lattice parameters: (a) phase I and (b) phase II.

displacement energy is then given by the following equation:^{14–16} $\Delta E = |\mu|^2(1 - 3 \cos^2 \theta)/r^3$ where r denotes the distance between two transition dipoles (μ). The net interaction in crystals is obtained by summing the interaction over all molecules to a given molecule. As may readily be seen, most of the interaction would come from the nearest neighbors because the dipole–dipole interaction falls off as the inverse cube of distance. The present treatment has variously been employed in the interpretation of the absorption spectra in molecular crystals or dye aggregates as shown below: anthracene, perylene, naphthalene, and tetracene,¹⁵ J aggregates of cyanine dyestuffs^{17–19} and dithioketopyrrolopyrrole pigment.²⁰

The above equation of the dipole–dipole coupling tells us that the excited-state level is shifted towards lower energies (redshift) for $\theta < 54.7^\circ$ or towards higher energies (blue shift) for $\theta > 54.7^\circ$. In addition, no spectral displacement takes place when $\theta = 54.7^\circ$. In the present calculation, the transition moment μ is first calculated from the xyz coordinate sets of x-ray structures^{4,13} on the basis of the INDO/S Hamiltonian.²¹ The result is given as transition dipole lengths in Table II, and the transition moment points the direction of the long axis of the molecule. Next, the exciton displacement energy ΔE is calculated as follows. Since the distance r and θ are known constants of the crystal structure for each crystal modification,^{4,13} the displacement energies are evaluated for each pair of the nearest-neighbor molecules (ten pairs for both modifications I and II) and summed over a sphere of about 35 Å in the lattice. The values obtained in this way are set out in Table II in the reciprocal centimeters.

The minus sign in Table II denotes an energy shift towards lower energies (redshift); whereas the plus sign indicates a shift to higher energies (blueshift). The largest contribution to the redshift is clearly made by the stack pairs in

TABLE II. Spectral shift due to exciton coupling effects: $\Delta E = |\mu|^2(1 - 3 \cos^2 \theta)/r^3$.

Type of molecule pairs	Number of molecules	Site ^a	r (Å)	θ (°)	ΔE (cm ⁻¹)
Phase I: Ten nearest neighbors around the molecule at (1/4, -1/4, 1/2) and their displacement energies.					
$\mu = 2.328$ (Å) ^b					
Stack pair	2	(1/4, 3/4, 1/2)	4.741	47.44	-2203
Diagonal pair 1	2	(3/4, -3/4, 1/2)	10.341	50.00	-137
Diagonal pair 2	2	(-1/4, 5/4, 1/2)	12.324	36.92	-308
Diagonal pair 3	4	(-1/4, -1/4, 0)	16.000	85.38	150
					10
					-4696
Phase II: Ten nearest neighbors around the molecule at (1/2, 1/2, 1/2) and their displacement energies.					
$\mu = 2.313$ (Å) ^b					
Stack pair	2	(3/2, 1/2, 1/2)	4.737	48.18	-1955
Diagonal pair 1	2	(1/2, 1/2, -1/2)	9.507	71.58	505
Diagonal pair 2	2	(-2, 1/2, -1/2)	12.166	40.00	-262
Diagonal pair 3	4	(-1/2, 0, 0)	17.328	74.2	93
					10
					-3052

^aThe molecular site is expressed in fractional coordinates.

^bTransition dipole length (μ).

both modifications, where the distance r is around 4.7 Å and the angle θ is 47° – 48° . Additionally, the diagonal pairs contribute, to some extent, to the red- or blueshifts, depending on the distance and angle between two transition dipoles. The total spectral shift amounts to -4696 cm⁻¹ for modification I and -3052 cm⁻¹ for modification II, showing that the spectral shift is larger in modification I by 1644 cm⁻¹ than in modification II. This tendency agrees with experimental determination (Fig. 3). Furthermore, this value becomes 567 cm⁻¹ when the dielectric correction is made with a value of 2.9 obtained from ellipsometry for modification II. The calculation is in fairly good agreement with the experimental value of about 413 cm⁻¹.

E. Interpretation of the band at 610 nm

As discussed in the preceding section, the absorption band at 610 nm shows up as a result of the ordering of molecules and can be attributed to the exciton coupling effect. The present interpretation is also borne out by the spectral shape of the reflection bands measured on single crystals (Fig. 3) as well as the spectral change of an evaporated film in the temperature range between 220 and 320 °C described in Sec. II B. In both cases, the reflection or absorption spectrum is characterized by an intense longer-wavelength band while the shorter-wavelength band is very weak in intensity. The present spectral distribution occurs, in particular, in single crystals due to the strong exciton coupling induced by perfectly ordered array of the molecules. On the other hand, the black phase shown in Fig. 1 can be characterized by an intermediate state between an amorphous and a crystalline state, in which the molecules are not perfectly ordered. In this quasiordered state, two kinds of absorption bands will appear: one is due to isolated molecules (473 nm) and the other is due to exciton coupling effects (610 nm).

F. Summary of electronic characterization

(1) PDC exhibits a vivid red color as evaporated and is characterized by an amorphous phase. The red color is structure insensitive and is typical of isolated, randomly oriented molecules in the amorphous phase.

(2) PDC undergoes a color change from red to black, giving two absorption bands in the visible region: 473 and 610 nm. The black phase is indicative of an intermediate state between an amorphous and an ordered state. The transition state gives two absorption bands: one is due to individual molecules (473 nm) and the other is due to exciton coupling effects (610 nm).

III. APPLICATION TO OPTICAL DISKS

A. Operation principle

Based on the electronic characterization of PDC, we apply the phase change phenomenon to write-once optical disks based on AlGaInP laser diodes of 635 nm. As we have seen, the absorption band around 473 nm in the black phase is due to isolated, randomly oriented molecules; whereas the absorption band around 610 nm arises from exciton coupling in a quasicrystalline system (Fig. 1), so we can switch the optical absorption around 610 nm by ordering the molecules (on state of the absorption), or by blocking the existing ordered array of molecules (off state of the optical absorption). Below we will describe a new write-once system with a reflectivity change from low to high, or high to low. The present system is based on our previous system using dithioketopyrrolopyrrole pigment for GaAsAl laser diodes of 780 nm.^{22–24} The appealing feature of the system is to use a solid solvent as an initiator for the molecular rearrangement.

B. Hydrazone compound as a solid solvent

An idea for the solid solvent was developed and introduced, in our previous disk system^{22–24} in order to locally induce a phase change. By solid solvent, we mean a compound that is solid at room temperature and which melts or gives some vapor pressure at elevated temperatures. The 4-diethyl-aminobenzaldehyde-1,1-diphenyl-hydrazone (mp: 96 °C) was, for example, found to be a good solid solvent for the present system. The solid solvent, when heated by laser, loosens the crystal lattice and induces molecular rearrangement in the recording layer composed of PDC and a solid solvent. The solid solvent can also diffuse, to some extent, into the interstitial sites of the PDC lattice to disturb intermolecular interactions. The latter process plays an important role in the system from low to high.

C. Optical disk with a reflectivity change from low to high

The optical disk from low to high starts from the state with an absorption of 610 nm ("black") and ends up with quenching of this absorption ("red") by laser irradiation, disturbing the existing ordered system of molecules.

Figure 10 shows the structure of the write-once recording layer composed of PDC and a solid solvent prepared on a polycarbonate substrate. On the pregrooved substrate, we

FIG. 10. Structure of the optical disk with a reflectivity change from low to high.

evaporate the solid solvent under high vacuum, about 100 Å, followed by an evaporation of PDC, about 500 Å. The evaporated film is subsequently exposed to acetone vapor for several seconds to cause the phase change. We then coat an Al-reflection layer by vacuum evaporation, and a photopolymer protection layer is finally applied by spin coating.

Information is written and readout basically by a laser diode at 635 nm. However, in the present experiment, an Ar⁺ laser of 514 nm was used, since the absorption coefficient of the band at 514 nm is almost equivalent to that of 635 nm. Optical recording is performed with a power of 50 mW at a scanning rate of 400 mm/s, and the reflectivity change is measured by means of a microscope spectrophotometer. The recorded stripe by laser irradiation is about 100 μm in width. The present condition of laser writing is known to approximately correspond to that of the dynamic test of our previous disk system at 780 nm (linear velocity: 1.2–1.4 m/s with a writing power of 9 mW).²³

The optical energy is first absorbed in the PDC layer due to an intense absorption and converted into thermal energy to heat the solid solvent layer. Some vapor is then produced in the solid-solvent layer. At the same time, the solvent molecules slightly diffuse into the PDC layer. This thermal diffusion disturbs the existing ordered array of molecules, leading to the quenching of the optical absorption at 635 nm. At this moment, the reflectivity of the recording layer changes from low to high.

Figure 11(a) shows the reflectivity change of the write-once recording layer as a function of wavelength before and after laser writing. A large reflectivity change over 55% from low to high is clearly observed at 635 nm. Figure 11(b) shows the transformed absorption spectra of the recording layer before and after laser writing. These spectra are derived from the reflection spectra through a transformation of $A = -\log R$ where A and R denote the optical density and reflectivity, respectively. It is apparent that the optical absorption at 635 nm has completely disappeared by laser writing. The absorption spectra of the recording layer before and after laser writing greatly resemble those in Fig. 1.

D. Optical disk with a reflectivity change from high to low

The optical disk from high (red) to low (black) utilizes the thermal transition from a state with a small absorption shoulder to the black phase (Fig. 5). With an absorption shoulder at 635 nm, optical energy is absorbed and converted into thermal energy. This, in turn, initiates the phase change

FIG. 11. Optical disk before and after writing: (a) reflectivity change and (b) transformed absorption spectra.

to give an intense optical absorption at 635 nm. The evaporated film with an absorption can easily and directly be prepared by slow evaporation of PDC under high vacuum.

Figure 12 shows the structure of the write-once optical recording layer which operates from high to low. Since the present disk works without any solid solvent, it provides a simpler disk structure. Optical energy is first absorbed in the perylene layer due to an absorption shoulder at 635 nm and converted into thermal energy which, in turn, induces the phase change. Then, the absorption shoulder at 635 nm rapidly grows up to an absorption peak. At this moment, the reflectivity of the recording layer changes from high to low.

Figure 13(a) shows the reflectivity change of the write-once recording layer as a function of wavelength before and after laser writing. A reflectivity change of about 20% from high to low is clearly observed at 635 nm. Figure 13(b) shows the transformed absorption spectra of the recording layer before and after laser writing. It is apparent that the

FIG. 12. Structure of the optical disk with a reflectivity change from high to low.

FIG. 13. Optical disk before and after writing: (a) reflectivity change and (b) transformed absorption spectra.

optical absorption shoulder at 635 nm has completely grown up to an absorption peak by laser writing. The absorption spectra of the recording layer before and after laser writing greatly resemble those in Fig. 5.

E. Summary of the application to optical disks

(1) The phase transition of PDC from an amorphous state to the crystalline state or vice versa can be applied to optical disks in such a way as to order molecules or to disturb ordered molecules.

(2) The solid solvent is a useful initiator to disturb the structure sensitive, ordered array of molecules, leading to the quenching of the optical absorption at 635 nm. This transition gives a reflectivity change from low to high.

(3) A small absorption shoulder at 635 nm is utilized to initiate the transition from an amorphous to the crystalline state. In this case, the reflectivity changes from high to low.

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