

The First Discotic Metallomesogen Derived from Phthalocyaninatooxotitanium for a Novel Photoconductive Liquid Crystal

Julio Santiago, Takushi Sugino, and Yo Shimizu*

Department of Organic Materials, Osaka National Research Institute, AIST-MITI, Midorigaoka 1-8-31, Ikeda, Osaka 563-8857

(Received March 18, 1998; CL-980203)

The first phthalocyaninatooxotitanium discotic liquid crystal has been synthesized for a novel photoconductive liquid crystal. The thermal behaviour of 2,3,9,10,16,17,23,24 octakis(octadecylthio)phthalocyaninatooxotitanium(IV) was investigated by polarised light microscopy and differential scanning calorimetry (DSC) and X-ray diffraction, to reveal that it exhibits two hexagonal columnar mesophases.

Phthalocyaninatooxotitanium (PcTiO) are one of the most interesting photoresponsive materials because of their high photoconductivity.^{1,2} These have been found to have utility as xerographic photoreceptors and GaAsAl printers.³ Many studies of the solid state film show that the charge generation efficiency of PcTiO derivatives is strongly dependent on the crystal structure.⁴

On the other hand, the photoconductivity of discotic liquid crystals has been studied extensively.^{5,6} In particular, a fast hole mobility ($0.1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$) was reported for a plastic crystalline phase of a triphenylene discotic liquid crystal.⁷ However, up to now there is no study of liquid crystalline phthalocyaninatooxotitanium derivatives. Therefore, studies of the charge carrier generation process as well as the determination of the charge carrier mobility in the liquid crystalline phase of PcTiO derivatives are expected to provide important information regarding its applications.

In this communication, we describe the synthesis and thermal properties of the first discotic liquid crystal having a PcTiO core (Figure 1).

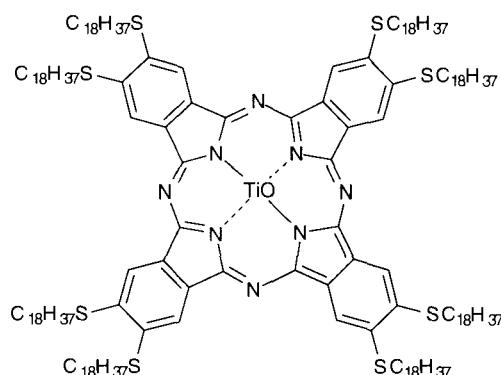


Figure 1. Molecular structure of 1.

The synthesis of 2,3,9,10,16,17,23,24-octakis(octadecylthio)phthalocyaninatooxotitanium(IV), **1**, was carried out by heating a mixture of 4,5-bis(octadecylthio)phthalonitrile, Ti(OBu)_4 and urea in n-octanol at

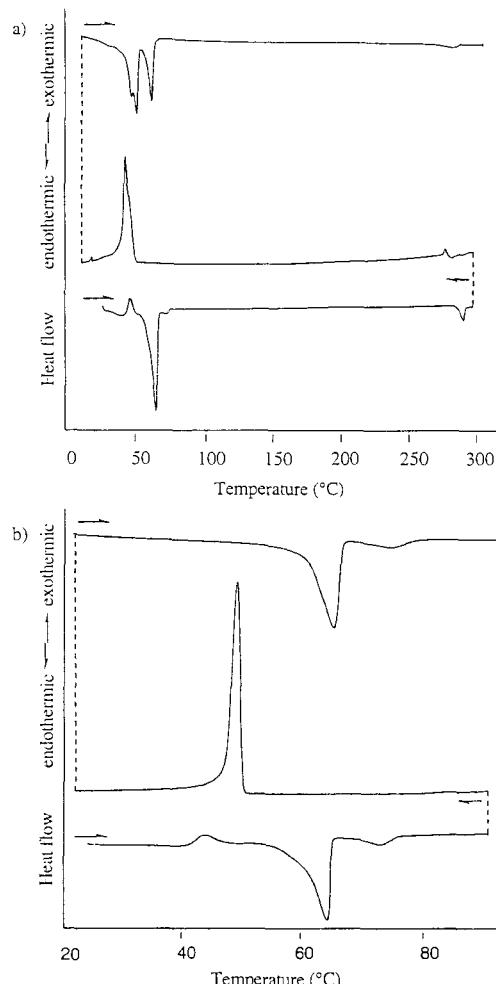


Figure 2. DSC traces of 1. The maximum temperatures of heating are a) $300 \text{ }^\circ\text{C}$ (heating and cooling rate: $5 \text{ }^\circ\text{Cmin}^{-1}$) and b) $90 \text{ }^\circ\text{C}$ (heating and cooling rate: $1 \text{ }^\circ\text{Cmin}^{-1}$).

$150 \text{ }^\circ\text{C}$ under N_2 for 6 h.⁸ 4,5-Bis(octadecylthio)phthalonitrile was obtained by the reaction of 4,5-dichlorophthalonitrile and octadecanethiol with K_2CO_3 in DMF at $150 \text{ }^\circ\text{C}$ for 1 h. Characterization of the product was performed by UV-visible absorption, IR and NMR spectroscopies and elemental analysis.⁹ These results were in good agreement with those reported previously in the literature.^{2,10}

Figure 2a shows the DSC traces of **1**. On the first heating run (bottom) an exothermic peak at $41 \text{ }^\circ\text{C}$ (13.4 kJmol^{-1}) and two endothermic peaks at $59 \text{ }^\circ\text{C}$ (106.5 kJmol^{-1}) and $68 \text{ }^\circ\text{C}$ (11.7 kJmol^{-1}) were detected. The clearing point was recognized at $292 \text{ }^\circ\text{C}$ (9.6 kJmol^{-1}) by a microscopic observation of the textures. On

the second heating run, new peaks appear at 35 °C, 43 °C and 54 °C. These are probably induced by slight modification of the compound under heating up to the clearing point. The exothermic peak at 41 °C was not observed during the second heating run which suggests that it is due to an exothermic crystal-crystal rearrangement. Figure 2b shows the DSC traces of a fresh sample heated up to 90 °C. The two endothermic peaks at 59 °C and 68 °C were observed both in the first and second heating runs. This indicates that no decomposition or chemical modification occurs up to 90 °C. However, the peak at 68 °C was not detected in the cooling process.

The microscopic observation of **1** heated up to 150 °C revealed that it melts at 60 °C and the texture obtained changes slightly at 70 °C. Both mesophases could not be identified only by texture observations. But the corresponding phase transitions were also observed on the cooling process and were reproducible in repeated heating-cooling cycles. The texture formed spontaneously on cooling from the clearing point (292 °C) was similar to that obtained for a mesophase of an analogous phthalocyaninatooxovanadium complex which was assigned to be D_{hd} phase.¹¹ However, no change of texture was recognized at 70 °C and the crystallization on cooling was observed at 36 °C.

The results of powder X-ray diffraction measurements for the two mesophases are shown in Figure 3. X-ray diffraction patterns of **1** at 65 °C and 150 °C are very similar in the narrow angle region. Three peaks were observed with a spacing ratio of 1 : 1/3 : 1/2, which is characteristic of a hexagonal columnar phase. In the wider angle region, X-ray pattern at 150 °C showed only a

broad halo centered at 20=20° (ca.4.6 Å) which is derived from the molten alkyl chains, whilst the pattern at 65 °C exhibited four additional peaks at 6.2 Å, 4.6 Å, 4.2 Å and 3.9 Å, indicating the higher molecular order for this mesophase. The peak at 3.9 Å probably corresponds to the stacking periodicity of molecules. However, the peak at 6.2 Å may indicate the presence of dimers in this mesophase. Further experiments are necessary to reveal the details.

In conclusion, optical microscopy, DSC and X-ray diffraction revealed that **1** is mesomorphic and the phase transition sequence is as follows, C - 59 °C - D_h - 68 °C - D_{hd} - 292 °C - I. Studies of the thermal stability (over 292 °C) and the photoconductive properties are in progress.

The authors thank Agency of Industrial Science and Technology (AIST) for providing AIST fellowship to Dr. J. Santiago and for the financial support based on a MITI's national research project "Harmonized Molecular Materials" operated in Industrial Science and Technology Frontier Program.

References and Notes

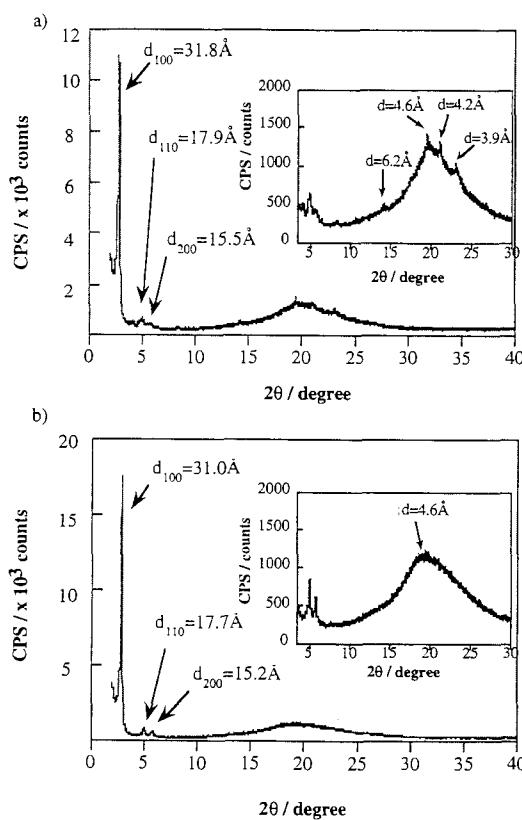


Figure 3. X-ray diffraction patterns of **1** at a) 65 °C and b) 150 °C.

- 1 M. Hanack and M. Lang, *Adv. Mater.*, **6**, 819 (1994); K.-Y. Law, *Chem. Rev.*, **93**, 449 (1993).
- 2 P. Haisch, G. Winter, M. Hanack, L. Lüer, H.-J. Egelhaaf, and D. Oelkrug, *Adv. Mater.*, **9**, 316 (1997); W.-F. Law, K.M. Lui, and D.K.P. Ng, *J. Mater. Chem.*, **7**, 2063 (1997).
- 3 A. Kawara, T. Tanaka, and A. Yajima, Mita Industrial Co. Ltd., Jpn. Kokai Tokkyo Koho JP 09281734 (1997); *Chem. Abstr.*, **124**, 352989v (1998).
- 4 J. Mizuguchi, G. Rihs, and H.R. Karfunkel, *J. Phys. Chem.*, **99**, 16217 (1995); T. Saito, Y. Iwakabe, T. Kobayashi, S. Suzuki, and T. Iwayanagi, *J. Phys. Chem.*, **98**, 2726 (1994).
- 5 C.-Y. Liu, H.-L. Pan, M.A. Fox, and A.J. Bard, *Chem. Mater.*, **9**, 1422 (1997); C.-Y. Liu, H.-L. Pan, H. Tang, M.A. Fox, and A.J. Bard, *J. Phys. Chem.*, **99**, 7632 (1995).
- 6 Y. Shimizu, A. Ishikawa, S. Kusabayashi, M. Miya, and A. Nagata, *J. Chem. Soc., Chem. Commun.*, **1993**, 656; Y. Shimizu, A. Ishikawa, and S. Kusabayashi, *Chem. Lett.*, **1986**, 1041.
- 7 D. Adam, P. Schuhmacher, J. Simmerer, L. Häussling, K. Siemensmeyer, K.H. Etzbach, H. Ringsdorf, and D. Haarer, *Nature*, **371**, 141 (1993).
- 8 J. Yao, H. Yonehara, and C. Pac, *Bull. Chem. Soc. Jpn.*, **68**, 1001 (1995).
- 9 H^1 -NMR ($CDCl_3$): δ 0.85 (*t*, 24H, CH_3) 1.2-1.6 (*br m*, 224H, $CH_3(CH_2)_{14}$), 1.76 (*br s*, 16H, $CH_2CH_2CH_2S$), 2.06 (*br s*, 16H, CH_2CH_2S), 3.50 (*br d*, 16H, CH_2S), 8.82 (*br*, 8H aromatic).
FT-IR (KBr/cm^{-1}): 966 (Ti=O str.).
UV-Vis ($CHCl_3$, λ_{max}/nm ($\log \epsilon / \text{mol}^{-1}\text{cm}^{-1}$)): 738 (5.55), 705 (4.73), 661 (4.76), 468 (4.69), 337 (5.04).
Found: C, 74.44; H, 10.83; N, 4.11; S, 9.30%. Calcd for $C_{176}H_{304}N_8OS_8Ti$: C, 74.10; H, 10.74; N, 3.93; S, 8.99%.
- 10 W.-F. Law, R.C.W. Liu, J. Jiang, and D.K.P. Ng, *Inorg. Chim. Acta*, **256**, 147 (1997).
- 11 S. Trantawong, T. Sugino, Y. Shimizu, A. Takeuchi, S. Kimura, T. Mori, and H. Takezoe, *Liq. Cryst.*, in press.