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Photoconductivity of Discotic Liquid Crystals: a Mesogenic Long-Chain Tetraphenylporphyrin and Its Metal Complexes

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A mesogenic long-chain tetraphenylporphyrin and its metal complexes(Ni(II), V=O(IV) and $Si(OH)_2$) were studied on the mesomorphism and photoconductivity in a symmetrical sandwich-type ITO cell. These complexes show so-called "lamellar-type" mesophases having a layered structure like smectic mesophase. The photocurrent behaviour of these compounds were compared to clarify the characteristic properties of photoconductivity for lamellar mesophases.

Keywards discotic liquid crystal; photoconductivity; carrier mobility; metallotetraphenylporphyrin; metallomesogen

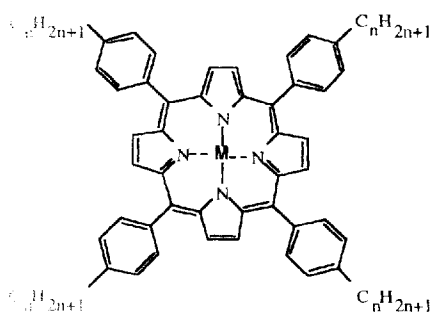
INTRODUCTION

Discotic liquid crystals have attracted much interest in their electronic properties as potential natures for applications to novel photonic and/or electronic devices. This is mainly owing to their characteristic molecular arrangements of a molecularly stacked columnar structure as a quasi-one-dimensional electronic conductor. In fact, photo-

conductivity and electronic conductivity of mesomorphic materials have been extensively studied in these several years and a fast hole mobility (0.1 cm^2 $V^{-1}s^{-1}$) was reported for a plastic columnar mesophase of a triphenylene discotic mesogen [1]. However, the most interesting subject of electronic charge migration phenomenon in mesophase is the charge migration behaviour in an intermediate state of solid and liquid where the molecules align with some fluctuation as well as with a long-range order. In addition, the fluctuation seems to be collective as a dynamic state of molecular aggregation.

Furthermore, the easy control of molecular alignment in mesophase could give rise to one more attractive aspect of mesophase materials which leads to a new technology for a thin film device with the higher performance of functions when one can obtain a film possessing a large area of a uniformity of molecular alignment.

On the other hand, porphyrin and phthalocyanine are well-known compounds as a molecular semiconductor, of which molecular structure consists of a extended π-conjugation system of electrons. The electronic states of these compounds, furthermore, could be modified by metallation(making a metal complex with various metal ions using one ligand). This could provide a best matching for charge generation at mesogen/electrode interface in order to get the highest performance as an electronic device. Thus, metallomesogens are a quite interesting category of mesogens for an electronic materials.



n =15, 12
M = 2H, Ni, V=O, Si(OH)$_2$

However, only a few discotic mesophases have been studied on the relation of photoconductivity to mesomorphism. As for discotic metallomesogens, even the manner of metal contribution to mesomorphism has not been clarified yet.

We have studied on

the mesomorphic behaviour and photoconductivity of a few long-chain metallotetraphenylporphyrins so far and several characteristic properties were found .

EXPERIMENTAL

All compounds were synthesized by the conventional method with some modifications. The investigation of mesomorphism has been carried out using a polarizing microscopy, DSC and X-ray diffraction apparatus.

The dark- and photo-currents were measured for a sandwich-type cell consisting of two ITO-coated glasses, polyimide film or glass beads and a mesogen film. A cell flame was prepared to have a configuration as shown in Fig.1. The space between both electrodes was filled with the mesogenic compound by capillarity on heating above the clearing point.

Microscopic observations of the cell showed that the sandwiched film of mesogen was formed in polydomain structures. All results shown in this work are of a polydomain film. Lamellar mesophases are too viscous to obtain a monodomain film by either modifying the cooling process or simple rubbing of ITO electrodes. The current was detected by a digital multimeter as closed-circuit current. Hole mobility was determined by TOF (Time-Of-Flight) method using a Nd:YAG laser and Optical Parametric Oscillator.

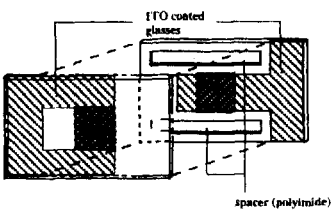


Fig.1 Cell assembly for current measurements.

The transient photocurrent was detected by a digital oscilloscope with a preamplifier. The measurements were carried out in Ar atmosphere.

RESULTS AND DISCUSSION

Phase transitions

Some long-chain metallotetraphenylporphyrins with a square planar geometry of the central metal ion have been so far studied on their mesomorphism to reveal that these are likely to show lamellar-type mesophases which have layered structures with disc-shape molecules[2]. The proposed structures of two lamellar mesophases seen for the metal-free compound and VO complex are shown in Fig.2. In contrast, it was found that the corresponding Al-OH complex with a pyramidal geometry forms a hexagonal columnar mesophase[3]. Furthermore, the Si complex with two axial hydroxo groups was found to show a lamellar mesophase with a columnar structure in the wider temperature range[4] and the Ni complex also exhibits the similar mesophase[5]. In addition, it was also found that the corresponding Mo=O complexes with an axial Cl and OH groups form a lamellar and tetragonal columnar mesophases, respectively[6,7]. These indicate that the intermolecular specific interactions could have a potential for the contribution to columnar formation, which surely leads to a diversity of columnar arrangement of tetraphenylporphyrin core.

However, the Al and Mo complexes are unfortunately not so suitable for current measurements due to the thermal decomposition.

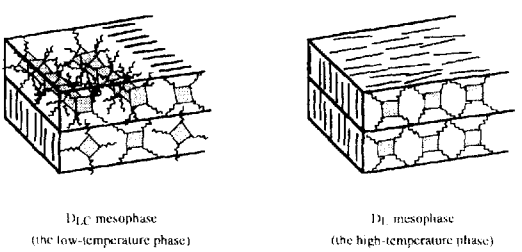


Fig. 2 Schematic representations of the proposed structures of two lamellar mesophases shown in the metal-free and VO compounds.

The phase transition parameters of the metal-free, Ni, VO and Si(OH)2 compounds are summarized in Table 1.

Table 1 Phase transition parameters of the mesogenic compounds

compound	Phase transitions/ °C
the metal-free (C15)	Cryst 56 D_{LC} 66 D_L 135 Iso
Ni complex (C15)	Cryst 68 D_{LC} 122 Iso
V=O complex (C15)	Cryst 51 D_{LC} 82 D_L 140 Iso
$Si(OH)_2$ complex (C12)	Cryst 84 D_{LC} 211 Iso

Photoconductivity

A. Temperature dependence

Fig.3 shows a typical pattern of temperature dependence of the photocurrent for the metal-free compound cell[8] and this is very similar to those of the Ni and VO complexes. The photocurrent shows rather complicated behaviour against the phase and temperature change, while the darkcurrent tends to almost obey Arrhenius law in all phases. At the phase transition of the low- to high-temperature lamellar meso-phases, the photocurrent stepwise increases and decreases at the mesophase–mesophase transition. Furthermore, the photocurrent gradually increases in the high temperature mesophase when the temperature approaches to the clearing point. The mobility measurement of positive carrier revealed

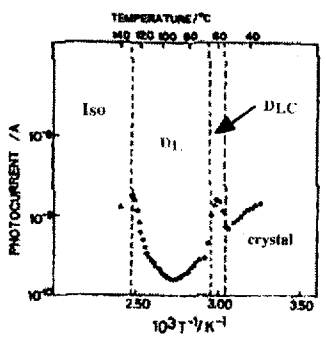


Fig.3 Temperature dependence of photocurrent of ITO/C15TPPH2/ITO cell. C15TPPH2: the metal free compound.

behaviour also exhibits a tendency to disappear when the lamellar mesophase does not have the columnar structure like the high-temperature phase of the metal-free compound.

C. Action Spectra and carrier generation mechanism

Action spectra of the positive electrode illumination for a ITO/C15TPPH2/ITO cell tend to show symbatic and antibatic relations in the wavelength region of low and high absorption intensities, respectively. The thinner cell showed a stronger symbatic relation, whilst the negative electrode illumination was not in a symbatic way, but in an antibatic one[12]. These results imply the photocarrier generation in this cell is on a combination of "extrinsic" and "intrinsic" ones. The former is a mechanism caused at the mesogen-ITO interface and the latter in the bulk region of a mesogenic film. It is considered that for the metal-free, Ni and VO compounds, the positive electrode illumination causes "hole injection" and the negative one for the Si complex induces "electron injection" in the extrinsic process.

On the other hand, the intrinsic process is effective for both electrode illumination to give the photocurrent. Thus, in the high temperature lamellar mesophase of the metal-free compound, it is considered that the extrinsic process is suppressed to the undetectable level of photocurrent and this may be due to the destruction of columnar structure in the high-temperature lamellar mesophase[13].

CONCLUSION

What these results indicate is that the mesophase transitions relating to the change of columnar structure may cause switching properties of photocarrier generation mechanism as for an extrinsic one. Furthermore, the extrinsic process could be modified by the exchange of metal ion ligating to the macrocyclic π-electronic conjugation system in coincidence with the electrode nature. The rectification behaviour

the surprising insensitivity to phase and temperature change[9]. This indicates the temeperature dependence of photocurrent is mainly derived from the phase and temperature dependence of the number of carriers effective for the observed current.

B. V-I characteristics

The V-I characteristics of these cells showed a very interesting and contrasting feature. For the metal-free, Ni and VO compounds, the V-I characteristics of photocurrent exhibit a rectification behaviour in which the larger photocurrent is obtained for the positive electrode illumination as shown in Fig.4[10]. However, the Si complex showed the opposite sign of the rectification where the larger photocurrent was obtained for the negative electrode illumination and the mobility measurements revealed the comparable values of mobilities of the positive and negative charges[11]. These indicate an electron injection from the electrode to the excited complex is caused by the negative electrode illumination, while a hole injection occurs for the positive one . This indicates the usage of metallomesogens could lead to the better performance of photoconductivity depending on the electrode nature by the modification of metal ion.

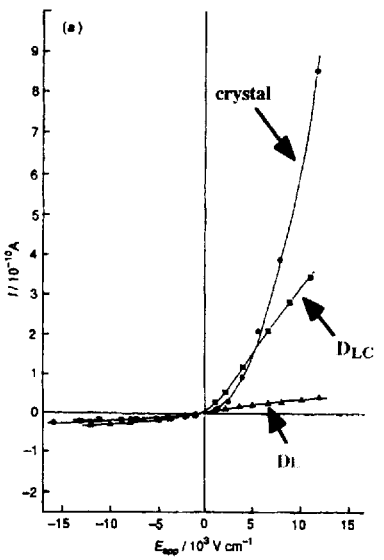


Fig. 4 V-I characteristics of the dark- and photo-currents for ITO/C15TPPH2/ ITO cell.

These rectification

changes as one of the results of these changes. Recently it has been reported that some chemical modifications introducing intermolecular specific interactions could lead to control of intra- and inter-columnar structures of discotic mesophases and this also leads to more interesting futures of liquid crystals as a new electronic materials

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