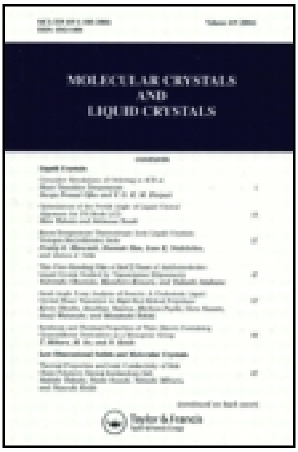

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Mesogenic Aluminum(III) Tetraphenylporphyrins: Effect of Monomer to Dimer Conversion on the Mesomorphic Properties

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MESOGENIC ALUMINUM(III) TETRAPHENYLPORPHYRINS: EFFECT OF MONOMER TO DIMER CONVERSION ON THE MESOMORPHIC PROPERTIES

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Abstract Hydroxoaluminum(III) complex of tetraphenylporphyrin with dodecyl chains at the *p*-site of the phenyl rings was found to show monomer to dimer conversion through the mesophase to isotropic phase transition, leading to drastic change of the phase transitiion sequence.

INTRODUCTION

Our recent studies on mesomorphic behaviour of metallotetraphenylporphyrins with square planar geometry(metal=Co, Ni, Cu, Zn, Pd, and Pt) revealed the mesophases appeared are of discotic lamellar(D_L) type, neither hexagonal nor rectangular.[1]

Metallomesogens potentially have a feature of controlling structure of molecular assemblies with intermolecular specific interaction derived from the presence of the metal atom in a molecular unit, and it could be designed. Molecular shape and such interactions are quite essential for forming

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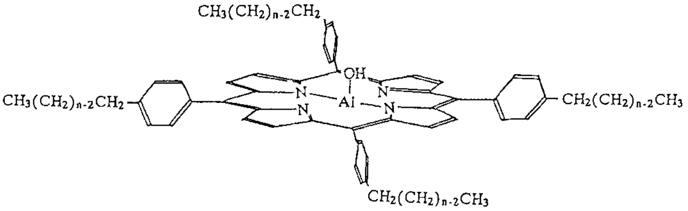
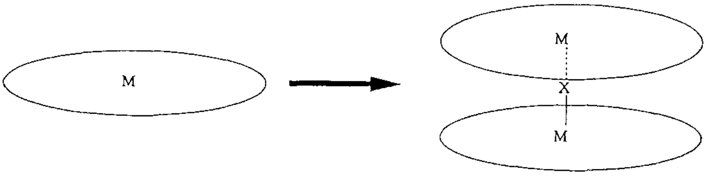
mesophases with some molecular arrangements related to *supramolecular chemistry*.

Recently it was found that the hydroxoaluminum(III) complex of the long-chain tetraphenylporphyrin, hydroxo[5,10,15,20-tetrakis(4-*n*-dodecylphenyl)porphinato]aluminum(III) abbreviated as C_{12}TPPAl(OH) shows discotic hexagonal disordered(D_{hd}) mesophase and the phase transition sequence is not enantiotropic, implying the occurrence of the μ-oxo dimerization in the fluid states.[2]

In this work, the μ-oxo dimer of C_{12}TPPAl(OH), μ-oxo-bis[5,10,15,20-tetrakis(4-*n*-dodecylphenyl)porphinatoaluminum(III)] abbreviated as $(C_{12}TPPAl)_2O$, was synthesized and investigated on the mesomorphic properties in relation to the monomer-to-dimer conversion.



CnTPPAl(OH) (n=12)



X: linkage group

EXPERIMENTAL

Synthesis

The μ-oxo dimer, $(C_{12}TPPAl)_2O$ was synthesized according to the literature[3] with slight modification. The monomer C_{12}TPPAl(OH) was heated at 190 °C for 6 hours under reduced pressure to give the dimer. Spectroscopic analyses were carried out to confirm the dimer structure. ν_{max}/cm^{-1}(KBr disc): 1043(AlOAl); $\delta_H(CDCl_3)$:0.92(t, 12H, CH_3), 1.3[m, 56H,

$(CH_2)_7]$, 1.57[m, 8H, $C_6H_4(CH_2)_3\underline{CH_2}]$, 1.65[m, 8H, $C_6H_4(CH_2)_2\underline{CH_2}]$, 2.00[m, 8H, $C_6H_4CH_2\underline{CH_2}]$, 2.98(t, 8H, $C_6H_4CH_2$), 7.36(d, 4H, the phenyl), 7.52(d, 8H, the phenyl), 7.84(d, 4H, the phenyl), 8.40(s, 8H, β of the pyrrole); Elemental analysis(%): Found C:83.88, H:9.33, N:4.36;Required C:83.65, H:9.46, N:4.24.

Measurements

The phase transitions were detected by Differentiall Scanning Calorimeter(Mac Science DSC3200) and the texture observation using polarizing microscope(Olympus, BH-2) equipped with a hot stage(Mettler FP80HT and FP82HT). X-Ray diffraction studies were carried out by Rigaku Geigerflex X-ray diffractometer(CuKα).

RESULTS AND DISCUSSION

The monomer crystal, $C_{12}TPPAl(OH)$, was found to exhibit discotic hexagonal mesophase(D_{hd})^2 and the phase transition sequence, however, is not of enantiotropic, as shown in Figure 1. When the original crystal is heated above the clearing temperature, slight bubbling was observed, indicating the occurrence of μ-oxo dimerization reaction. The μ-oxo dimer formation was confirmed by spectroscopic measurements, in which disappearance of the absorption band at 3654 cm^{-1} (OH stretching) and of the singlet signal of hydroxyl proton at -6.48 ppm for the IR and ^{1}H-NMR spectra, respectively, was seen.

$$2\,C_{12}TPPAl(OH) \longrightarrow (C_{12}TPPAl)_2O + H_2O$$

Figure 2 shows the phase transitions of the μ-oxo dimer, giving the coincidence of the phase transition sequence between the dimer and the monomer after isotropic melt. The phase transition temperatures for both the monomer and dimer are listed in Table I. The μ-oxo dimer exhibits three highly viscous states, though the monomer shows only one mesophase.

In X-ray diffraction measurements for the powder sample of $(C_{12}TPPAl)_2O$ as seen in Figure 3, four marked reflection peaks appeared in the lower angle region for the higher two mesophases *in temperature, of*

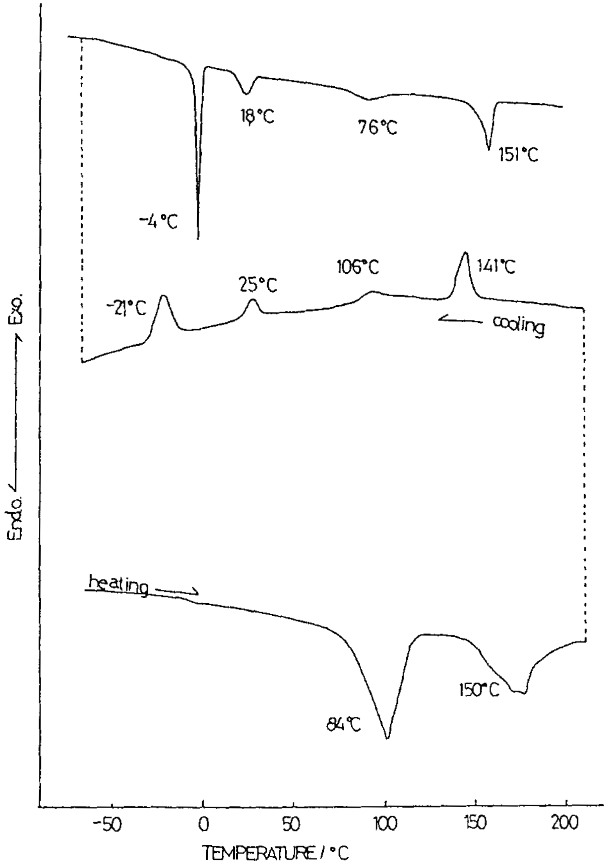


FIGURE 1 The DSC thermogram of the monomer, $C_{12}TPPAl(OH)$. Heating and cooling rate:5 °C/min.

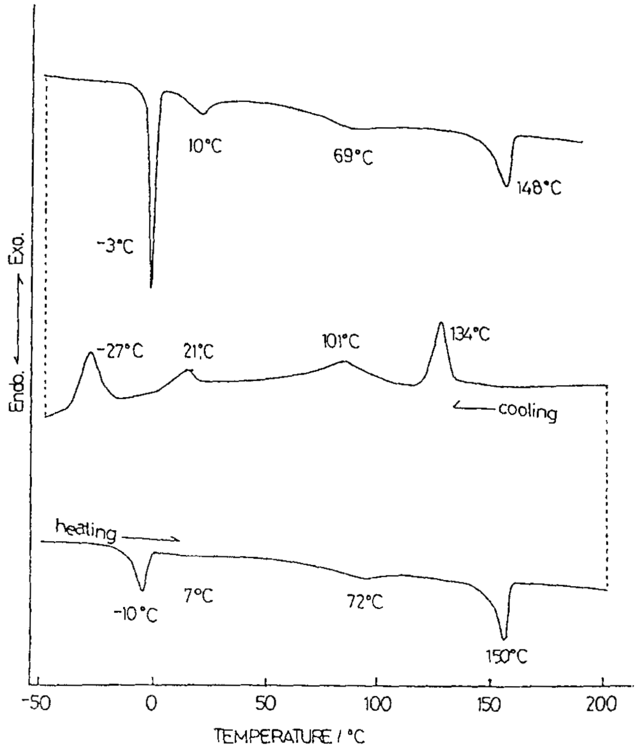


FIGURE 2 The DSC thermogram of the μ-oxo dimer, $(C_{12}TPPAl)_2O$. Heating and cooling rate:5 °C/min.

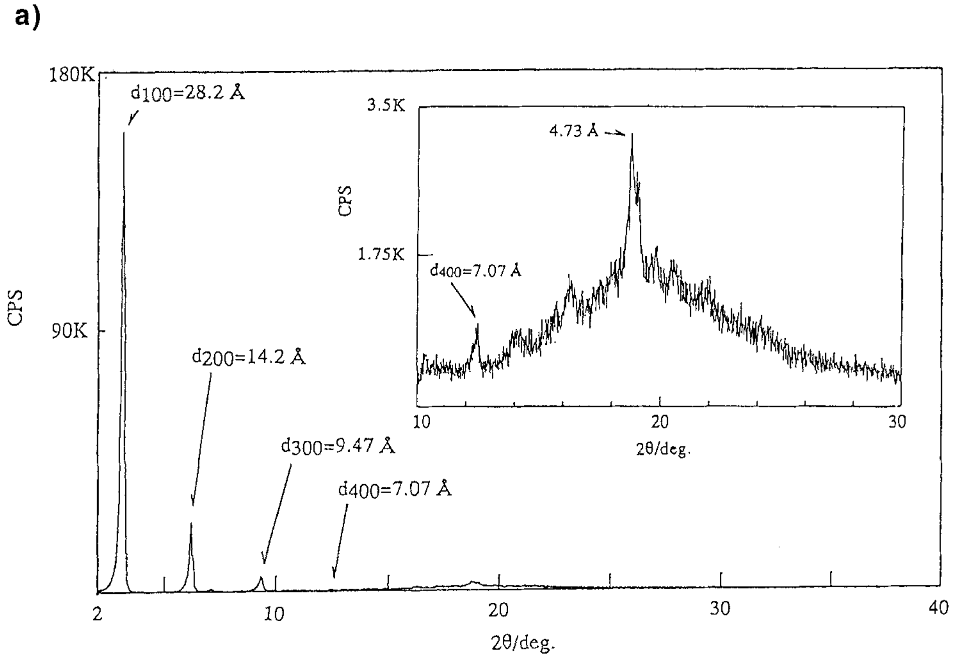
Table I Phase transition temperatures of C_{12}TPPAl(OH) and the dimer.1)

C_{12}TPPAl(OH)	Cryst.		D_{hd}		Iso.				
		84 °C		*ca.* 150 °C2)					
$(C_{12}TPPAl)_2O$	Cryst.		M(?)		D_{L1}		D_{L2}		Iso.
		-3 °C		10 °C		69 °C		148 °C	

1) Cryst.:crystal, M:mesophase, D_{L1} and D_{L2}:discotic lamellar phase, Iso.:isotropic liquid.
2) accompanied with conversion to the dimer.

which spacing ratio is 1:1/2:1/3:1/4, indicating that these mesophases have lamellar type ordering as usually seen in square planar tetraphenylporphyrin metallomesogens.[1] A peak located at *ca.*20 °(4.7Å) implies the columnar structure is present. This mesomorphism of the μ-oxo dimer is quite different from that of the monomer.

The layer spacings of these two mesophases are 28.2Å and 26.4Å. The side length of molecular square for C_{12}TPPAl(OH) is estimated to be *ca.*31Å. It indicates that the presence of molecular tilt or interdigitated chains in these D_L phases, whilst the another tetraphenylporphyrin metallomesogens with square planar geometry exhibit the comparable layer spacing of D_L phase to the molecular length. Assuming that, for the dimer, two molecular planes stack to each other with discrepancy of the position of the phenyl rings around the axis as seen for the same type of μ-oxo dimer of Fe(III) complex,[4] it could be seen as a quasi-octasubstituted discotic molecule, which is a more favourable molecular shape to formation of D_h phase. However, the dimer structure seems to be less favourable to molecular free rotation around the column axis, homogeneous continuity of molecular stacking along the columnar axis and column undulation, which are important factors for D_h phase formation. It is interesting that these two complexes seem to have quite different condition for the occurrence of mesomorphic nature from that for D_h mesophase of the oxo-bridged polymers of mesogenic metallophthalocyanines.[5]



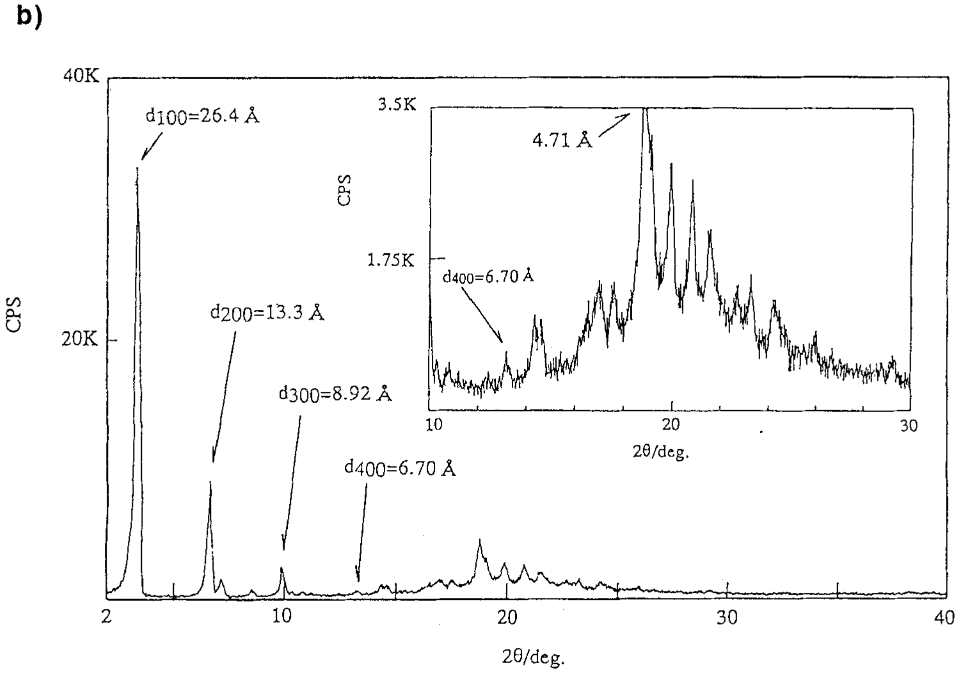


FIGURE 3 X-Ray diffraction patterns(powder) of $(C_{12}TPPAl)_2O$. a) at 130 °C and b) 50 °C.

CONCLUSION

In this work, comparison of mesomorphic behaviour was carried out between a hydroxoaluminum tetarphenylporphyrin mesogen and the μ-oxo dimer to reveal that the drastic change of the mesomorphic properties occurred.

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