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Yo Shimizu^a, Yasuo Miyake^{a,b}, Hiroyuki Yoshida^b, Hirosato Monobe^a, Michael J. Cook^c, Akihiko Fujii^b & Masanori Ozaki^b

^a Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology (AIST), Kansai Center, Ikeda, Osaka, 563-8577, Japan

^b Division of Electrical, Electronic and Information Engineering, Graduateschool of Engineering, Osaka University, Suita, Osaka, 565-0871, Japan

^c School of Chemistry, University of East Anglia, Norwich, UK

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A Possibility of 2-Dimensional Transport of Charged Carriers in Columnar Phases of Liquid Crystalline Semiconductors

YO SHIMIZU,^{1,*} YASUO MIYAKE,^{1,2} HIROYUKI YOSHIDA,²
HIROSATO MONOBE,¹ MICHAEL J. COOK,³
AKIHIKO FUJII,² AND MASANORI OZAKI²

¹Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology (AIST), Kansai Center, Ikeda, Osaka 563-8577, Japan

²Division of Electrical, Electronic and Information Engineering, Graduateschool of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

³School of Chemistry, University of East Anglia, Norwich, UK

1,4,8,11,15,18,22,25-hexahexylphthalocyanine was studied on the carrier mobility characteristics by a Time-Of-Flight (TOF) technique. The compound exhibits an ambipolar nature of charge transport and the carrier mobilities for hole and electron were determined to be 0.3 and 0.2 cm² V⁻¹ s⁻¹ in the hexagonal disordered columnar (Col_{hd}) mesophase and 0.3–1.4 and 0.4–0.5 cm² V⁻¹ s⁻¹ in the crystal. These values were obtained for poly-domain films. A possibility of 2-dimensional transport of carriers was discussed in terms of the molecular structure and orderings in both Col_{hd} and crystal phases.

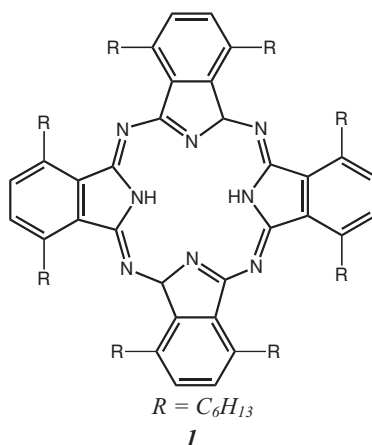
Keywords Organic electronics; liquid crystalline semiconductor; discotic liquid crystal; phthalocyanine; carrier mobility

1. Introduction

Recent studies on liquid crystalline semiconductors have shown characteristic properties derived from liquid crystallinity are so attractive as a new category of organic semiconductors for “Printed Electronics”. In addition to the fast mobility of charged carriers by electronic hopping transport in mesophases, good solubility into common organic solvents as well as its spontaneous alignment behaviour of molecules to form a large domain of film with uniformly aligned molecules are attractive properties for a potential application in thin film devices such as transistors and solar cells. In particular, discotics is an interesting category of liquid crystalline semiconductors due to the molecularly stacking columnar structures in which charges easily hop among the molecules along the columnar axis. This means columnar mesophase has a one-dimensional transport pathway for the charges and in fact, some compounds show a fast carrier mobility comparable to that of amorphous silicon ($>10^{-1}$ cm² v⁻¹ s⁻¹) [1–3]. However, such one dimensional pathway for charge transport is giving rise to somewhat difficulty in realizing fast drift mobility of carriers as a macroscopic

*Corresponding author. E-mail: yo-shimizu@aist.go.jp

point of view due to its narrow allowance for defects and dislocations being likely to happen in a “uniformly” aligned molecules of film. For example, hexabenzocoronene mesogens which possess an largely extended π electronic conjugation system as the central core of discotic mesogen exhibit a mobility in the order of $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for the columnar mesophase determined by a TOF technique [4], whilst the faster mobility of carriers was determined to be in the order of $10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [5]. The latter is the intrinsic mobility by Pulse-Radiolysis Time-Resolved Microwave Conductivity (PR-TRMC) method, which is not sensitive to the morphological conditions of films.



Iino et al. reported that a phthalocyanine discogen, 1, 4, 8, 11, 15, 18, 22, 25-hexaoctylphthalocyanine exhibits fast carrier mobility determined by a TOF method with an ambipolar nature for its Col_{hd} and Col_{rd} mesophases [6, 7]. It would a strange situation, when one considers that the eight octyl chains attached at 1, 4, 8, 11, 15, 18, 22, 25-sites could play an steric role for molecular stacking, meaning that its columnar mesophase should have disordered column in the direction of the columnar axis. This consideration would make us imagine so easily that the observed drift mobility is not so fast as that for the ordered columnar mesophase [8]. In fact, the mesophase coming up for the homologous series is of disordered columns [9].

Here we report the drift mobility of charged carriers for a homologue of the mesogenic phthalocyanine, 1, 4, 8, 11, 15, 18, 22, 25-hexahexylphthalocyanine (**1**) for both Col_{hd} and crystalline phases and some of the experimental evidences imply the charge transport takes place in the lateral direction of columnar axis.

2. Experimental

The compound was synthesized by the three-step reaction and the purification was carried out by repetitive column chromatography (silica-gel, hexane) followed by recrystallisation from toluene-methanol. The purification was executed until the photocurrent decay curves obtained in the TOF measurements no longer change their shape in which one can see a clear inflection point corresponding to the transit time of carriers drifting between two electrodes.

The phase transition temperatures, enthalpies and entropies were determined by DSC measurements at the heating and cooling rate at $1 \text{ }^\circ\text{C min}^{-1}$ (TA Instruments MDSC2650).

The XRD measurements were also carried out for the non-aligned sample using a Rigaku Rint 2000 X-Ray diffractometer and a hand-made temperature controllable cell. The optical textures formed on the phase transitions were observed by a polarized microscope (Olympus BH2) equipped with a temperature-controllable hot-stage (Mettler FP52 and the control unit FP82HT).

Drift mobility of carriers was determined by a Time-Of-Flight (TOF) technique of which system is facilitated with a polarized microscope (Olympus BX50) equipped with a temperature-controllable hot-stage prepared for conduction measurements [10]. The cell for mobility measurements is of a sandwich-type in which two ITO-coated substrates are used with polyimide film as spacer (thickness: 12.5 μm , the actual cell gaps were evaluated by an interference technique of light transmittance) and set into the hot-stage to observe the optical texture under the bias. The pulsed excitation of the compounds was executed using a N_2 gas laser (λ : 337 nm, pulsed width: 800 psec) which was guided into the hot-stage to shot the pulsed light through an optical fiber. The generated current transits were detected an oscilloscope (Hewlett Packard Infinium 54820A) and the transit times were determined on the observed photocurrent decay curves to calculate the mobility, μ following the equation, $\mu = d^2 t^{-1} E^{-1}$, where d , t and E are sample thickness, transit time and applied field.

3. Results and Discussion

Figure 1 shows DSC curves (a) measured at 5 $^\circ\text{C min}^{-1}$ and the XRD pattern for the mesophase of **1**. The phase transition temperatures were determined to be 161 and 170 $^\circ\text{C}$ for the melting and clearing temperatures, respectively. These are in good coincidence to those reported by Cook et al. [9]. The mesophase is assigned to be of Col_{hd} because of a typical reflection set where one sees the three marked reflections at the smaller angle region, d_{100} : d_{110} : d_{200} show its spacing ratio of 1 : 1/3 : 1/2 and no reflection was observed which corresponds to the stacking periodicity of molecules within a column (~ 3.5 Å).

The optical texture observation of Col_{hd} mesophase never shows homeotropic areas within the poly-domain film and this is quite deferent behaviour in comparison to that observed for the Col_{hd} mesophase of the octyl homologue which was reported to show a strong tendency for its homeotropic alignment attained spontaneously between slide glasses [7]. This may indicate that the ratio of molecular surface between the phthalo-cyanine core and the attached alkyl chains significantly affect its spontaneous alignment behaviour.

The photocurrent decay curves obtained by the TOF measurements of mobility exhibit a typical shape of decay curves as shown in Fig. 2. The drift mobility was easily determined to give ambipolar mobilities both in the Col_{hd} and crystal phases. The observed mobility is field independent and this is a typical character of liquid crystalline semiconductors [11]. Interestingly, the decay curves could be detected in a very clear manner for easy determination of the transit times even for the poly-domain crystalline phase as well as its Col_{hd} mesophase. One often sees that the transient decay curves of photocurrent clearly observed in a mesophase are likely to get dispersive when the phase transitioned to the crystalline solid with poly-domain structure of films, where the transit time could hardly be determined.

As Iino et al. reported, this compound shows an ambipolar character of mobility and this could be seen for both Col_{hd} mesophase and crystalline solid phase. Figure 3 exhibits the temperature dependence of mobility of **1**. Small temperature dependence in the Col_{hd} mesophase is a typical for liquid crystalline semiconductors [12]. However, for the crystalline solid phase, a remarkable difference is seen between the hole and electron mobilities. The hole mobility drastically increases as the temperature goes down ($0.4\text{--}1.4\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$),

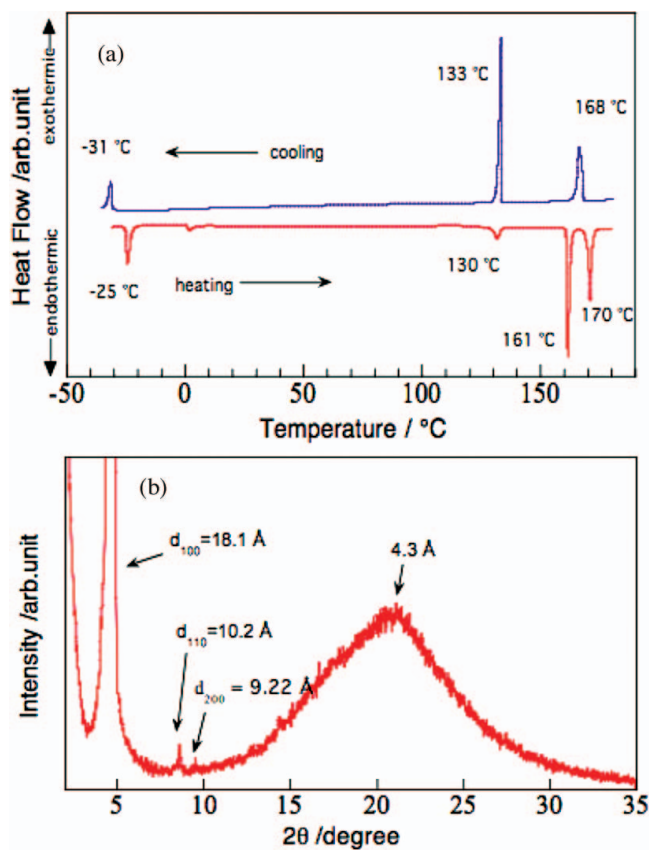


Figure 1. DSC curves (a) and an XRD pattern at 160 °C (b) of 1.

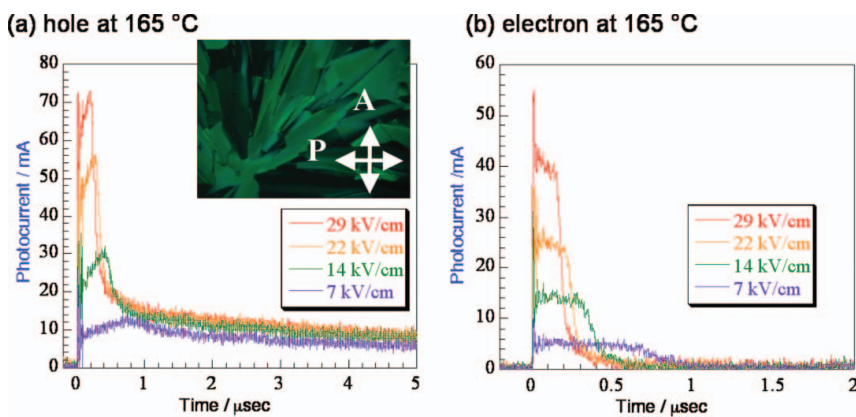


Figure 2. Photocurrent decay curves obtained for hole (a) and electron (b) in the Col_{hd} mesophase of 1. The photograph is of the optical texture of film in the cell used for the mobility measurements.

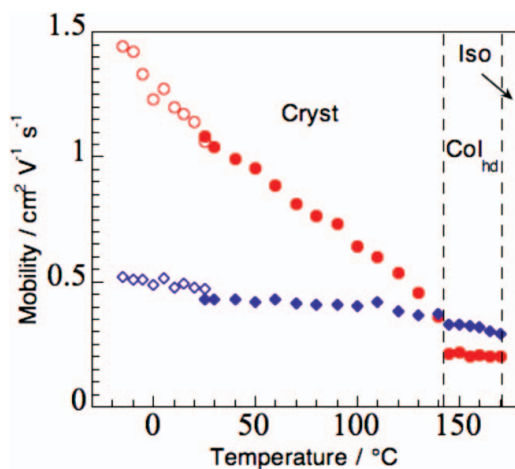


Figure 3. Temperature dependence of mobility for **1** (applied field: 14 kV cm^{-1}).

whilst the electron one shows a small dependence ($0.4\text{--}0.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). This behaviour in the crystal has not yet been reported for organic semiconductors with a liquid crystalline nature. These were obtained for their poly-domain films without any homeotropic area where the columnar axis stands perpendicular to the substrate surface and this axis is along the direction of easy electronic transport path and thus, this may indicate that even in the crystalline solid phase, domain boundaries do not give any significant influence on the charge transport efficiency as smectic liquid crystalline semiconductors [13].

Cook et al. reported a single crystalline structure of **1** and it reveals that the $\pi\text{--}\pi$ stacking periodicity extra-ordinary large ($\sim 8 \text{ \AA}$) [14] and this value indicates that it is very difficult for electrons to hop among the neighboring molecules in its direction. Considering the size of phthalocyanine ring and alkyl-attached one (**1**) as depicted in Fig. 4, molecules might be contact to each over the columns and efficient charge hopping, thus, may be possible.

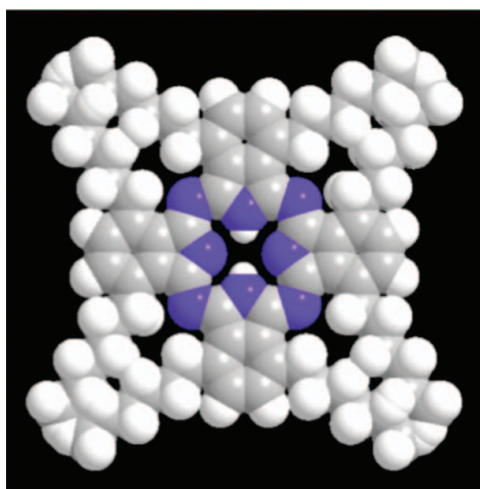


Figure 4. A molecular shape of **1** as a simple modeling.

4. Summary

A mesogenic phthalocyanine, 1, 4, 8, 11, 15, 18, 22, 25-hexahexyl-phthalocyanine (**1**) was studied on its drift mobility characteristics by a TOF method. The compound essentially exhibits an ambipolar nature and the mobility for the Col_{hd} mesophase is in the order of $10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ showing a small dependence on temperature and for the crystalline solid phase, temperature dependence of mobility is quite different to each, where small dependence could be seen for electron transport, though large dependence for hole transport reaching to $1.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature. All these were obtained for poly-domain films without any homeotropic area. This compound is so interesting in terms of a new molecular design concept for liquid crystalline semiconductors.

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