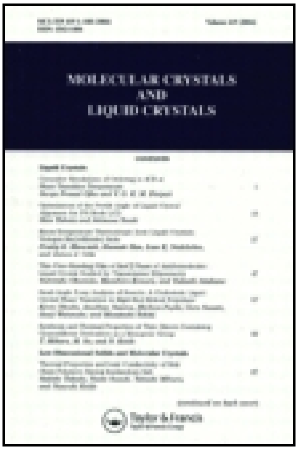

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Photoconductive Properties of a Mesogenic Long-Chain Tetraphenylporphyrin Oxovanadium(IV) Complex in a Symmetrical Sandwich-Type ITO Cell

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The photoconductive properties of 5,10,15,20-tetrakis(4-*n*-pentadecyl-phenyl)porphinatooxovanadium(IV) was investigated to be compared with those of the free base compound for a symmetrical sandwich-type ITO cell. The similar photocurrent rectification behavior to the free base tetraphenylporphyrin mesogen was shown. However, the observed photocurrent remarkably larger than that of the free base compound for all phases. The temperature dependence of the dark- and photo-currents were also investigated.

Keywords: discotic liquid crystals; photoconductivity; lamellaer phase; metallomesogen; porphyrin

INTRODUCTION

Metalloporphyrins have been extensively studied in these three decades for their physico-chemical properties from a biomimetic viewpoint[1,2]. Porphyrin skeleton has an extended π-conjugation system leading to a wide range of visible light absorption and *p*-type property as an electronic system. In particular to these characteristic properties, it is well-known relating that the analogous chlorophyll takes an important role in photosynthetic process and some metalloporphyrins show a remarkable photovoltaic effect in a cell with an appropriate structure[3-5]. These indicate that metalloporphyrins have potentiality for electronic charge transportation and excited energy migration[6,7]. However, these properties derived from the electronic state of molecules are subjected to a metal species inserted in the central core. Sometimes they are likely to show a drastic change of electronic properties in their molecular aggregations. Thus, a well-designed molecular architecture of porphyrins could realize a variety of high performance functional properties if the self-assembled structure is well-controlled[8,9].

On the other hand, mesogenic compounds are one of the most interesting categories of self-assembled systems from these points of view. Especially, discotic liquid crystals are strongly expected to show high order of the anisotropic properties for electronic charged carrier transportation as well as energy migration because of their characteristic structures like columnar mesophases. Several disc-shaped mesogens derived from a porphyrin skeleton have been reported so far[6,7]. However, as for the mesomorphic behavior of long-chain tetraphenylporphyrin and its metal complexes, only a few reports have been published to reveal the occurrence of unfamiliar mesophases of so-called "discotic lamellar mesophase", which have layered structures formed by disc-shaped molecules and is just like smectic mesophases of rod-like molecules[10]. The lamellar mesophases exhibited by a series of long-chain metallotetraphenylporphyrins tend to show very high viscosity, indicating the high molecular order of aggregations which were evidenced by many reflection peaks in the wide angle region of X-ray diffraction pattern. This fact, in other words, indicates that the lamellar mesophases of tetraphenylporphyrin mesogens may have some effective routes in their mesomorphic structures appropriate for charged carrier migration and/or hopping.

In 1986, the first report about the photocurrent behavior was published for an ITO sandwich-type cell into which was injected a long-chain tetraphenylporphyrin without any metal ions in the central core, the free base derivative ($C_{15}TPPH_2$)[11]. The phase transition dependence of photocurrent on the positive electrode illumination clearly showed a marked increase of photocurrent at the crystalline to lamellar phase transition, while the photocurrent stepwise decreases at the phase transition between two lamellar mesophases. Furthermore, the V-I characteristics of photocurrent exhibits a remarkable rectification behavior for both crystalline and low-temperature lamellar phases, though it disappears at the phase transition between two lamellar mesophases[12]. This was tried to explain in terms of a variant mechanism of photocarrier generation in the cell on the phase transitions[13-15].

In this work, a new long-chain metallotetraphenylporphyrin, 5,10,15,20-tetrakis(4-*n*-pentadecylphenyl)porphinatooxovanadium(IV) ($C_{15}TPPVO$), was synthesized and investigated the photoconductive properties to be compared with those of the free base compound for a symmetrical sandwich-type ITO/$C_{15}TPPVO$/ITO cell. The similar photocurrent rectification behavior to the corresponding free base $C_{15}TPPH_2$ was shown for $C_{15}TPPVO$. However, the observed photocurrent was increased remarkably. The temperature dependence of the steady-state photo- and dark-currents were also investigated. $C_{15}TPPVO$ shows two lamellar mesophases, ML' and ML phases, between the crystalline and the isotropic phases, similar to the free base compound. The phase transition parameters of $C_{15}TPPVO$ are summarized in Table 1.

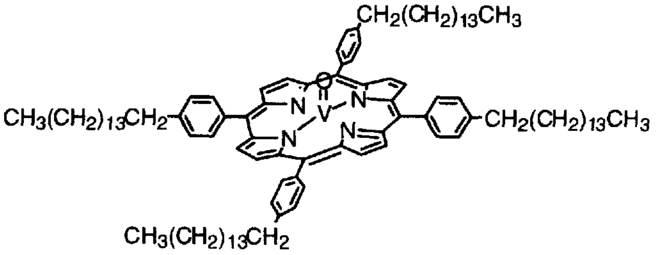

TABLE 1 Phase transition temperatures and enthalpies of C15TPPVO

	crystal		ML'		ML		iso
T / °C		51		82		140	
ΔH / kJ mol^{-1}		62		27		27	

EXPERIMENTAL

Synthesis

The synthetic procedures for para-substituted tetraphenylporphyrin free base ($C_{15}TPPH_2$) were on the basis of the literatures with slight modifications[16,17]. The details were described previously.[13] The insertion of oxovanadium(IV) was accomplished by literature methods[18,19]. The corresponding free base porphyrin $C_{15}TPPH_2$ (0.563 g, 0.387 mmol) and for excess amount of oxovanadium(IV) sulfate (2.10 g, 12.9 mmol) were mixed in 150 ml of *N,N*-dimethylformamide and the mixture was refluxed for 6 hours. After cooling to the room temperature and refrigerating for one night, the solution was filtrated to give a solid and washing with acetone gave red-violet crystals with metallic luster. Purification of the product was carried out by column chromatography (neutral activated alumina, using chloroform as eluent) and recrystallized from benzene-acetone (1:9), followed by Soxhlet extraction with methanol. 0.492 g of red-violet crystal with metallic luster was obtained (yield: 88%). Furthermore, the completion of the reaction was confirmed by the disappearance of the absorption peak at 650 nm for the free base porphyrin.

Chemical Analysis

$C_{15}TPPVO$: ^{1}H-NMR (500 MHz, $CDCl_3$, δ in ppm): 0.87 (t, 12H, CH_3), 1.27 (m, 80H, $(C\underline{H}_2)_{10}CH_3$), 1.44 (quintet, 8H, $C_6H_4CH_2CH_2CH_2C\underline{H}_2$), 1.53 (quintet, 8H, $C_6H_4CH_2CH_2C\underline{H}_2$), 1.86 (quintet, 8H, $C_6H_4CH_2C\underline{H}_2$), 2.88 (t, 8H, $C_6H_4C\underline{H}_2$), 7.47 (d, 8H, *metat* to the phenyl carbon attached to the *meso* position of porphyrin ring), 7.90 (d, 8H, *ortho* to the phenyl carbon attached to the *meso* position of porphyrin ring), 8.75 (s, 8H, β position of the pyrrole moiety). λ_{max} (ε_{max})/nm (1 mol^{-1} cm^{-1}) (benzene): 426 (535000), 482 (2690), 510 (3550), 549 (25000), 586 (3690).

Photoconductive Measurements

All measurements were carried out to obtain steady-state photo- and dark-currents in the constant temperature conditions for a symmetrical sandwich-type cell. The cells were prepared using ITO-coated glass electrodes separated by silica beads in the diameter of 2 μm and fixed by a silicon cement for 3.3 μm-thick cell. The effective area of the electrodes was patterned to be 1 cm^2. The cell thickness was evaluated by interferometry using a UV-Vis spectrophotometer. $C_{15}TPPVO$ was introduced into the cell by capillary action in the isotropic phase (ca. 150 °C) and the cell was cooled down to the room temperature so slowly (ca. 1 °C / min). Microscopic observations of the cell revealed that the thin film of $C_{15}TPPVO$ was formed to have polydomain structures. Thus, all measurements in this work were for a polydomain film. Lamellar mesophase is highly viscous and it was impossible to obtain a homogeneous monodomain film only by modifying the cooling process. Electrical contact to the electrodes was made using electroconductive silver paste and a copper wire. A Xenon-lamp (Ushio UXL-500D) was used as a light source and the light was monochromated by a scanning monochrometer (Jasco CT-10) to illuminate the sample cell in a temperature controllable cryostat under an inert atmosphere (Argon gas). The V-I characteristics of dark- and photo-currents were measured using an electrometer (Advantest R8340) as closed-circuit under bias. The temperature of the sample stage was controlled to within 0.2 K using a temperature controller (Chino SU10). The illumination light intensity was fixed to 0.34 mW cm^{-2} at the wavelength of 550 nm for all measurements.

RESULTS AND DISCUSSIONS

Figure 1(a) shows the V-I characteristics of the darkcurrent for a symmetrical sandwich-type ITO cell of 3.3 μm-thick in the crystalline, ML’, and ML phases of C_{15}TPPVO. Symmetrical features are clearly shown for the applied electric field of ±20000 V cm^{-1}. The conductivity σ can be determined to be $\sim 10^{-15}$ Ω^{-1} cm^{-1} for the crystal and ML’ phases and $\sim 10^{-14}$ Ω^{-1} cm^{-1} for the ML phase. The conductivity of C_{15}TPPVO is comparable with that of free base $C_{15}TPPH_2$.

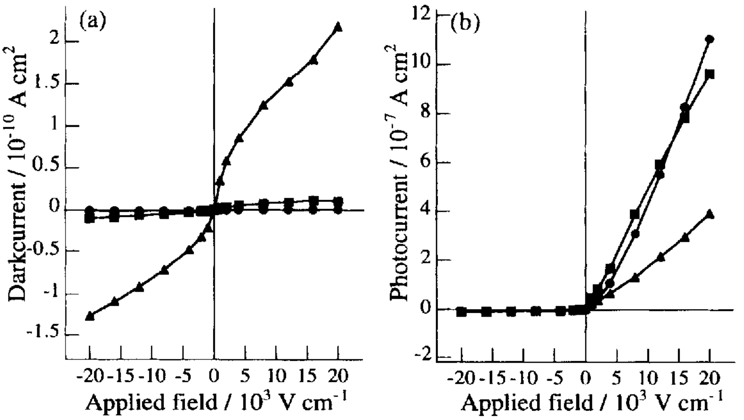

FIGURE 1 Applied electric field dependence of (a) dark- and (b) photo-currents in an ITO/C_{15}TPPVO/ITO (3.3 μm-thick) cell for the crystalline (25 °C; ●), ML’ (60 °C; ■) and ML (100 °C; ▲) phases of C_{15}TPPVO under 550 nm with 0.34 mW cm^{-2} light illumination.

Figure 1(b) shows the photocurrent-applied voltage characteristics of the cell for the crystalline, ML' and ML phases. Marked rectification of photocurrent is apparent for all phases of the cell. A positive electrode illumination causes a larger photo-current which increases with bias. For the ML phase, however, the photocurrent generated by positive electrode illumination is much reduced than for the other highly ordered phases. For the ML' phase, the photocurrent is comparable with that in the crystalline phase of C_{15}TPPVO, while that of C15TPPH2 is decreased from that in the crystalline phase.

Figure 2 shows the dark- and photo- currents as a function of temperature for a 3.3 μm-thick cell. The applied electric field was 8000 V cm^{-1} (2.64 V) under 550 nm light illumination of the positive electrode. The temperature dependence of the darkcurrent obeyed the Arrhenius' equation in the both mesophases (ML' and ML) and the isotropic phase. The value of the activation energy for the conduction in each phase were calculated to be 0.91 eV, 0.79 eV and 0.70 eV for the ML', ML and the isotropic phases, respectively. In the high temperature region of the ML phase, the darkcurrent was increased rapidly probably because of pretransitional effect. It seems that an additional contribution of the ionic conduction may be involved due to the impurities of the sample in which ionic species could be more transferable with increasing of molecular motion of C_{15}TPPVO.

On the other hand, the photocurrent shows a different behavior from that of darkcurrent. The phase transitions provides remarkable changes of the photocurrent and the temperature dependence in mesophases shows a gradual decrease. At the crystal to ML' transition, the photocurrent increases stepwise and decreases at the ML' to ML one. In particular, it drastically decreases at the clearing to an undetectable level. Furthermore, a strange behavior can be recognized for the ML mesophase that the photocurrent decreases in the lower temperature region, while it increases in the higher one.

These results imply that in the positive electrode illumination, the electronic conduction such as charge hopping process is dominant for charge migration process rather than ionic conduction. It is reasonably considered that because of the high viscosity of C_{15}TPPVO, the charged porprhyrin molecule could not be mobile itself in the crystalline, ML' and ML phases. Furthermore, in the ITO/C_{15}TPPVO/ITO cell, hole conduction could be expected the photocurrent observed to dominate for the following two reasons. Firstly, the intrinsic defects are thought to be mainly *p*-type impurities, and secondly, the work function of ITO is less than that of CnTPPM system. The positive carrier mobilities of

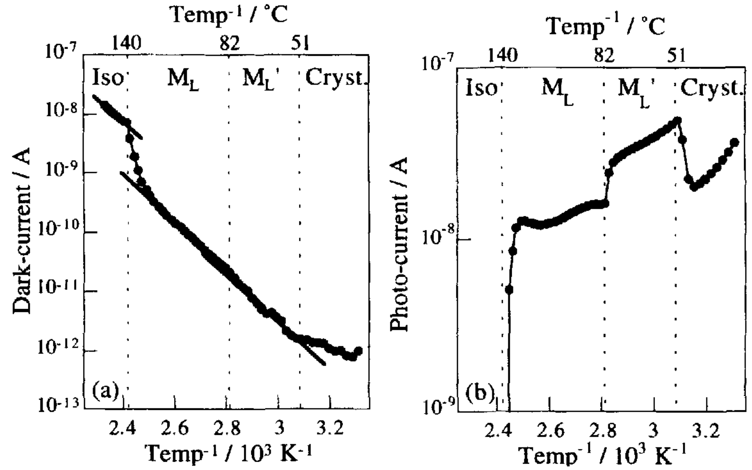

FIGURE 2 Temperature dependence of (a) dark- and (b) photo-current in the positive electrode illumination under 8000 V cm^{-1}.

M_L' and M_L phases of $C_{15}TPPH_2$ for a ITO/$C_{15}TPPH_2$/ITO cell were reported[20]. However, it seems to be strange that the mobility of M_L' phase is comparable to that of M_L phase in the order of 10^{-4} cm^2 V^{-1} s^{-1}, while the photocurrent showed a remarkable change at M_L' to M_L transition. This may indicate the efficiency of carrier generation and/or the effective carrier number in the migration process drastically changes at the phase transition.

The observed photoconductivity of $C_{15}TPPVO$ is much higher than that of $C_{15}TPPH_2$ about two order of the magnitude. In particular, a higher photoconductivity of $C_{15}TPPVO$ was observed in the M_L' mesophase than that of the free base compound. This may arise from the efficiency of carrier generation of $C_{15}TPPVO$ is larger than that of $C_{15}TPPH_2$ probably owing to the difference of the ionization potential and/or the effective carrier number which decreases with the recombination process in charge migration. Both carrier generation efficiency and carrier migration process should be considered for the interpretation of these phenomena.

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