Carrier Mobility of Discotic Lamellar Mesophases of 5,10,15,20-Tetrakis(4-*n*-pentadecylphenyl)porphyrin

Hirosato Monobe, Shoji Mima, and Yo Shimizu*
Department of Organic Materials, Osaka National Research Institute, AIST-MITI, 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577

(Received June 2, 2000; CL-000533)

The carrier mobility of discotic lamellar mesophases was evaluated by Time-of-Flight (TOF) method for mesogenic 5,10,15,20-tetrakis(4-*n*-pentadecylphenyl)porphyrin and was found to be in the order of 10^{-4} cm^2 V^{-1} s^{-1}. In spite of the higher order of molecular orientation in the lamellar mesophases, it is comparable with that of hexagonal disordered columnar mesophase. This is the first report of charged carrier mobility of a discotic lamellar mesophase.

Recent studies of discotic liquid crystals have revealed that some of columnar mesophases show unexpectedly fast mobility of charged carrier in spite of their large extent of molecular fluctuation.[1] As for some hexagonal columnar mesophases, it was shown that the molecular order within a column significantly affect the charge transport properties and the carrier mobility decreases with the disorder.[2] The highly ordered mesophases, therefore, are quite interesting in their charge transportation behavior. Up to now, no other columnar mesophases than the hexagonal ones has been investigated on their carrier mobility as well as photoconductivity, though a variety of columnar mesophases are found.[3] One of the highly ordered columnar mesophases is so-called "discotic lamellar" phase and it is a smectic-like mesophase of disc-shaped molecules.[4] Studies of photoconductivity for two kinds of discotic lamellar mesophases showed some characteristic properties of photocurrent in relation to the mesomorphic phase transitions for an ITO sandwich-type cell of a long-chain tetraphenylporphyrin.[5]

On the other hand, recently, it was found that calamitic liquid crystals revealed showing fast charge mobilities which depends on the molecular order in the smectic E and in the smectic A phases.[6] Discotic and calamitic liquid crystals attracted attention as organic carrier transport materials. The relation of charge migration phenomena to molecular fluctuation in mesophase is quite interesting in order to understand the characteristics of mesophase materials.

In this letter, the first evaluation of carrier mobility in a discotic lamellar mesophase is reported for 5,10,15,20-tetrakis-(4-*n*-pentadecylphenyl)porphyrin, abbreviated as C15TPPH$_2$, which was carried out by Time-of-Flight (TOF) method.

C15TPPH$_2$ shows the phase transition behavior in the following scheme.

	crystal		M$_{LC}$		M$_L$		isotropic
T / °C		56		66		135	
ΔH / kJ mol^{-1}		92		31		27	

The existence of a columnar structure is proposed for the low-temperature lamellar (M$_{LC}$) mesophase based on the spectroscopic results, while the high-temperature one (M$_L$) is a non-columnar or broken columnar mesophase.[7] Interestingly, the sudden disappearance of photocurrent rectification was observed at the phase transitions from the low- to high-temperature mesophases and an extrinsic mechanism where an electron is injected into the ITO from the excited porphyrin is related to the rectification behavior.[8]

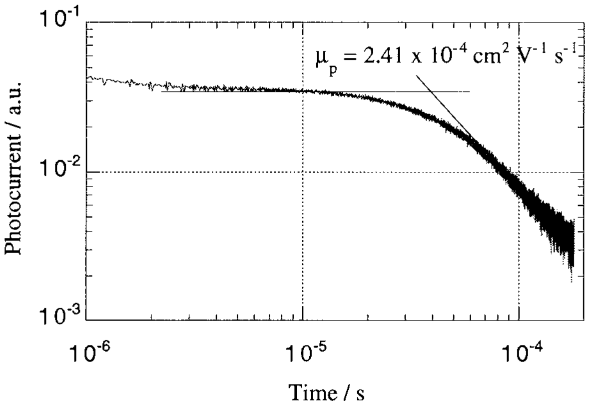

Figure 1. A photocurret transient in the high-temperature discotic lamellar phase (90 °C) of ITO/C15TPPH$_2$/ITO for the positive charge carrier obtained by TOF method. wavelength of laser pulse: 420 nm, electric field strength: 40000 Vcm^{-1}, sample thickness: ~4 μm.

Figure 1 shows a transient photocurret decay curve obtained by TOF method. For almost all measurements in this work, such a typical and clear decay curve was seen and this indicates that the charged carriers are mobile without any significant dispersion in spite of the multi-domain structure of the mesogenic film. Temperature dependence of carrier mobility in the positive electrode illumination for this cell is depicted in Figure 2. The observed values of carrier mobility are in the order of 10^{-4} cm^2 V^{-1} s^{-1}. Surprisingly, it is almost independent of the phase (two lamellar mesophases and crystal) as well as the temperature. The cell used for the mobility measurements is not of mono-domain film of the mesogen. The lamellar mesophases of C15TPPH$_2$ have high viscosity and consequently it is so hard to obtain a uniform alignment in the film as a large domain. According to the recent works by Funahashi et al., domain boundaries of conventional rod-like liquid crystalline systems essentially do not affect the charge migration efficiency and it is proposed to be a characteristic property of charge transportation in liquid crystals.[6,9] Thus, the observed mobility is, at least, faster than 10^{-4} cm^2 V^{-1} s^{-1}. For some mesophases with hexagonal arrays of columns, the carrier mobility either does not depend on the temperature or decreases with temperature.[10] In our case, an independent nature of carrier mobility for temperature was observed. The evaluated carrier mobility of the lamellar mesophases (10^{-4} cm^2 V^{-1} s^{-1}) was

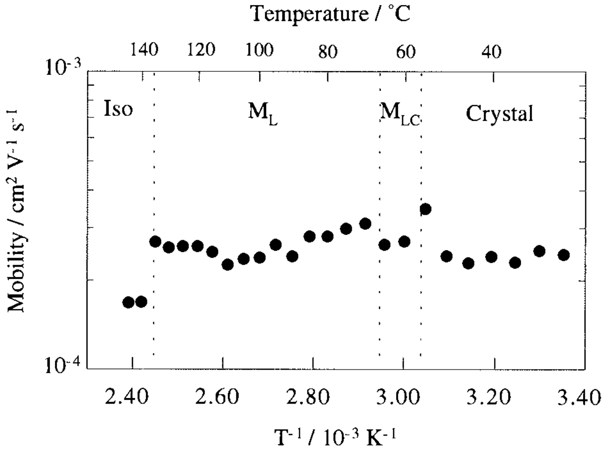

Figure 2. Arrhenius plot of C15TPPH2 hole mobility versus the reciprocal of temperature at an electric field of 40000 Vcm^{-1}. The mobility is calculated using the well known relation $\mu = l / t_T E$, where l is the sample thickness, E the electric field strength, and t_T the transit time.

smaller than that in the hexagonal columnar phase for an alkylthiotriphenylene derivative (10^{-3} cm^2 V^{-1} s^{-1}) and that in the more ordered structures such as the helical columnar phase (10^{-1} cm^2 V^{-1} s^{-1}).[1]

On the other hand, the temperature dependence of steady-state photocurrent (Figure 3) shows distinctive stepwise change. The photocurrent increases at the phase transition from crystal to the low-temperature lamellar phase, while it decreases at the transition from the low- to high-temperature lamellar ones. In general, the observed current is directly related to two factors, the number of carrier and the mobility. The mobility behavior on the phase transitions, thus, indicates that the stepwise change of the photocurrent for the phase transitions is mainly due to the change of the number of effective carriers in the cell. In addition, the photocurrent decreases in the lower temperature region of the high-temperature lamellar mesophase and increases in the higher temperature region, showing a minimum point at ca. 80 °C. Thus, the mobility behavior indicates that the number of effective carriers gradually decreases from the mesophase-mesophase transition temperature to the minimum point, while it increases steeply in the higher temperature region.

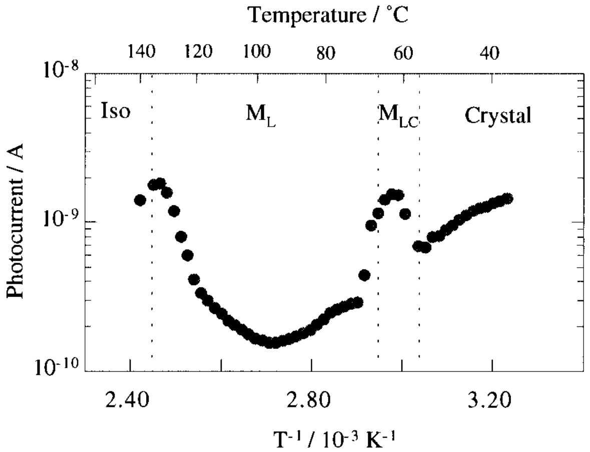

Figure 3. Temperature dependence of photocurrent for ITO/C15TPPH2/ITO cell. sample thickness: 25 μm, bias: 4000 Vcm^{-1}, wavelength of illumination light: 620 nm.

This is the first evaluation of carrier mobility for discotic lamellar mesophases. Our results indicate that the number of effective charged carriers generated in an ITO/C15TPPH$_2$/ITO cell is strongly dependent on temperature and further studies are now in progress.

The authors acknowledge Agency of Industrial Science and Technology, Ministry of International Trade and Industry for the financial support based on a national R&D research project entitled "Harmonized Molecular Materials" operated by Industrial Science and Technology Frontier Program.

References

1 D. Adam, P. Schuhmacher, J. Simmerer, L. Häussling, K. Siemensmeyer, K. H. Etzbach, H. Ringsdorf, and D. Haarer, *Nature*, **371**, 141 (1994).
2 J. Simmerer, B. Glüsen, W. Paulus, A. Kettner, P. Schuhmacher, D. Adam, K. H. Etzbach, K. Siemensmeyer, J. H. Wendorf, H. Ringsdorf, and D. Haarer, *Adv. Mater.*, **8**, 815 (1996).
3 S. Chandrasekhar, *Liq. Cryst.*, **14** , 3 (1993).
4 H. Sakashita, A. Nishitani, Y. Sumiya, H. Terauchi, K. Ohta, and I. Yamamoto, *Mol. Cryst. Liq. Cryst.*, **163**, 211 (1988).
5 Y. Shimizu, A. Ishikawa, S. Kusabayashi, M. Miya, and A. Nagata, *J. Chem. Soc., Chem. Commun.*, **1993**, 656; Y. Shimizu, H. Monobe, S. Mima, T. Higashiyama, T. Fuchita, and T. Sugino, *Mater. Res. Soc. Symp. Proc.*, **559**, 211 (1999).
6 M. Funahashi and J. Hanna, *Appl. Phys. Lett.*, **73**, 3733 (1998).
7 Y. Shimizu and T. Higashiyama, *Proc. SPIE-Int. Soc. Opt. Eng.*, **3319**, 177 (1998).
8 Y. Shimizu, T. Higashiyama, and T. Fuchita, *Thin Solid Films*, **331**, 279 (1998).
9 M. Funahashi and J. Hanna, *Appl. Phys. Lett.*, **76**, 2575 (2000).
10 A. M. van de Craats, J. M. Warman, M. P. de Haas, D. Adam, J. Simmerer, D. Haarer, and P. Shuhmacher, *Adv. Mater.*, **8**, 823 (1996).