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Electronic Characterization of N,N'-Bis(2-phenylethyl)perylene-3,4:9,10-bis(di-carboximide) and its Application to Optical Disks

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Abstract

The title compound is a commercial black pigment based on the perylene skeleton. It exhibits two distinct colors (red and black) in the solid state which correspond to an amorphous and a crystalline phase. The red color (500 nm) is due to randomly-oriented, individual molecules in the amorphous phase; whereas the black phase is composed of two absorption bands: one (473 nm) is due to individual molecules and the other (610 nm) is due to exciton coupling effects. The color change depends mainly on the appearance or disappearance of the absorption band around 610 nm. The present optical switching at 610 nm can be applied to an optical disk system based on an AlGaInP laser diode. An information storage system has been developed in which the absorption at 610 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.

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 photoreceptors[2] as well as photovoltaic elements[3]. Previously, we have reported that **PDC** exhibits a color of vivid red as evaporated and undergoes a color change from red to black as shown in Fig.1 when exposed to acetone vapor or heated above 100°C for several seconds[4]. The present color change corresponds to a phase change from an amorphous to a crystalline state as shown by X-ray diffraction analysis. The optical absorption band around 473 nm in the black phase has been attributed to isolated, randomly oriented molecules; whereas the absorption band around 610 nm arises from exciton coupling effects in a quasi-ordered system of the molecules[4] (Fig. 1). This conclusion indicates that we can basically switch on the optical absorption around 610 nm by ordering the molecules, or switch off by blocking the existing ordered array of molecules. An attempt is therefore made in the present investigation to apply the above switching phenomenon to an information storage system operating at 635 nm based on an AlGaInP laser diode. The present system is similar in operation principle to our previous one using 1,4-dithioketo-3,6-diphenyl-pyrrolo-[3,4-c]-pyrrole for a laser diode of 780 nm[5-7].

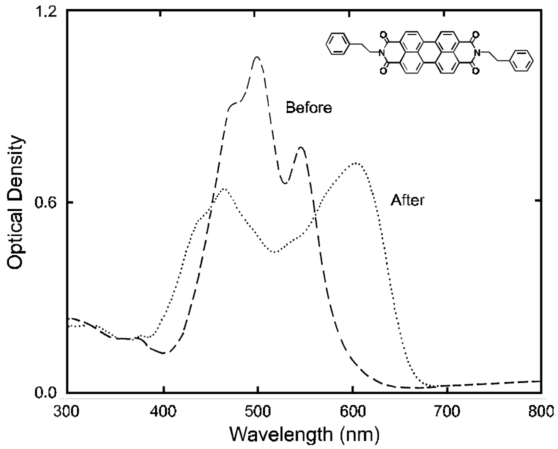

Figure 1. Absorption spectra of evaporated PDC before and after vapor treatment (film thickness: ca. 1000Å).

Result and Discussion

Phase Change from an Amorphous to the Crystalline State

Fig. 2 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 is distinctly recognized due to vapor treatment as shown by diffraction peaks assigned as indicated. The symbols I and II beside the parentheses in Fig. 2 denote modifications I[8] and II[9], respectively.

It is interesting to note that the color change also takes place thermally as shown in Fig. 3, in which gradual spectral changes are plotted as a function of time for heat treatment at 100°C. The spectral change proceeds with time, accompanied by isosbestic points at 350 and 560 nm. After 30 seconds, an absorption shoulder begins to appear and grows up to an absorption peak.

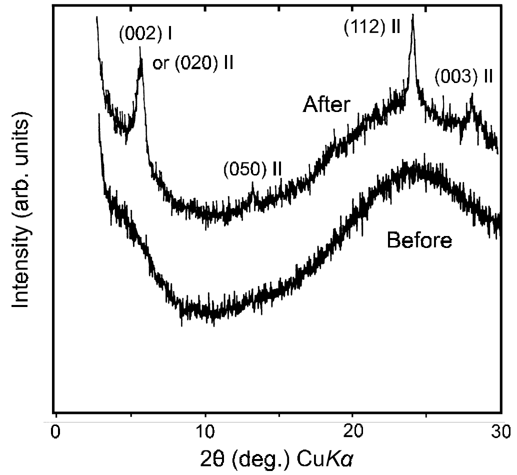

Figure 2. X-ray diffraction diagrams of evaporated PDC before and after vapor treatment.

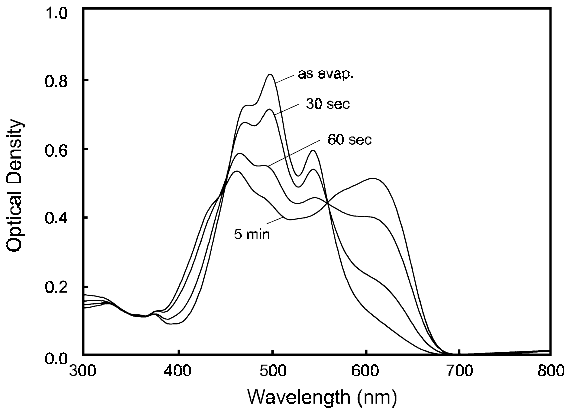

Figure 3. Spectral changes as a function of heat-treatment time at 100℃.

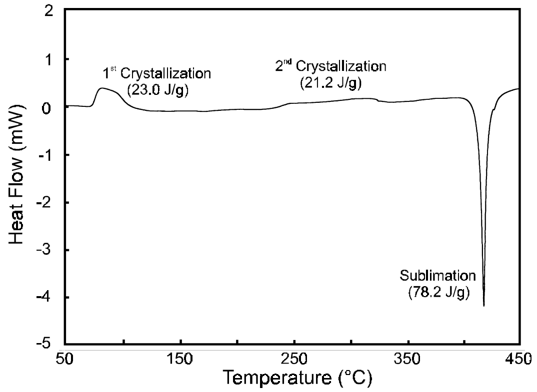

Figure 4. DSC measurements of PDC showing the heat flow as a function of temperature.

The phase change can also be demonstrated by DSC measurements (differential scanning calorimetry) as shown in Fig. 4. A broad exothermic peak of 23 J/g is clearly observed around 75-100°C which corresponds to the phase transition from an amorphous state (λ_{max}=500 nm) to the crystalline state (λ_{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 increase in absorption intensity; whereas the intensity of the band at 473 nm is greatly diminished.

Hydrazone Compound as a "Solid Solvent"

An idea for "solid solvent" has newly been developed and introduced in optical disk systems in order to locally induce a phase change[6,7]. By "solid solvent", we mean a compound that is solid at room temperature and which melts or gives some vapor pressure at elevated temperatures. 4-Diethyl-aminobenzaldehyde-1,1-diphenyl-hydrazone (mp: 96°C) was found to be a good solid solvent for the present system. In the recording layer composed of a recording media (PDC) and a solid solvent, the solid solvent is expected to loosen the crystal lattice at elevated temperatures to induce molecular rearrangements. The solid solvent can also diffuse, to some extent, into the interstitial sites of the PDC lattice to disturb intermolecular interactions. The latter process especially plays an important role in the system with a reflectivity change from low to high described below.

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 635 nm ("black") and ends up with quenching of this absorption ("red") by laser irradiation, disturbing the existing ordered system of molecules.

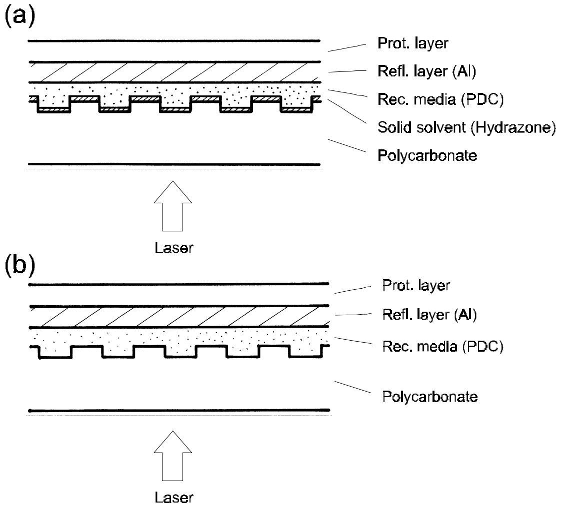

Figure 5. Structure of the optical disk: (a) with a reflectivity change from low to high and (b) with a reflectivity change from high to low.

Fig. 5(a) shows the structure of the write-once recording layer composed of PDC and a solid solvent prepared on a polycarbonate substrate. On the pre-grooved substrate, we evaporate the solid solvent under high vacuum, about 100 Å, followed by an evaporation of PDC, about 500 Å. We then coat an Al-reflection layer by vacuum evaporation, and a photopolymer protection layer is finally applied by spin coating.

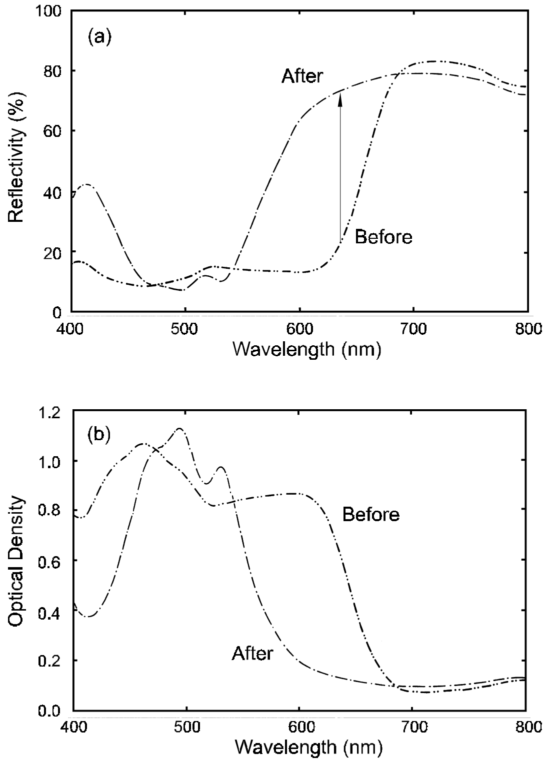

Figure 6. Optical disk with a reflectivity change from low to high: (a) reflection spectra and (b) transformed absorption spectra.

Information is written and read-out by a laser diode at 635 nm. For the write process, optical energy is first absorbed in the perylene 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 perylene 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.

Fig. 6(a) shows the reflectivity changes of the write-once recording layer as a function of wavelength before and after laser writing measured by means of a microscope-spectrometer. A large reflectivity change over 55% from low to high is clearly observed at 635 nm.

Fig. 6(b) shows the transformed absorption spectra of the recording layer before and after laser writing. 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.

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. 3). With an absorption shoulder at 635 nm, optical energy is absorbed and converted into thermal energy. This, in turn, initiates the phase change to give an intense optical absorption at 635 nm.

Fig. 5(b) 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. Again, information is written and read-out by a laser diode at 635 nm. 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.

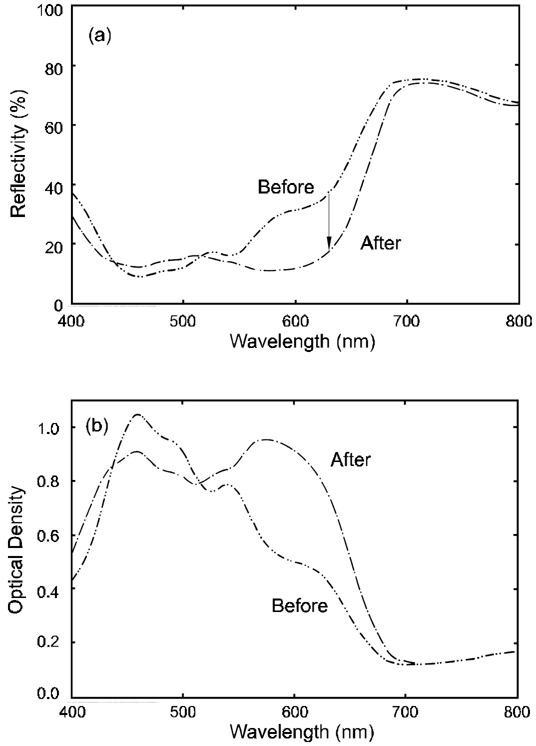

Figure 7. Optical disk with a reflectivity change from high to low: (a) reflection spectra and (b) transformed absorption spectra.

Fig. 7(a) shows the reflectivity changes 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. Fig. 7(b) shows the transformed absorption spectra of the recording layer before and after laser writing. It is apparent that the 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.1.

Summary and Concluding Remarks

1. Transition 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 the ordered molecules.
2. “Solid solvent” is an 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 620 nm is utilized to initiate the transition from an amorphous state to the crystalline state. In this case, the reflectivity changes from high to low.

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Biography

Jin Mizuguchi received his B. Sc. in Chemistry from Sophia Univ. in 1970, Dr. of Sc. from Univ. of Tokyo in 1982, Venia Docendi from Univ. of Bern in 1994. Dr. Mizuguchi joined Sony Corporation in 1970 and worked there in the field of organic semiconductors. In 1985, he left Sony Corporation and joined Ciba-Geigy AG in Switzerland. He was involved in the research and development of organic pigments with applications to laser printers and optical disks. In 1995, he was nominated to professor for materials science at the Yokohama National University. His current interest is electronic characterization of organic pigments on the basis of molecular structure, crystal structure and intermolecular interactions.