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PHOTOCONDUCTING BEHAVIOR IN RELATION TO PHASE TRANSITIONS. 5,10,15,20-TETRAKIS(4-PENTADECYLPHENYL)PORPHYRIN

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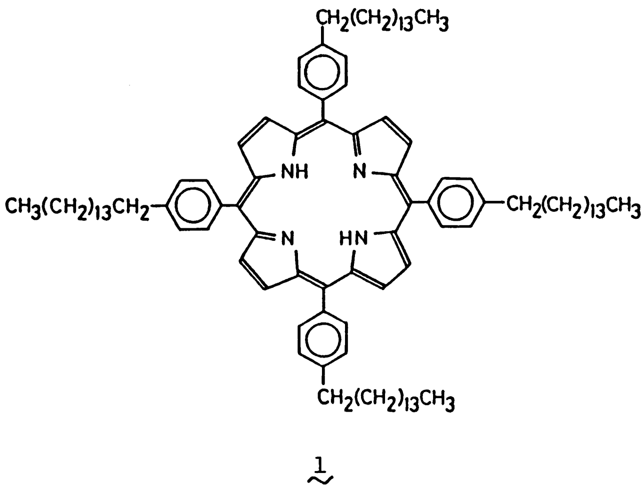
5,10,15,20-Tetrakis(4-pentadecylphenyl)porphyrin(1) exhibited large changes of the photo- and the dark-current ratio(i_p/i_d) through the phase transitions, which ranged from 300 to 0.22 between 27 °C (the crystalline phase) and 140 °C (the isotropic liquid phase) for a sandwich - type cell of ITO(25 μm -thick). The photocurrent decreased as the temperature increased, while the inverse situation was shown for the darkcurrent.

5,10,15,20-Tetraphenylporphyrin(TPP) has been extensively studied from photoelectrochemical viewpoints because of the strong light-absorption in the visible region.[1)]

Recently, it was found that the title compound 1 has three phases below the transition temperature to the isotropic liquid phase.[2)] The phase transition temperatures are as follows;

$$\text{crystal} \underset{(22.0\ °C)^*}{\overset{56.0\ °C}{\rightleftharpoons}} m_1 \overset{65.5\ °C}{\rightleftharpoons} m_2 \overset{134.5\ °C}{\rightleftharpoons} \text{isotropic}$$

*) In parentheses, the crystallization temperature on cooling at 5 °C/min.



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The phases m_1 and m_2 were found to have quasi-mesomorphic properties, though the molecular alignments of the states have not been revealed yet.

The investigation of the photoconductivity of 1 is interesting from the viewpoint of its behavior in relation to the phase transitions.

The material was prepared by the usual method of TPP synthesis[3)] and purified by column chromatography(activated alumina, benzene) after oxidation of the by-product, a chlorin derivative.[4] Further purifications were carried out by the Soxhlet extraction with methanol-ethanol followed by recrystallization from benzene-acetone, and finally by the zone refining method. This compound **1** is soluble in many organic solvents(benzene, dichloromethane, chloroform etc.) except for ethanol, methanol and acetone.

The cell used for measurements is a sandwich-type, which consists of two ITO glass electrodes(an effective area: 1 cm^2) and a spacer of polyimide film(25 μm). The sample was injected by capillarity into the cell space on the hot stage in a cryostat(ca. 140 °C). Once the cell was cooled down to about 20 °C, the system was pumped out for about an hour, and then replaced with dry nitrogen gas. All measurements were carried out in a dry nitrogen atmosphere.

The temperature dependences of the darkcurrent(i_d) and the photocurrent(i_p) are shown in Figs. 1 and 2, respectively. The photocurrent as shown in Fig. 2 was observed when the positive electrode was illuminated at 620 nm under 4000 V/cm. The incident light intensity was 0.34 mW/cm^2.

The i_d in each phase increases with temperature. The current gaps were observed at three phase transitions. The temperature dependence obeyed the Arrhenius' equation and the values of the activation energy for the conduction in each phase were calculated to be 0.28 eV, 0.69 eV and 0.30 eV for the crystalline, m_1 and m_2 phases, respectively.

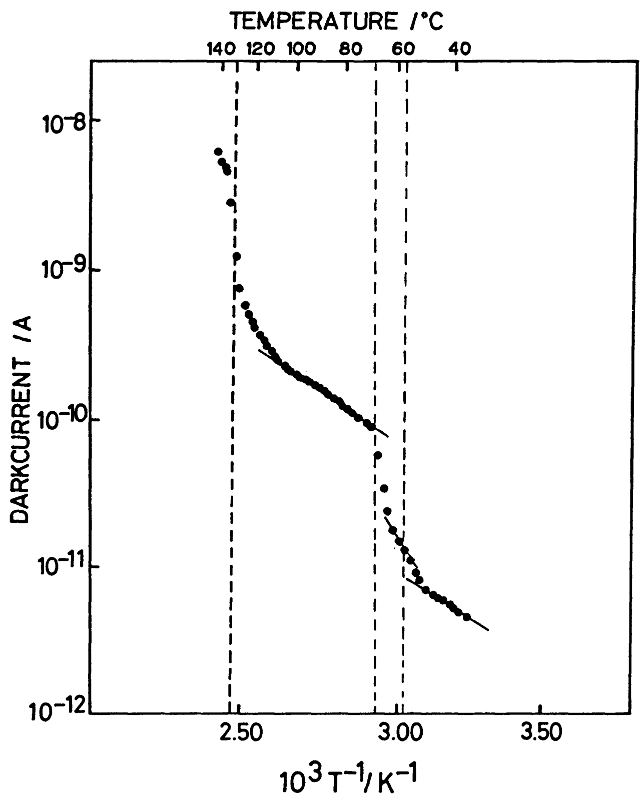

Fig.1. Temperature dependence of the darkcurrent under 4000 V/cm.

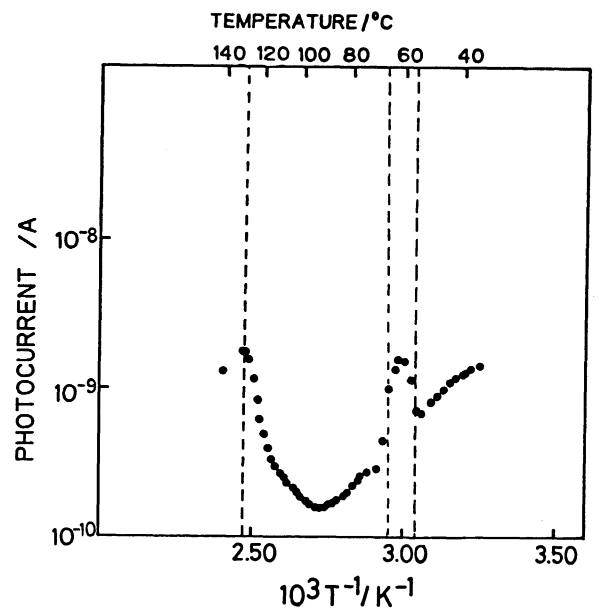

Fig. 2. Temperature dependence of the photocurrent at 620 nm under 4000 V/cm.

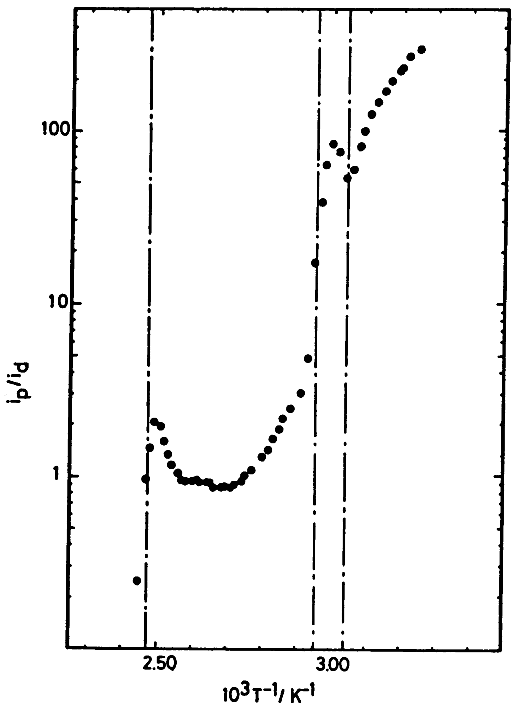

Fig. 3. Temperature dependence of the current ratio(i_p/i_d) of **1**.

thick cell appeared to be red-shifted and the photocurrent in the region of strong light-absorption is much smaller than that in the region of weak one, as shown in Fig. 4.

The trend that the action spectrum becomes coincident with the absorption spectrum is shown as the cell thickness decreases. The result of the illumination of the negative electrode was also shown to be approximately the same as that of the illumination of the positive one, except for the smaller value of the i_p in the former case than that in the latter case.

These results indicate that the photocurrent is generated by the light-absorption of the compound itself and is re-

On the other hand, the i_p in each phase changes curiously as the temperature increases in the case of the illumination of the positive electrode. The i_p value decreases in the crystalline phase as the temperature rises and in the m_1 phase the i_p increases with temperature, but decreases in the m_2 phase. However, in the m_2 phase the i_p has a minimum value at ca. 90 °C . These complexities of the photocurrent behavior seem to be due to the pretransitional phenomenon of **1** in the heating run. The photocurrent was not detected at zero bias(ca. < 10^{-14} A).

Thus, these photocurrent behavior indicates that the photoconductivity of **1** is severely related to the states, i.e.,the molecular alignments and interactions in each phase.

The ratio(i_p/i_d) is shown in Fig. 3. The ratio changes from 300 to 0.22 between 27 °C (the crystalline state) and 140 °C (the isotropic liquid state). Especially, it shows a marked change at the m_1 to m_2 transition.

Compared with the absorption spectrum of the film of **1**, the action spectrum for a 25 μm-

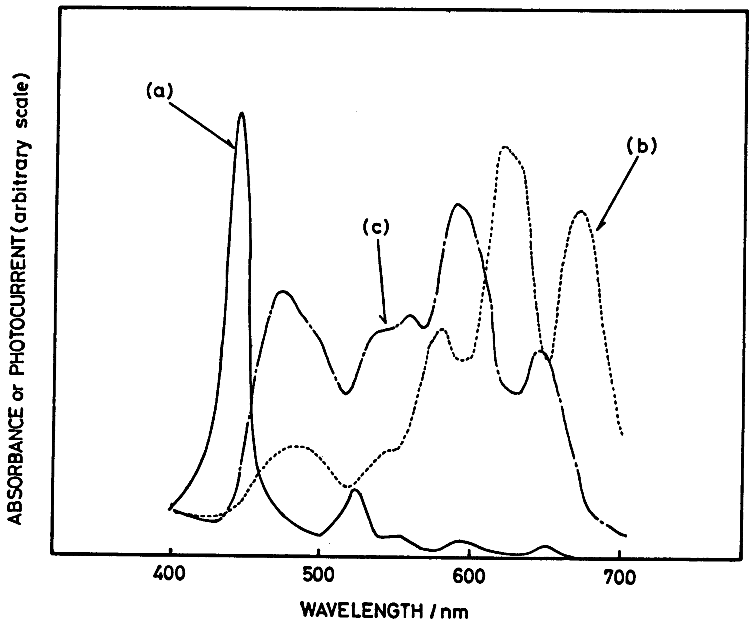

Fig. 4. Absorption and action spectra of **1** for the crystalline phase. (a)absorption, (b) action for 25 μm-thick cell and (c)action for 6 μm-thick cell.

lated to the carrier recombination and trapping processes in the region where the carriers are generated and in the region where the carriers transport toward the counter electrode, respectively.

The light exponent γ was calculated to be 0.89 in the crystalline phase from Fig. 5. This value is comparable to the results of the metal-TPP derivatives(0.8 - 1.0).[5]

As far as we know, this is the first example that the photoconductive behavior was investigated in the relation to the phase transitions of a TPP derivative with long aliphatic chains. Further investigations are now under proceeding.

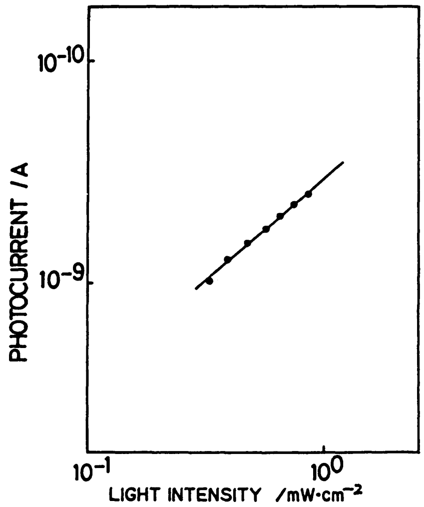

Fig. 5. Incident light intensity dependence of the photocurrent for a 25 μm-thick cell at 620 nm under 4000 V/cm by the illumination of the positive electrode.

References

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