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Liquid Crystals

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Online publication date: 19 May 2010

To cite this Article Sugino, Takushi , Santiago, Julio , Shimizu Corresponding author, Yo , Heinrich, Benoît and Guillon, Daniel(2004) 'Mesomorphic properties of a tetraphenylporphyrin metallomesogen with a weak hydrogen bond interaction between axial ligands: dihydroxo[5,10,15,20-tetrakis(4-*n*-dodecylphenyl)porphinato]silicon(IV)', *Liquid Crystals*, 31: 1, 101 – 108

To link to this Article: DOI: 10.1080/0267829032000159097

URL: <http://dx.doi.org/10.1080/0267829032000159097>

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Mesomorphic properties of a tetraphenylporphyrin metallomesogen with a weak hydrogen bond interaction between axial ligands: dihydroxo[5,10,15,20-tetrakis(4-*n*-dodecylphenyl)porphinato]silicon(IV)

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(Received 25 June 2003; accepted 17 August 2003)

A new metallomesogen, the dihydroxo[5,10,15,20-tetrakis(4-*n*-dodecylphenyl)porphinato]-silicon(IV) complex, C₁₂TPPSi(OH)₂, was synthesized and its mesomorphism was investigated in terms of the axial hydrogen bond interaction in the stacked columnar structure. It was found that this compound exhibits a 3D plastic lamellar mesophase with a columnar structure, and the axial hydroxyl groups are connected by a very weak hydrogen bond interaction in the column. This causes a dramatic increase of the clearing point for the mesophase, even though the stacking periodicity is far larger (*c.* 9 Å) than that typically found for a columnar mesophase (*c.* 3.5 Å).

1. Introduction

The empirical molecular structure–mesomorphism relationships established for columnar mesophases have been analysed in terms of symmetry along the axis perpendicular to the molecular plane, the length and type of peripheral chains and the linking group connecting the alkyl chain to the core. Asymmetry with respect to the columnar axis was found to show no definitive influence on the columnar mesomorphism and thermal stability. By contrast, it was clearly shown that the excluded volume of the peripheral chains and the linking groups is critical in determining the mesophase thermal stability, in a similar manner to calamitic systems. In recent studies of columnar mesophases obtained with discotic molecules, it was reported that lateral intermolecular interactions such as hydrogen bonding by the peripheral groups play an important role in the enhancement of columnar mesomorphism [1].

Extensive studies of metallomesogens consisting of disc-shaped molecules have been performed and some

new aspects of their mesomorphism were revealed [2]. The effect of the metal ions on the mesomorphism generally emerges as an enhancement of the mesomorphic thermal stability. Also the electronic properties of these materials are expected to depend largely on the type of metal ions incorporated and the molecular structure of the mesogen, which leads to a range of mesophase structures. The interest in metallomesogens for studies of structure–mesomorphism relationships is that specific intermolecular interactions arising from an axial ligand can be utilized, and the effect of these axial ligand interactions on the mesomorphism would be evaluated. In particular, this will be highly specific for columnar mesophases. Such a study would be very difficult in hydrocarbon-based discotic mesogens.

In recent years, we have systematically investigated the mesomorphic properties of metal complexes derived from 5,10,15,20-tetrakis(4-*n*-dodecylphenyl)porphyrins (C₁₂TPPM: M = Co, Ni, Cu, Zn, Pd and Al(OH)). It was shown that the long chain metallotetraphenylporphyrins with square planar geometry (M = Co, Ni, Cu, Zn and Pd) exhibit lamellar mesophases [3], while the

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hydroxoaluminum(III) complex shows a hexagonal columnar (Col_h) mesophase [4]. Furthermore, it was found that the complex is transformed to a μ -oxo dimer on heating at around the clearing temperature (*c.* 150°C) which shows a lamellar-type mesophase [5]. Additionally, the corresponding oxomolybdenum complex with a chlorine ion as an axial ligand was prepared and the mesomorphic phase transition behaviour was investigated. The molybdenum complex shows a lamellar plastic mesophase [6]. These results strongly suggest that the mesomorphism is strongly dependent on the specific interaction between the stacked disc-shaped molecules within a column via the axial ligands.

In addition, porphyrins and phthalocyanines are of great interest because of their electronic properties; some interesting phenomena have been observed in their photoconductivity in the mesophase structures, which are likely to change depending on the metal ion species [7–9]. In these cases, intra- and inter-columnar structures are essential for these properties.

Recently, dihydroxo[5,10,15,20-tetrakis(4-*n*-dodecylphenyl)porphyrinato]silicon(IV) ($\text{C}_{12}\text{TPPSi}(\text{OH})_2$, compound **1**), which has a silicon ion as a central metal with two hydroxyl groups as the axial ligand, was synthesized. Investigation of the mesomorphic behaviour revealed the existence of a highly ordered lamellar phase which has a wider temperature range than those of the metal complexes with square planar geometry [10].

In this article, the mesophase structure and hydrogen bonding interactions for a series of long chain tetraphenylporphyrins are discussed with the emphasis placed on the effect of axial interaction on the mesomorphism.

2. Experimental

2.1. Characterization

UV-visible spectra were recorded on a Shimadzu UV 2500PC absorption spectrometer. IR spectra were obtained, using KBr pellets, on a Perkin Elmer Peragon 1000 FTIR spectrometer equipped with a Linkam FTIR600 hot stage and LK600FTIR control unit. The phase transition temperatures and enthalpies were determined by differential scanning calorimetry (DSC) on a TA instrument modulated DSC (MDSC 2920). The heating and cooling rates were 5°C min⁻¹. Microscopy was performed with an Olympus polarizing microscope equipped with a Mettler FP 82HT heating stage and FP 80HT control unit. X-ray diffraction (XRD) measurements were carried out at several temperatures using a linear monochromatic $\text{Cu-}\alpha_1$ beam obtained with a sealed tube generator and a bent quartz monochromator together with a curved counter Inel CPS 120. For this set-up, the temperatures of samples were controlled within $\pm 0.05^\circ\text{C}$ [11].

2.2. Synthesis

All solvents were purified and dried by standard procedures and stored under argon before use [12]. $\text{C}_{12}\text{TPPH}_2$ was prepared by a slight modification of established procedures [13]. SiCl_4 (Wako Pure Chemical Industries, Ltd.) was used without further purification. Purification of the products was carried out by column chromatography using neutral Al_2O_3 (activity I, Merck).

The dihydroxosilicon(IV) complex **1** was prepared following a method described in the literature [14] (see the scheme). To a cooled mixture (10–20°C) of 0.78 g (0.6 mmol) of $\text{C}_{12}\text{TPPH}_2$ and 30 ml of dry pyridine, 6 ml (48 mmol) of SiCl_4 was added under argon flow. The glass tube containing the mixture was sealed *in vacuo* (*c.* 10 mm Hg), and heated at 180°C for 2 days. After cooling to r.t., 30 ml of MeOH was added and the mixture was filtered. The solvent was evaporated and the resulting residue purified by column chromatography: neutral Al_2O_3 and CH_2Cl_2 then $\text{CH}_2\text{Cl}_2/\text{AcOEt}$ (100/1 to 10/1) as eluent. Recrystallization from hexane gave **1** as a red-violet powder (0.40 g, 48%). ¹H NMR (500 MHz, CDCl_3): δ –6.81 (s, 2H, OH), 0.88 (t, 12H, CH_3), 1.29 (m, 56H, $\text{CH}_3(\text{CH}_2)_7$). 1.44 (m, 8H, $\text{C}_6\text{H}_4\text{-CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 1.52 (m, 8H, $\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CH}_2$), 1.87 (m, 8H, $\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2$), 2.89 (t, 8H, $\text{C}_6\text{H}_4\text{CH}_2$), 7.50 (d, 8H, *meta* Phenyl-H), 7.99 (d, 8H, *ortho* Phenyl-H), 8.90 (s, 8H, β pyrrole-H). UV-vis (CH_2Cl_2) λ_{max} (ϵ_{max} , mol⁻¹ dm³ cm⁻¹): 593 (10 100), 555 (20 800), 423 (529 400), 312 (20 800) nm. IR (KBr): 3628 (O–H), 2923, 2853, 1009, 852 (Si–O) cm⁻¹. Anal: calcd for $\text{C}_{92}\text{H}_{126}\text{N}_4\text{O}_2\text{Si}$, C 81.97, H 9.42, N 4.16; found, C 81.67, H 9.72, N 4.15%.

3. Results and discussion

The DSC thermogram of **1** is shown in figure 1 and two peaks are seen on heating and cooling. The microscopy observation of textures revealed that **1** exhibits only one enantiotropic mesophase, the viscosity of which is rather high and similar to a soft solid. The phase transitions at 84 and at 211°C correspond to the melting of the brittle solid and to the isotropization, respectively. The temperature range of the mesophase is reasonably large (127°C). The phase transition temperatures, enthalpies and entropies are summarized in table 1. No chemical transformations or decomposition were detected. In addition, the μ -oxo polymerization reported for a mesogenic phthalocyanine silicon complex [15] did not occur in this work.

The XRD pattern for the mesophase indicates the existence of a layered structure and of a partially molten state of the peripheral alkyl chains as shown in figure 2. The *d*-spacings corresponding to the former reflections are in the ratio 1:1/2:1/3, indicating a layered structure (layer thickness of about 35 Å) [16]. The latter

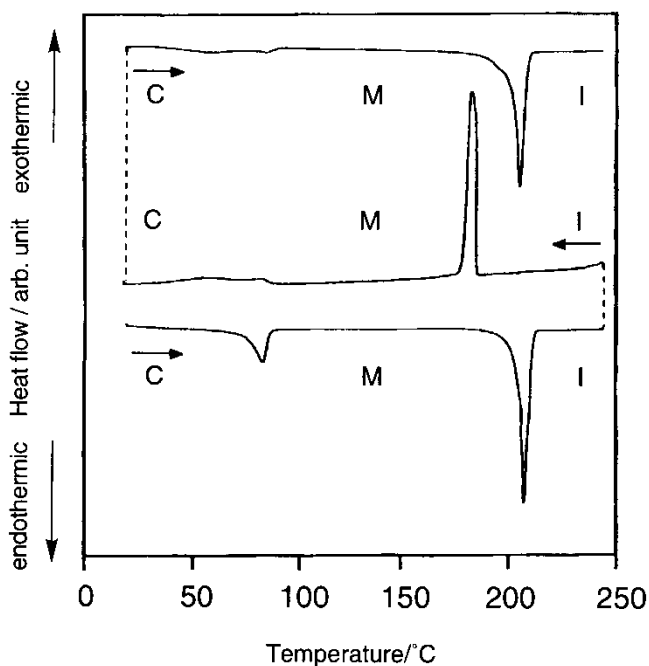
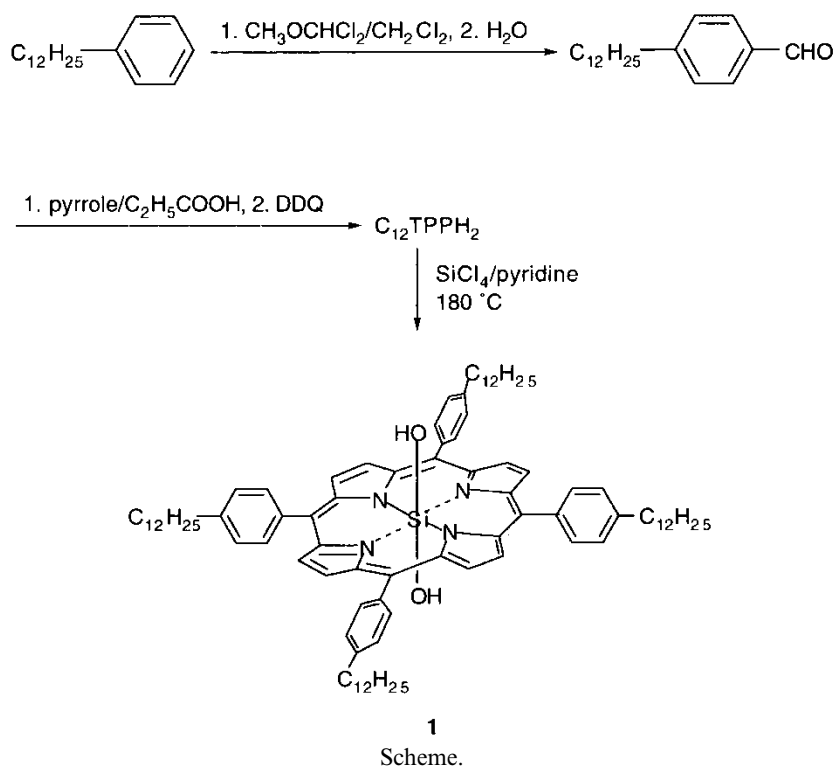


Figure 1. DSC thermogram of **1**. Heating and cooling rates are $5^\circ\text{C}/\text{min}$. C=crystal phase, M=mesophase, I= isotropic phase.

reflection corresponds to a d -spacing of about 4.3 \AA . However, the width of this diffuse peak is rather narrow, indicating a partially molten state of the aliphatic

Table 1. The phase transition temperatures, enthalpies and entropies of compound **1**.

Transition	$T/^\circ\text{C}$	$\Delta H/\text{kJ mol}^{-1}$	$\Delta S/\text{J K}^{-1} \text{ mol}^{-1}$
C-M	84	11	30
M-I	211	36	75

chains. These results are in agreement with the texture observed by microscopy, which revealed a rather viscous phase. This is also compatible with the observation of reflections in the wide angle region. The list of reflections observed is shown in table 2 along with their indices.

This set of assignments shows that the mesophase can be considered as a 3D plastic mesophase with a tetragonal lattice (lattice constant: $a=b=34.8 \text{ \AA}$, $c=9.03 \text{ \AA}$), in which the molecular planes are arranged face-to-face (figure 3).

A reflection is also observed at 9.03 \AA , indicating that the molecules stack to form a columnar structure with a periodicity larger than expected and normally observed one for a typical disc-shaped mesogen with a π -conjugated system [17]. For example, the face-to-face distance between porphyrin planes is inferred to be 4.50 \AA . The observed value of 9.03 \AA is twice of 4.50 \AA , indicating a long range ordered stacking of pairs of molecules. It is well known that tetraphenylporphyrin is not a planar molecule due to the steric hindrance

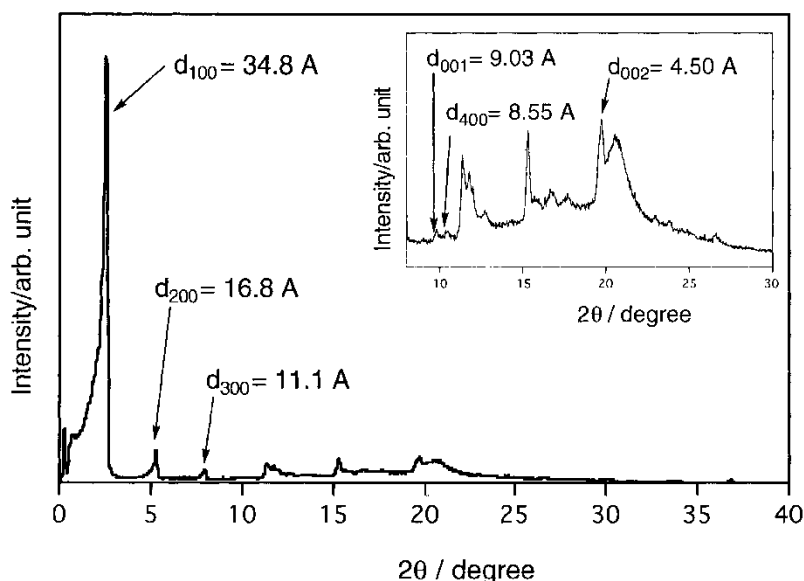


Figure 2. X-ray diffraction pattern of **1** at 150°C (in the mesophase).

Table 2. *d*-Spacings determined by X-ray diffraction experiments for complex **1** on the first heating run at 150°C.

$\theta_{\text{obs}}/^\circ$	$d_{\text{obs}}/\text{\AA}$	<i>hkl</i>	$d_{\text{calcd}}/\text{\AA}$
1.269vs	34.8	100	34.8
2.634s	16.8	200	37.4
3.982s	11.1	300/130	11.6/11.0
4.895	9.03	001	9.03
5.171	8.54	400/111	8.70/8.48
5.698s	7.76	240/121	7.78/7.81
5.897s	7.50		
6.006	7.36	221	7.28
6.360	6.95	311/340	6.98/6.96
7.657s	5.78	350	5.83
7.869	5.63	600	5.80
8.319	5.32	260	5.50
8.865	5.00	700	4.97
9.861s	4.50	002/102	4.52/4.48
10.27br, s	4.32	molten alkyl 212/202	4.34/4.37
11.50	3.86	422/480	3.91/3.89
11.92	3.73	390/900	3.67/3.87
13.33	3.34	210/642	3.41/3.30

Tetragonal: $1/d^2 = (h^2 + k^2)/a^2 + l^2/c^2$, $a = b = 34.8 \text{ \AA}$, $c = 9.03 \text{ \AA}$.

between the phenyl protons and pyrrole protons which results in a conformation in which the phenyl ring is perpendicular to the central porphyrin plane being the most stable [18]. In a fluid state such as a mesophase, the phenyl ring is thought to be able to rotate or fluctuate in a flip-flop manner around the bond connected with the porphyrin moiety, given it takes place in solution [19]. Considering the general Si–O bond length (1.5–1.7 Å) [20], and a recent report by Aida *et al.* [21] that the OH groups of unsubstituted tetraphenylporphyrin silicon (IV) complex are attached

perpendicularly to the porphyrin plane in the solid state, the distance 4.5 Å seems to be quite reasonable for the face-to-face stacking periodicity. In this context, the free rotational motion of phenyl rings could be suppressed due to the shorter distance of the periodicity than the required space for free rotation (*c.* 2.5 Å).

On the other hand, it is well known that phthalocyanine molecules are likely to stack in a staggered conformation when they form a columnar structure in a crystalline solid [22], and this trend is also seen for columnar mesophases in which a dimeric stacking periodicity can be deduced from the XRD pattern [23]. These considerations could lead to an explanation for the observation of the reflection corresponding to a dimeric pair of molecular stacks by **1** (figure 4). In fact, the observed value for d_{100} (34.8 Å at 150°C) is significantly larger than the estimated molecular diameter, *c.* 31 Å for the molecular model with fully extended chains and this supports a staggered stacking arrangement.

Comparing the mesomorphic behaviour of **1** with that of the analogous tetraphenylporphyrin and its metal complexes reported to date, the behaviour of **1** is quite different from those of the corresponding metal-free and metal complexes with a square planar geometry which show two types of layered mesophase. Also very different mesomorphism is seen for the corresponding hydroxoaluminum complex which shows a hexagonal columnar mesophase [4]. However, the mesophase seen for **1** may be similar to the low temperature lamellar mesophase exhibited by those analogues [3]. The thermal stability of the low temperature lamellar phase

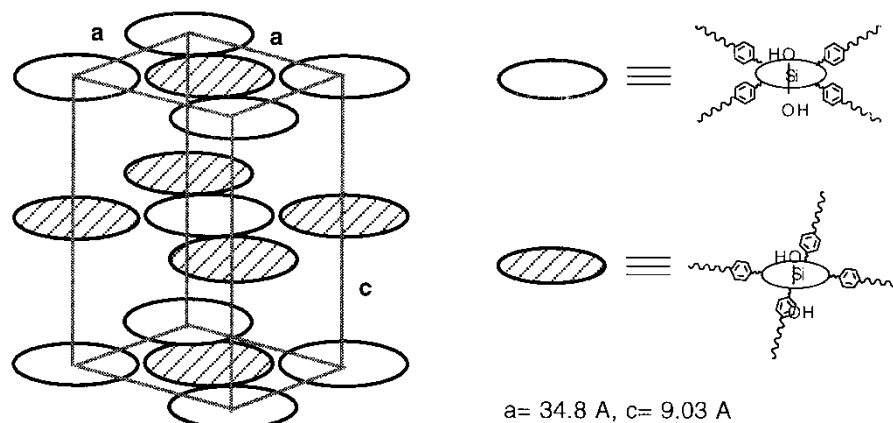


Figure 3. A schematic illustration of the lattice of the 3D plastic mesophase of **1**.

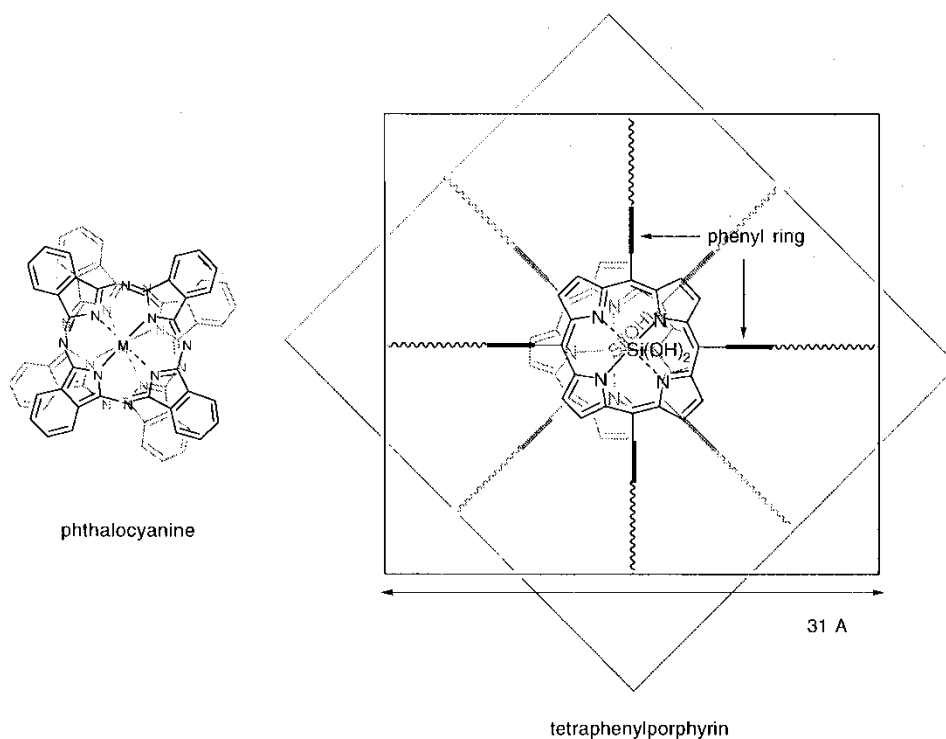


Figure 4. Comparison of the staggered conformations for phthalocyanine and tetraphenylporphyrin.

shows a dramatic increase for **1** when compared with the results for these other compounds for which the temperature range of the low temperature lamellar phase has a maximum of 30°C (the Pd complex) as shown in table 3.

This view of the molecular stacking in the columnar structure formed by **1** implies intermolecular interactions between the molecules along the columnar axis which is related to the hydroxyl groups attached on both sides of the porphyrin plane. Figure 5 shows a schematic illustration of the molecular stacks in a

column in which an intermolecular hydrogen bond interaction acts as a linkage between two porphyrin planes. The temperature dependence of the IR spectra was measured to investigate such an interaction. When the hydroxyl groups interact in a hydrogen bond, the bands associated with the Si–O and O–H stretching vibrations are modified according to the strength of interaction. Figure 6 shows the temperature dependence of the band maxima for the O–H and Si–O bands. The O–H and Si–O stretching bands of **1** were observed at 3627 and 850 cm⁻¹, respectively, at room temperature.

Table 3. Phase transition temperatures, enthalpies and entropies of metal complexes of 5,10,15,20-tetrakis(4-*n*-dodecylphenyl)porphyrin.

Metal ion	Transitions	$T/^\circ\text{C}$	$\Delta H/\text{kJ mol}^{-1}$	$\Delta S/\text{JK}^{-1}\text{mol}^{-1}$	Ref.
Co	C-M _L	28	39	132	[3]
	M _L -D _L	50	13	39	
	D _L -I	161	30	69	
Ni	C-D _L	44	51	162	[3]
	D _L -I	129	22	56	
Cu	C-M _L	32	51	170	[3]
	M _L -D _L	56	14	44	
	D _L -I	188	32	70	
Zn	C-M _L	37	85	276	[3]
	M _L -D _L	52	5.4	17	
	D _L -I	220 ^a	—	—	
Pd	C-M _L	30	42	137	[3]
	M _L -D _L	60	13	39	
	D _L -I	186	29	63	
Si(OH) ₂	C-M _L	84	11	30	
	M _L -I	211	36	75	
Al(OH)	C-Col _{hd}	84	74		[4]
	Col _{hd} -I	>150 ^b	—	—	
Al-O-Al	C-M _L	69			[5]
	M _L -I	148			

^aWith decomposition.

^bWith μ -oxo dimerization.

These wavenumbers are almost the same as that observed for another dihydroxosilicon(IV) porphyrin complex [24].

The O–H stretching band gradually shifted to higher wavenumbers with increasing temperature. However, the shift is very small, indicating that the hydrogen bond interaction is weak. Two stepwise changes in the position of the band maxima were observed at the phase transition between crystal and mesophase and between mesophase and the isotropic phase. For example, the O–H stretching band was shifted to 3631 cm^{-1} at 150°C , and jumped to 3677 cm^{-1} at the isotropization temperature. This means that the weak hydrogen bond interaction is released in stepwise fashion at these phase transitions because of the increased internal fluctuations on heating.

In contrast, the wavenumber of the Si–O stretching band (851 cm^{-1} at room temperature) decreased with temperature (848 cm^{-1} at 150°C) and shifted suddenly to a smaller wavenumber (832 cm^{-1}) at around the isotropization temperature. These results imply that the hydrogen bond interaction between molecules in a column via two axial OH groups was largely unchanged in the crystal and the mesophase but was remarkably weakened at the transition to the isotropic phase.

Figure 7 shows the temperature dependence of the XRD spacings d_{100} and d_{002} of **1**. These interlayer and

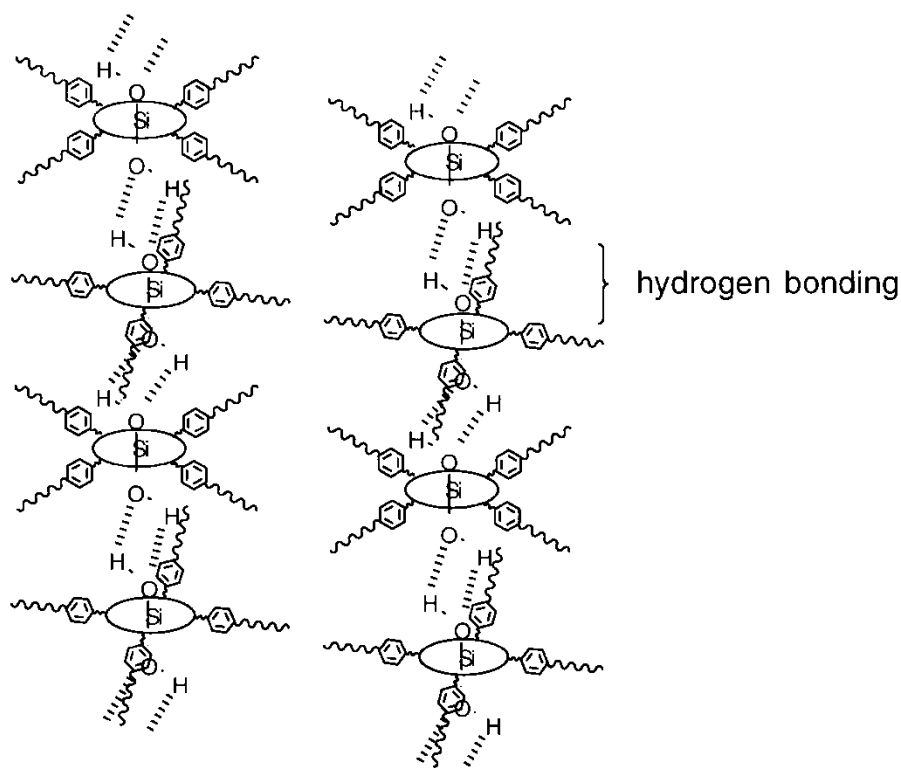


Figure 5. A schematic illustration of a possible stacking of molecules within a column of the mesophase.

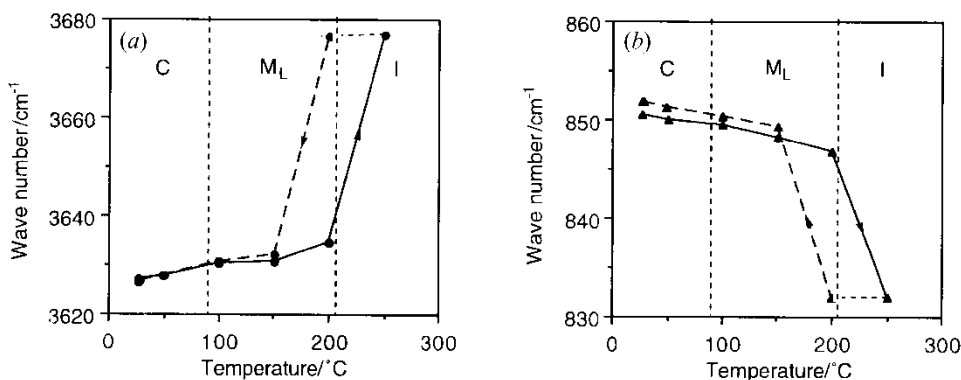


Figure 6. Temperature dependence of the infrared vibrational band maxima for (a) O–H and (b) Si–O stretching modes in **1**.

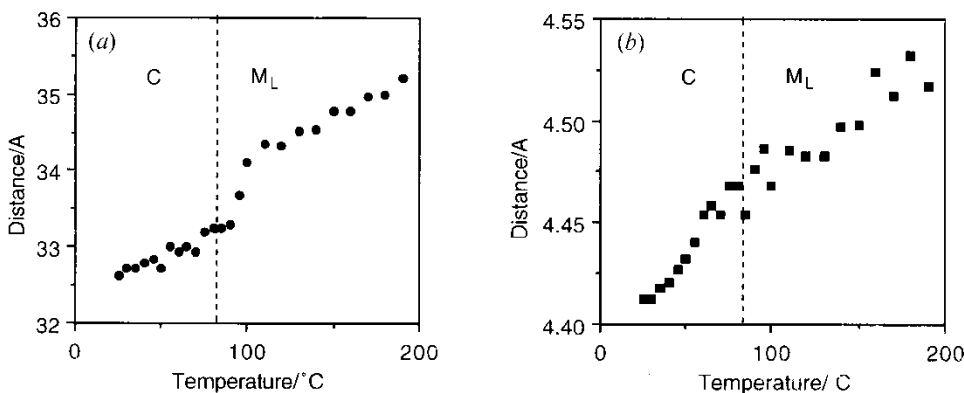


Figure 7. Temperature dependence of (a) d_{100} and (b) d_{002} for **1**.

intracolumnar stacking distances increase with temperature and, in particular, both d -values increase in a stepwise fashion at the phase transition corresponding to crystal melting. Interestingly, the temperature dependence of the intracolumnar stacking distance is the same as that of the two infrared bands shown in figure 6. The interaction is strong in the crystalline solid and becomes weaker at the first melting at 84°C. The enhanced molecular dynamic properties in the mesophase could provide a wider space for the mesogenic molecules to fluctuate more freely and this is also suggested by the temperature dependence of d_{100} , for which a stepwise increase of the lattice constant a at the phase transition from the crystalline solid to mesophase is observed.

Therefore, it can be clearly seen that the intermolecular hydrogen bonding interaction in **1** plays an important role in stabilizing the stacking structure along the columnar axis, resulting in a wider temperature range of the 3D plastic mesophase with a tetragonal lattice formed by columns of the dihydroxosilicon complex.

4. Conclusion

We have investigated the phase transition behaviour of a dihydroxosilicon(IV) complex **1** of a long chain tetraphenylporphyrin, and the effect of the hydrogen bond interaction along the columnar axis on the mesomorphism. This complex shows only a 3D plastic mesophase with a tetragonal lattice of columns in which pairs of staggered molecules stack. The temperature range of the mesophase is larger than 100°C and isotropization occurs at 211°C. Comparison with the phase transition behaviour of the corresponding metal-free tetraphenylporphyrin and its metal complexes having a square planer geometry. ($M = H_2, Co, Ni, Cu, Zn$ and Pd) shows that **1** has the highest thermal stability. IR studies show that the intermolecular hydrogen bond interaction between the axial hydroxyl groups, along the columnar axis is related to the mesomorphism, and leads to the stabilization of the columnar structure. The mesomorphic behaviour is completely different from that of the corresponding hydroxoaluminum(III) complex possessing an axial OH ligand, which shows a hexagonal columnar mesophase.

The authors thank the Ministry of Economy, Trade and Industry (METI) for financial support based on the national R&D project 'Molecular Harmonized Materials' operated in the Industrial Science and Technology Frontier Programme. J.S. acknowledges the Science and Technology Agency (STA) for providing STA fellowship. The French-Japanese International Program of Scientific Collaboration. PICS No.1434 is gratefully acknowledged.

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