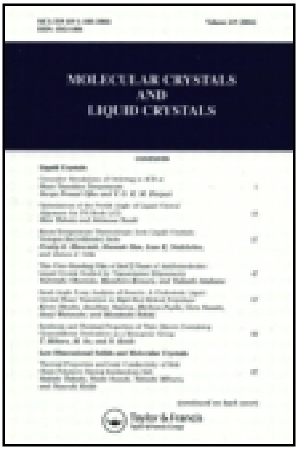

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Effect of Intermolecular Axial Interaction on Columnar Mesomorphism in Long-Chain Metallotetraphenylporphyrins

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Effect of Intermolecular Axial Interaction on Columnar Mesomorphism in Long-Chain Metallotetraphenylporphyrins

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The mesomorphic phase transition behavior of a series of long-chain metallotetraphenylporphyrin complexes (C12TPPM, M: Co, Ni, Cu, Zn, Pd, Pt, V=O, Al(OH), Mo=O(OH) and $Si(OH)_2$) were compared to reveal that the intermolecular interaction by the axial group significantly affects the columnar arrangement. Furthermore, it was indicated that the more rigid columnar backbone with a capability of free rotation of disc-shaped molecules leads to the formation of hexagonal and tetragonal arrays of columns.

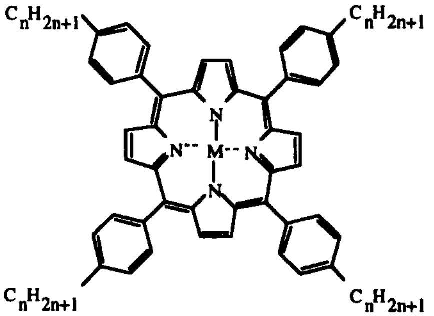
Keywords: metallomesogen; axial ligand; metallotetraphenylporphyrin; columnar mesophase

INTRODUCTION

Columnar mesophases formed by disc-shaped molecules of which structure has an extended π-electronic conjugation system have been paid some attention to new applications based on their potentials for electronic functionality[1]. In fact, recent studies of charged carrier migration for columnar mesophase have revealed a specific feature of an intermediate state of matter between crystalline solid and isotropic liquid. A fast carrier mobility (10^{-1} $m^2V^{-1}s^{-1}$) was reported for a plastic columnar mesophase of a hexaalkylthiotriphenylene against the fluctuations of molecules within a column[2]. High anisotropy of electronic conduction and the characteristic electric properties of columanr mesophase are owing to the columnar structure of molecular stacks[3] and therefore, it is quite interesting and important to control the state of columns in mesophase in order to obtain more efficient electronic properties as a function.

As it is an essence of columnar mesophase that disc-shaped molecules stack in the face-to-face manner, the interaction of disc-shaped molecules perpendicular to the molecular plane is most significant for the formation of columnar structure. In addition, it seems to be related to a manner of columnar arrangement. Some metallomesogen of disc-shaped molecules could provide a field where one can studies on the effect of face-to-face interaction on the mesomorphism for disc-shaped molecules with some modifications of the axial ligand.

Some long-chain metallotetraphenylporphyrins with a square planar geometry of the central metal ion have been so far studied on their mesomorphism to reveale that these are likely to show lamellar-type mesophases which have layered structures with disc-shape



n=12 : C12TPPM

M : 2H, Co, Ni, Cu, Zn, Pd, Pt
Al(OH), Si(OH)2, MoOCl

This work
M: MoO(OH), V=O

molecules[4]. In contrast, it was found that the corresponding Al-OH complex with a pyramidal geometry forms a hexagonal columnar mesophase[5]. 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[6]. In addition, it was also reported the corresponding Mo=O complex with an axial Cl atom also forms a lamellar mesophase[7].

In this work, Mo=O(OH) and V=O complexes of the same ligand, 5,10,15,20-Tetrakis(4-n-dodecylphenyl)porphyrin, were synthesized and investigated on the phase transition behavior to be compared with those of the metallotetraphenylporphyrin mesogens already reported. The former is characterized by hydrogen bonding interaction between Mo=O and OH, while the latter case is expected to show a dipolar interaction or a ligation of the oxygen atom to a vanadium ion in the neighbouring molecules. These intermolecular interactions are expected to have a potential for the contribution to columnar formation, which may lead to a different array of columns from the known mesogens of metallotetraphenylporphyrin.

EXPERIMENTAL

Synthesis of MoO(OH) complex, abreviated as C12TPPMoO(OH), were carried out by the method of Ledon *et al.* with some modifications[8]. The VO complex(C12TPPVO) was obtained according to a conventional procedure. The product analyses were performed by measurements of UV-visible and infrared absorption spectra(Shimadzu UV-visible spectrometer and Perkin Elmer Paragon 2000 infrared spectrophotometer, respectively) as well as elemental analysis. The investigation of mesomorphisms has been done using a polarizing microscopy (Olympus BH-2 equipped with Mettler FP80 hotstage and FP82 controller), DSC(TA Instument, 2920 MDSC) and X-ray diffraction(Rigaku Geiger Flex with a hand-made hotstage) apparatus.

RESULTS AND DISCUSSION

Phase transitions of C12TPPMoO(OH)

The DSC curves were shown in Fig.1 to reveal that this compound has a mesophase between –4 °C and 163 °C, supported by the microscopic observation. The XRD pattern of this phase (Fig.2) exhibit a broad halo centered around 4.5 Å and a weak but sharp reflection at 4.7 Å corresponding to the periodicity of face-to-face distance of molecules. Furthermore, four reflections appear in the small angle region and the spacings are in a ration of 1: 1/√2 : 1/2 : 1/3, indicating a columnar mesophase with tetragonal array.

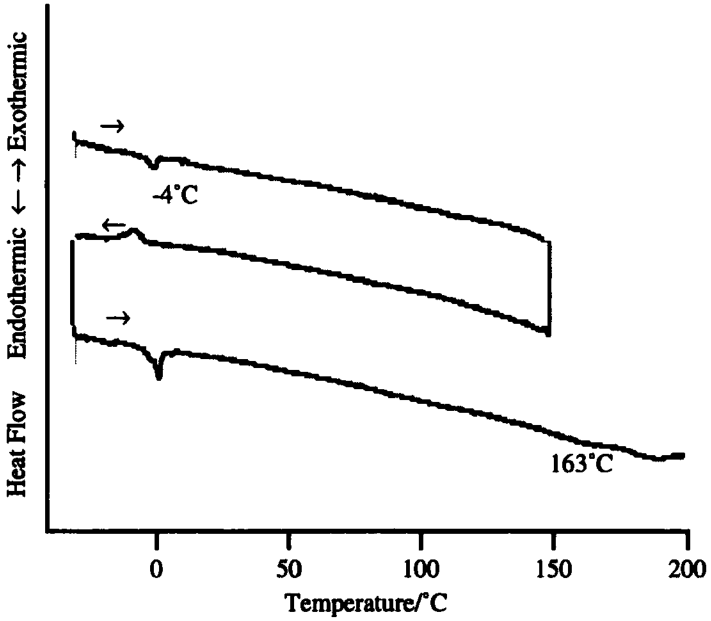


FIGURE 1 DSC traces of C12TPPMoO(OH). Heating and cooling rates: 5 °C min^{-1}.

Phase transitions of C12TPPVO

C12TPPVO shows the similar phase transition behavior to those of a series of metallotetraphenylporphyrin lamellar mesogens reported so far. The phase sequence is C 21 °C Mᴌᴄ 65 °C Mᴌ 153 °C Iso. The polarizing microscopic observation of textures revealed two mesophases are very viscous, but not brittle crystal. The XRD measurements indicate these two phases are in principle, classified to be lamellar mesophases (smectic-like layered ordering).

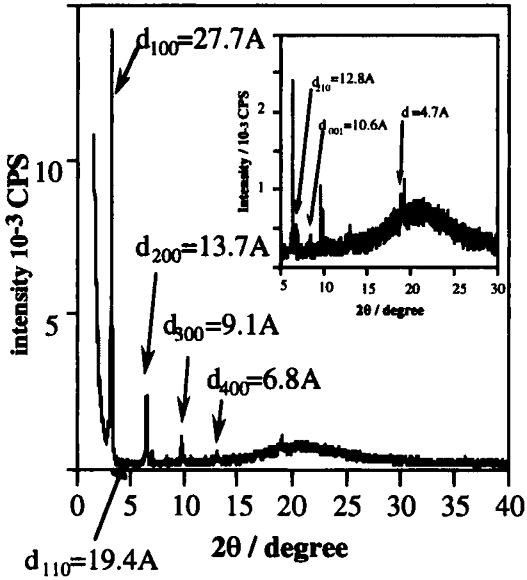


FIGURE 2 A XRD pattern of C12TPPMoO(OH) at 120 °C.

The phase transition behavior of the these metal complexes is summarized in Fig.3 with those of other complexes possessing axial groups.

Comparison of the phase transition behavior

According to the publication[4], a series of C12TPPM with a square planar geometry (Co, Ni, Cu, Zn, Pd and Pt) shows lamellar-type mesophases and this is probably related to the prevented free rotation of molecules around the columnar axis caused by the *meso*-phenyl groups.

In the case of $Si(OH)_2$ complex, the mesophase obtained is a lamellar one and infrared spectroscopic studies indicate that a hydrogen bonding interaction between the axial OH groups is very weak, meaning that the columnar backbone is not so rigid [9].

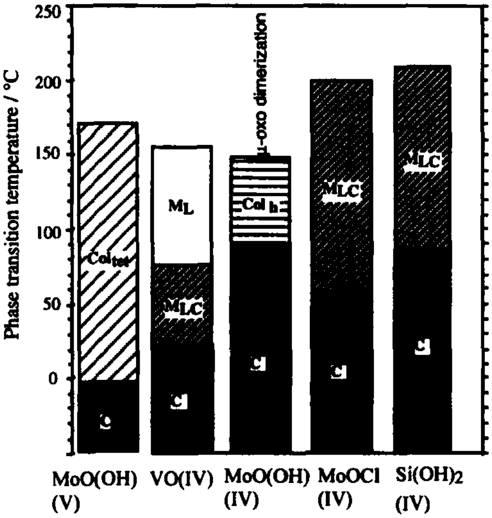


FIGURE 3 Comparison of the phase transition behavior for C12TPPM with axial groups.

However, the AlOH complex shows a typical columnar mesophase with a hexagonal arrangement of columns and the infrared studies implies that the formation of columnar structure is related to the property of Al^{3+} ion as a Lewis acid. In this case, it is proposed as the mechanism that the oxygen atom is likely to be an anion in the molten state which plays a role as a Lewis base for the formation of a polymeric system of -Al-O-Al-O- [10]. This interaction would lead to the stabilization of columnar structure.

As for the present work, infrared spectra of the VO complex was investigated to reveal the V=O-V=O interaction. It was reported that a strong V=O to V=O interaction leads to the remarkable lower shift (> 100 cm^{-1}) of the wavenumber of V=O stretching band[11]. The temperature dependence of V=O stretching band of C12TPPVO showed that the wavenumber shift is clearly very small and this means V=O-V=O interaction is very weak. This indicates the VO complex has the same situations for an interaction in the axial direction as those for C12TPPM to exhibit the similar phase transtions.

On the other hand, it is quite interesting that the MoO(OH) complex shows a columnar mesophase with tetra-gonal arrangement, while the corresponding MoO(Cl) complex has only a lamellar mesophase. Furthermore, the MoO(OH) complex shows a low melting point which may be due to some flexibility of the hydrogen bond linkages among porphyrin planes (Fig.4).

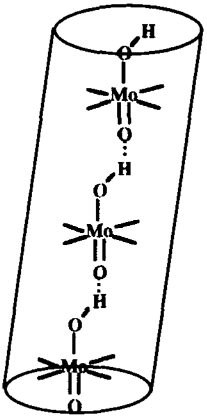


FIGURE 4 A schematic representation of a hydrogen bond system of MoO(OH) complex.

The observed values of face-to-face periodicity in XRD measureents for these complexes are *ca.* 5 Å, 4.7 Å, 4.5 Å, 4.37 Å and 4.9 Å for AlOH, MoO(OH), Si(OH)2, V=O and MoOCl, respectively. The molecular thickness of tetraphenyl-porphyrin core is estimated about 4.3 Å including the rotating phenyl groups. This may indicate that the columnar mesomorphism of metallotetraphenylporphyrins with four peripheral chains appears when the face-to-face distance within a column is larger than 4.6-4.7 Å. In other words, columnar mesomorphism requires free rotation around the axis. However, the MoOCl complex forms only a lamellar mesophase, though it has a large periodical distance (4.9 Å). The MoOCl complex does not have any groups for intermolecular specific interactions in the axial deirection. This may indicate some regidity of columnar backbone is required for stable columnar structure with hexagonal and tetragonal arrangements.

CONCLUSION

It is shown that metallomesogens are a quite useful tools for studies on relation of intermolecular interaction to columnar mesomorphism. A series of metallotetraphenylporphyrins with four peripheral chains were investigated on their mesomorphism to indicate that free rotation of disc-shaped molecules around the stacking axis should be allowed for columnar mesophase and a rigid backbone of a column is an important factor for a manner of column arrangement.

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