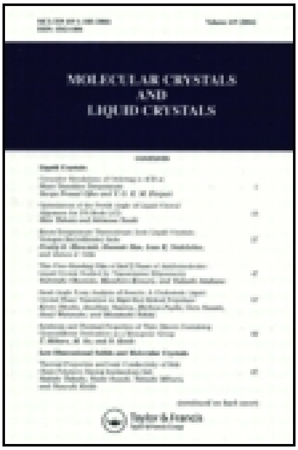

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The First Oxotitanium Phthalocyanine Metallomesogen as a Liquid Crystalline Photoconductor: 2,3,9,10,16,17,23,24-Octakis(n-octadecylthio) phthalocyaninatooxotitanium(IV)

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The First Oxotitanium Phthalocyanine Metallomesogen as a Liquid Crystalline Photoconductor: 2,3,9,10,16,17,23,24-Octakis(n-octadecylthio) phthalocyaninatooxotitanium(IV)

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The title compound was synthesized as a liquid crystalline photoconductor. Its thermal behavior is strongly dependent on the thermal history of the material. It exhibits polymorphism in the solid state and a columnar hexagonal disordered mesophase in a wide temperature range from 68 °C to 292 °C.

Keywords: metallomesogens; metallophthalocyanines; discotic liquid crystal; photoconductivity

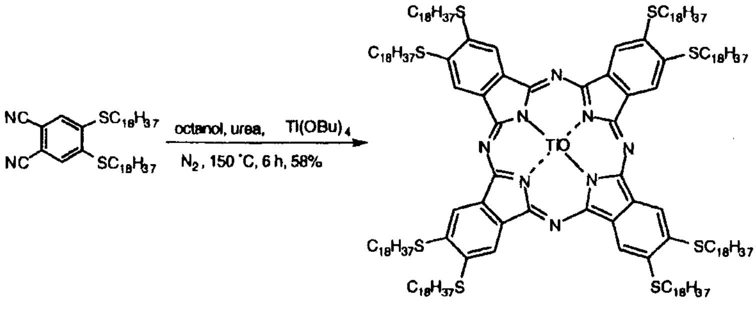
INTRODUCTION

Among metallophthalocyanines, phthalocyaninatooxotitanium derivatives (PcTiO) has paid much attention because of their high photoconductivity and its industrial application in xerography.[1] The mechanism of the charge carrier generation in these materials is a subject of an intensive research, but it is not very well understood yet.[2] Many studies of the solid state film show that the charge generation efficiency of PcTiO derivatives is strongly dependent on the crystal structure.[3] It means that the organization of the molecules in the bulk is crucial for the photoconductive properties of the material. Discotic liquid crystals offers new molecular arrangements different than those found in the solid state[4] and 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.

Recently, in a preliminary communication we describe the synthesis and thermal properties of the first discotic liquid crystal having a PcTiO core, **1**.[5] According to the preliminary data we deduced that **1** exhibited two columnar phases of hexagonal type.

In this work, we describe in detail the synthesis of **1** and present new data that allow us a better understanding of the thermal behavior of the first metallomesogen with titanium as metal.

The synthesis of **1** was performed according to the Scheme 1. The initial 4,5-Bis(octadecylthio)phthalonitrile was prepared by slight modification of the published procedure.[6]



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SCHEME 1

EXPERIMENTAL

Synthesis

2,3,9,10,16,17,23,24-Octakis(n-octadecylthio)phtalocyaninato-oxotitanium(IV) (1): A mixture of 4,5-Bis(octadecylthio)phthalonitrile (2.718 g, 3.9 mmol), $Ti(OBu)_4$ (0.365 g, 1.07 mmol), urea (0.117 g, 1.95 mmol), and 1-octanol (0.6 g, 4.61 mmol) was heated at 150°C under N_2 for 6 h. Then, 3 ml of methanol was added to the mixture and it was continuously heated for additional 30 min.[7] After cooling to room temperature, a dark violet solid was obtained by filtration. This solid was washed with toluene, methanol and water. The crude compound was purified by chromatography (neutral Al_2O_3, chloroform-hexane 1:1) followed by recrystallization from chloroform-acetone to give a dark brown powder: 1.6 g (58%). H^1-NMR ($CDCl_3$): δ 0.85 (*t*, 24H, C*H*$_3$) 1.2-1.6 (*br m*, 224H, $CH_3(C$*H*$_2)_{14}$), 1.76 (*br s*, 16H, C*H*$_2CH_2CH_2S$), 2.06 (*br s*, 16H, C*H*$_2CH_2S$), 3.50 (*br s*, 16H, C*H*$_2$S), 8.82 (*br*, 8H aromatic). FT-IR (KBr/cm^{-1}): 966 (Ti=O str.). UV-Vis ($CHCl_3$, λ_{max}/nm (logε /l mol^{-1}cm^{-1})): 738 (5.55), 705 (4.73), 661 (4.76), 468 (4.69), 337 (5.04). Elemental analysis of $C_{176}H_{304}N_8OS_8Ti$ (2852.82): found (calculated): C 74.44 (74.10), H 10.83 (10.74), N 4.11 (3.93), S 9.30 (8.99).

Measurements

The phase transitions were detected by a Differential Scanning Calorimeter (TA Instruments, 2920 MDSC) and the texture was observed by a polarizing microscope (Olympus, BH-2) equipped with a hot stage (Mettler, FP80HT). X-Ray diffraction studies were carried out by using a Rigaku Geigerflex X-ray diffractometer (CuKα). The temperature dependent FT-IR was measured by using a FT-IR spectrometer (Perkin Elmer, Paragon 1000) equipped with a microscope (Olympus, SZ-STB1) and a hot stage (Linkam, LK-600FT-IR). The elemental analysis was performed with a Perkin Elmer CHNS/O analyzer 2400.

RESULTS AND DISCUSSION

From the DSC trace of **1** (Figure 1) two facts can be observed: a) The DSC trace during the first heating is not reproducible on the second heating. b) Not all the endothermic peaks observed during the first heating were detected on the cooling process. These observations suggest that the sample decomposes slightly after reaching the clearing point (292 °C) or the phase transition temperatures are depending on the conditions of the experiments (rates of the heating-cooling process or thermal history of the sample).

The DSC traces of **1** were basically the same for the heating and cooling rates from 0.1 °C/min to 10 °C/min. However, when a fresh sample was heated up to 90 °C, the two endothermic peaks were observed at 59 °C and 68

°C 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 or it occurs together with the transition at 59 °C.[5]

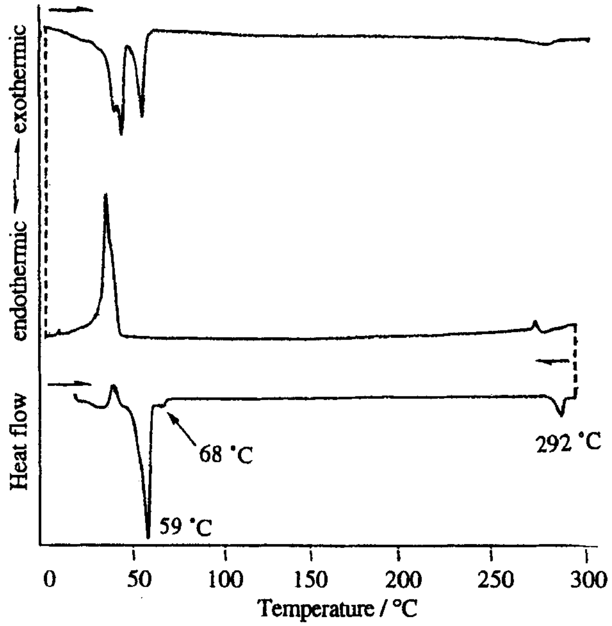

FIGURE 1 DSC traces of **1** heated up to 300 °C (rate: 5 °C/min).

In a new experiment, the reversibility of each peak during the first heating run was studied. As we can observe in Figure 2, after heating up to 65 °C (just after the first endothermic peak), cooling to 0 °C and then heating up to 80 °C, the ratio of intensities of the peaks at 59 °C and 68 °C were inverted. Continuous treatment of this sample, cooling to 0 °C and heating up to 80 °C makes those peaks reappear in their original intensities ratio. This behavior can be explained as shown in Figure 3, considering that the original sample is a mixture of two crystalline forms: C_1 (major component) and C_x, where C_x is a metastable form which change to another one, C_2, in an exothermic process at 41 °C. The big endothermic peak at 59 °C corresponds to the transition C_1-

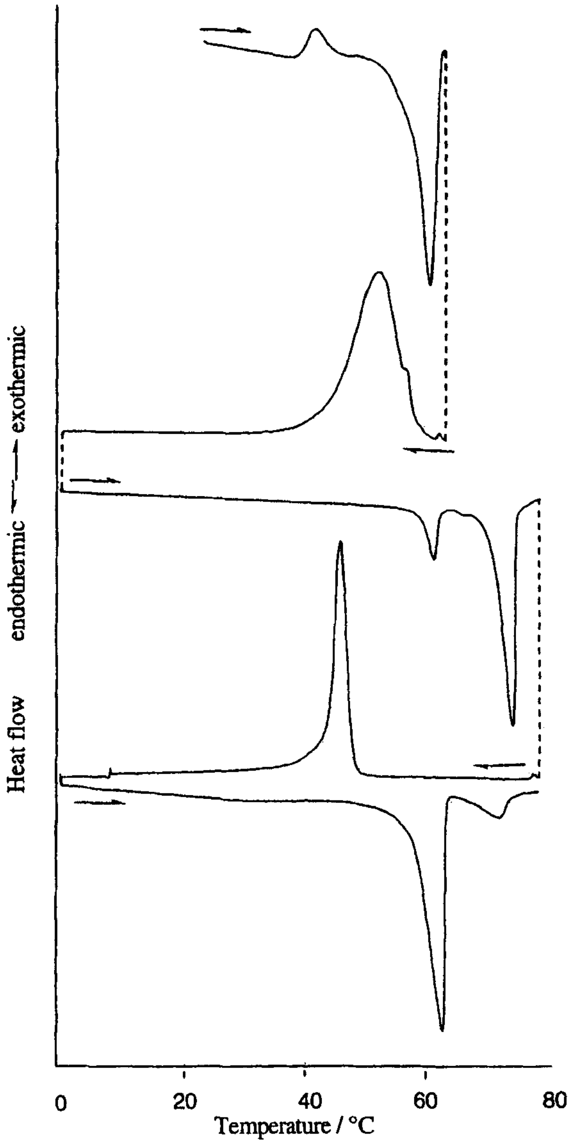

FIGURE 2 DSC traces of 1 heated and cooling (rate: 1 °C/min) successively between 0 °C and 80 °C.

Col_{hd} and the small peak at 68 °C to the transition C_2-Col_{hd}. At 65 °C the sample is a mixture of Col_{hd} and C_2 forms. Cooling from this temperature leads to producing a mixture of C_1 and C_2 forms, but now the C_2 form is the major component because in the crystallization process these crystals act as a nucleation agent to favorise the formation of C_2 form. This is reflected in the change of intensities for the transitions C_1-Col_{hd} and C_2-Col_{hd}. In this case, the sample at 65 °C is a mixture of Col_{hd} and C_2, in which C_2 is the major component. This is confirmed by X-ray diffraction experiments. A typical pattern for crystals was obtained at this temperature. At 80 °C, the sample shows only a Col_{hd} phase. Cooling from this temperature leads to having a mixture of C_1 and C_2, in which C_1 is again the major component,. It is probably due to the difference of easiness of the nucleation from the Col_{hd} phase.

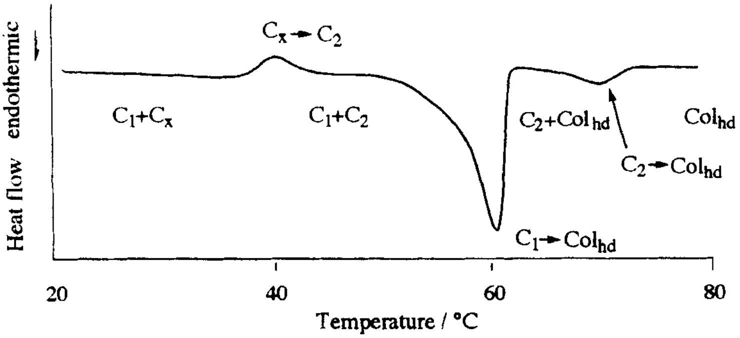

FIGURE 3 Interpretation of the DSC trace of **1** during the first heating run.

The microscopic observation of **1** revealed that it melts at 60 °C and the texture obtained changes slightly at 70 °C but no clear mesomorphic texture was observed. The texture formed spontaneously on cooling from the isotropic liquid was similar to that obtained for a mesophase of an analogous phthalocyaninatooxovanadium complex which was assigned to be Col_{hd} phase.[6] However, no change of texture was recognized at 70 °C and the crystallization was observed at 36 °C.

The X-ray diffraction pattern of **1** at 150 °C is shown in Figure 4. It is a typical one for a Col_{hd} phase: three peaks were observed in the small angle region with a spacing ratio of $1 : 1/\sqrt{3} : 1/2$, and a broad halo centered at $2\theta=20°$ (ca.4.6 Å) is observed in the wider angle region. whilst the pattern at 65 °C is similar to the one at 150 °C, but it exhibits additional small peaks at 21.5 Å, 6.2 Å, 4.6 Å, 4.2 Å and 3.9 Å, which were also present in the pattern of the crystal phase. These peaks are probably due to the presence of the C_2 crystalline form.

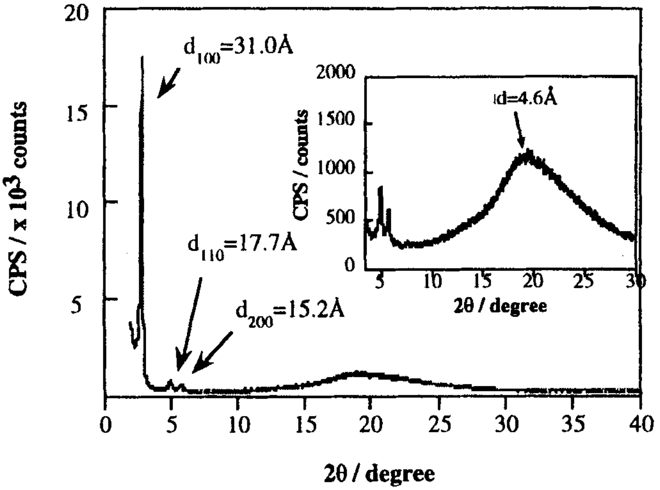

FIGURE 4 X-Ray diffraction powder pattern of **1** at 150 °C.

The temperature dependent FT-IR is also consistent with the existence of polymorphism in the solid state and the dependence of the transition temperatures with the thermal history of the sample. The vibration band at 1058 cm^{-1} is very sensitive to the phase transition, and shift from 1058 cm^{-1}, in the crystal phase, to 1071 cm^{-1}, in the Col_{hd} phase. Unfortunately, this vibration band could not be assigned yet. On the other hand, no evidence of a polymeric arrangement ($Ti=O \Rightarrow Ti=O \Rightarrow$) was observed. The frequency of the vibration band due to the Ti=O bond, 966 cm^{-1}, does not change with the increase of the temperature. This fact contrast with the vanadyl phthalocyanine analog, in which some evidences of the polymeric arrangement $V=O \Rightarrow V=O \Rightarrow$ was found to contribute to the stabilization of the Col_{hd}.[8]

CONCLUSION

The title compound exhibits a polymorphism in the solid state. At least four crystalline forms were deduced to exist according to the interpretation of the DSC traces. Additionally, a Col_{hd} phase in a broad temperature range was clearly determined. The total melting point of this material depend on its thermal history. It changes between 59 °C and 72 °C. No evidence of polymeric arrangement of the type (Ti=O⇒Ti=O⇒) was observed.

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