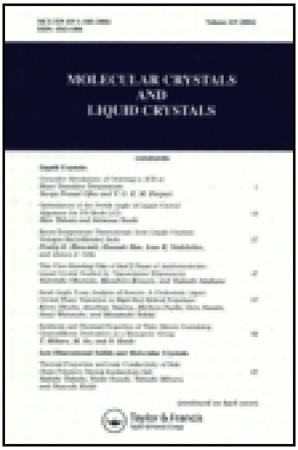

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Mesomorphic Properties of Porphyrin Silicon(IV) Metal Complexes

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Mesomorphic Properties of Porphyrin Silicon(IV) Metal Complexes

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We have introduced a silicon metal in 5, 10, 15, 20-tetrakis(4-*n*-dodecylphenyl)porphyrin core to have the complexes possessing two axial ligands ($C_{12}TPPSi(X)_2$, X=OH (**1**) or OCH_3 (**2**)) in terms of highly conducting liquid crystalline materials. The mesomorphic properties were investigated by differential scanning calorimetry (DSC), optical microscopy, and X-ray diffraction technique.

Keywords: metallomesogens; porphyrin silicon(IV) metal complexes; photoconductivity

INTRODUCTION

Metallomesogens derived from porphyrins and phthalocyanines have

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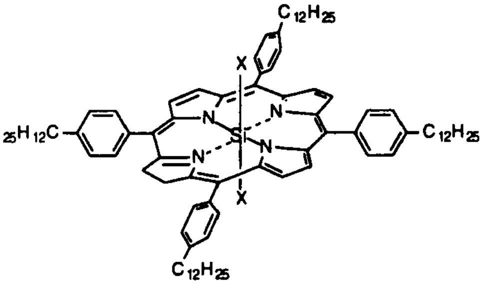
been received much attention from viewpoints of the electronic properties and the potential for supramolecular assemblies[1]. Furthermore, if the metal allows the introduction of strong covalent bond between the flat porphyrin rings, the chemical and electrical properties of these materials are modified[2]. Suitable axial ligands on the metal lead to making polymers. In this case, we obtain the so-called *spinal columnar liquid crystal*[3]. The design and synthesis of such polymers have been stimulated by its promising applications as a new electronic materials. However, most of the early studies in this field of chemistry were devoted to the solid state for both the phthalocyanine[4] and porphyrin[5] derivatives. These compounds demonstrated some interesting semiconducting properties as in a case of the unsubstituted $\{[PcSiO]I_x\}_n$ in Kevlar fibers[6]. As for porphyrin derivatives, mesogenic porphyrins were reported for disc-like octasubstituted porphyrins[7] and rod-like disubstituted porphyrins[8].

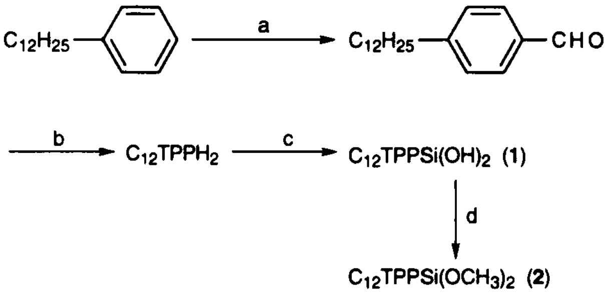
In this work, we report the syntheses and mesomorphic properties of a dihydroxo(dodecyltetraphenylporphinato)silicon(IV) **1** and the corresponding dimethoxosilicon(IV) derivative **2**, abbreviated as $C_{12}TPPSi(X)_2$ with X=OH and OCH_3, respectively. Additionally these are the first porphyrin silicon(IV) metallomesogens. Studies of the mesomorphic behaviour of these porphyrin complexes will allow a better understanding of the influence of the axial groups on the thermal behaviour, which has been recently demonstrated for a hydroxoaluminium complex of tetraphenylporphyrin[9].



X= OH (**1**), OCH_3 (**2**)

EXPERIMENTAL

Synthesis



Scheme 1. Synthesis of porphyrin silicon complexes **1** and **2**: (a) $TiCl_4$, $CH_3OCHCl_2/CH_2Cl_2/H_2O$, 50%; (b) pyrrole/$CH_3CH_2COOH$/DDQ, 20%; (c) $SiCl_4$/pyridine, 180 °C, 2 days/MeOH, 48 %; (d) MeOH/CH_2Cl_2/reflux, 5 h, 86%.

$C_{12}TPPSi(OH)_2$ (1).

The dihydroxosilicon complex **1** was prepared by modification of a published procedure[10]. ^1H-NMR (500 MHz, $CDCl_3$): δ -6.81 (s, 2H, O*H*), 0.88 (t, 12H, 4xCH_3), 1.29 (m, 56H, 4x$CH_3(CH_2)_7$), 1.44 (m, 8H, 4x$C_6H_4CH_2CH_2CH_2CH_2$), 1.52 (m, 8H, 4x$C_6H_4CH_2CH_2CH_2$), 1.87 (m, 8H, 4x$C_6H_4CH_2CH_2$), 2.89 (t, 8H, 4x$C_6H_4CH_2$), 7.50 (d, 8H, meta meso *Ph*), 7.99 (d, 8H, ortho *Ph*), 8.90 (s, 8H, β pyrrol-*H*). IR (KBr) : 3628 cm^{-1}(O-H). Anal. calcd for $C_{92}H_{126}N_4O_2Si$: C, 81.97; H, 9.42; N, 4.16. Found: C, 81.67; H, 9.72; N, 4.15.

$C_{12}TPPSi(OCH_3)_2$ (2).

A mixture of **1** and MeOH was refluxed for 5 h to give **2** as a violet oily mass at room temperature. This compound is very moisture-sensitive. ^1H-NMR(500 MHz, $CDCl_3$): δ -2.45 (s, 6H, 2xCH_3), 0.87 (t, 12H, 4xCH_3), 1.28 (m, 56H, 4x$CH_3(CH_2)_7$), 1.42 (m, 8H, 4x$C_6H_4CH_2CH_2CH_2CH_2$), 1.50 (m, 8H, 4x$C_6H_4CH_2CH_2CH_2$), 1.84 (m, 8H, $C_6H_4CH_2CH_2$), 2.87 (t, 8H, 4x$C_6H_4CH_2$), 7.47 (d, 8H, meta meso *Ph*), 7.93 (d, 8H, ortho *Ph*), 8.86 (s, 8H, β pyrrol-*H*). Anal. calcd for $C_{94}H_{130}N_4O_2Si$: C, 82.04; H, 9.52; N, 4.07. Found: C, 81.99; H, 9.50; N 3.85.

Measurements

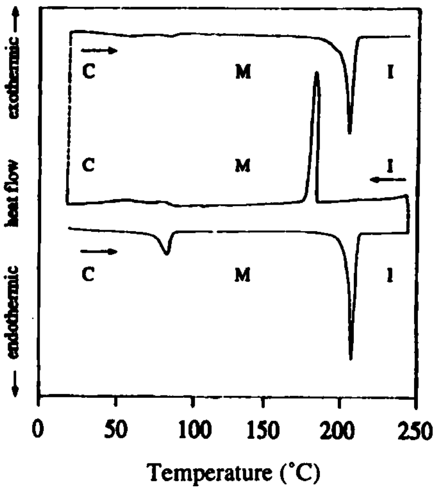
^{1}H-NMR spectra were recorded on a JEOL JNM-Alpha-500 spectrometer using Me_4Si as an internal standard. IR spectra were obtained for KBr pellets by a Perkin Elmer Pergon 1000 FT-IR spectrometer. The phase transition temperatures and enthalpies were determined by differential scanning calorimetry (DSC) using a TA instruments modulated DSC (DSC 2920). Microscopic studies were performed with an Olympus polarizing microscope equipped with a Mettler FP 82HT heating stage and FP 80HT control unit. X-ray diffraction (in Lindemann capillary) measurements were carried out according to the technique described elsewhere[11].

Photoconductivities were measured as a closed circuit current for a symmetrical sandwich-type cell (ITO/C_{12}TPPSi(OH)$_2$/ITO) with 33 μm thickness of C_{12}TPPSi(OH)$_2$ film and the photocurrent was detected by an electrometer. A sample was injected into the cell space (33 μm thickness with a polyimide film) by capillarity. The cell was placed on a temperature controllable stage in a cryostat under Ar atmosphere.

RESULTS AND DISCUSSION

DSC measurements

In order to establish the phase transition behaviour of compound **1**, DSC measurement was performed. The DSC thermogram of **1** is shown in Figure 1 and the phase transition temperatures, enthalpies and entropies are listed in Table 1. In both heating and cooling processes, **1** showed an enantiotropic property with two endo- or exothermic phase transitions. Only one mesophase with a wide range of temperature was observed between 84 and 211 °C.



C: Crystal phase, M: Mesophase, I: Isotropic phase

Figure 1. DSC thermogram of $C_{12}TPPSi(OH)_2$. heating and cooling rate: 5 °C/min

Table 1. Phase transition temperatures T (°C), enthalpies ΔH ($kJmol^{-1}$), and entropies ΔS ($JK^{-1}mol^{-1}$) of **1**.

compound	transitions	T (°C)	ΔH ($kJmol^{-1}$)	ΔS ($JK^{-1}mol^{-1}$)
$C_{12}TPPSi(OH)_2$	C–M	84	10.8	30.2
	M–I	211	36.4	75.2

X-ray measurements

X-ray measurements were done to identify the mesophase of complex (**1**). The ratio of d spacings corresponding to four reflection peaks in the small angle region is 1 : 1/2 : 1/3 : 1/4, which indicates the mesophase has lamellar type ordering (smectic type of ordering) (Figure 2) and this order is conserved in the solid state at room temperature on the cooling process. A typical smectic type of ordering texture was appeared in a polarizing microscope. This type of molecular ordering is also observed in the corresponding ligand and its metal complexes (Co, Ni, Cu, Zn, Pd, V=O, and Mo(=O)Cl) [12, 13]. Additionally a broad halo around 2θ= 20 ° was seen, indicating that this phase should be mesomorphic. However, a few sharp reflections were also detected in the wide angle region which can result from the existence of a columnar structure in the smectic layer.

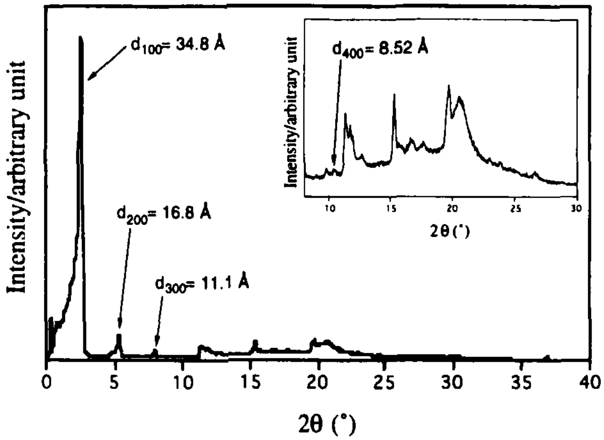


Figure 2. X-ray dffraction patterns of C_{12}TPPSi(OH)$_2$ at 150 °C.

Photoconductive property

The phtoconductive property of complex **1** was also investigated for the crystal in an ITO/C_{12}TPPSi(OH)$_2$/ITO cell. Applied field dependence of the photocurrent (positive electrode illumination) and darkcurrent is shown in Figure 3. An ohmic contact was obtained for the darkcurrent in the field strength up to 8000 Vcm^{-1}. The photocurrent was larger than darkcurrent by almost one order of magnitude. The photocurrent behaviour of complex **1** is completely different from that of a metal free porphyrin (C_{15}TPPH$_2$)[14]. A photocurrent rectification observed in C_{15}TPPH$_2$ was not recognized for **1**. This result indicates that the mechanism of carrier generation of **1** is dominated by an intrinsic process.

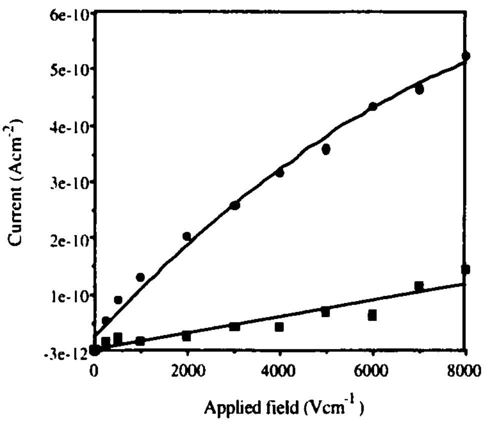


Figure 3. Applied field deppendence of photocurrent (●) and darkcurrent (■) of **1** in an ITO/C_{12}TPPSi(OH)$_2$/ITO cell for the crystal (30 °C) under 620 nm light illumination with an intensity of 0.409 mWcm^{-2}.

CONCLUSION

We have synthesized the first porphyrin silicon mesogen **1** and **2** and investigated the mesomorphic and phtoconductive properties in the solid state of **1**. Complex **2** is highly hygroscopic and it was so difficult to determine the mesomorphic behaviour. Complex **1** exhibits a lamellar type of mesophase in a temperature range from 84 to 211°C. This mesophase would be a phase with 3D ordering because of the presence of a few sharp reflection peaks obtained in the wide angle region (ca. $2\theta = 20$ °) in addition to the diffuse scattering from the molten chains in X-ray diffraction studies and the phase transition enthalpy ($\Delta H = 10.8$ kJmol^{-1}) from the crystal phase to mesophase is smaller than those of analogous metal porphyrins showing lamellar types of mesophase[12]. The photoconductivity was observed for an ITO/C_{12}TPPSi(OH)$_2$ [crystal]/ITO cell.

References

[1] *Metallomesogens*, edited by José Luis Serrano (VCH, Weinheim; New York: Basel; Cambridge; Tokyo, 1996).

[2] (a) T.J. Marks, *Science*, **227**, 881 (1985). (b) T.J. Marks, *Angew. Chem. Int. Ed. Engl.*, **29**, 857 (1990).

[3] (a) C. Sirlin, L. Bosio and J. Simon, *J. Chem. Soc., Chem. Commun.*, 379 (1987). (b) C. Sirlin, L. Bosio and J. Simon, *J.* Chem. *Soc., Chem. Commun.*, 236 (1988). (c) M. Hanack, A. Beck and H. Lehmann, *Synthesis*, 703 (1987).

[4] (a) M. Hanack, K. Mitula, G. Pawlowski and L.R. Subranamian, *J. Organomet. Chem.*, **204,** 315 (1981). (b) I.W. Shim and W.M. Risen, *J. Organomet. Chem.*, **260,** 171 (1984).

[5] M. Ikonen, D. Guez, V. Marvaud and D. Markovitsi, *Chem. Phys. Letters,* **231,** 93 (1994).

[6] T. Inabe, J.W. Kyding and T.J. Marks, *J. Chem. Soc., Chem. Commun.,* 1084 (1983).

[7] (a) B.A. Gregg, M.A. Fox, and A.J. Bard, *J. Chem. Soc. Chem. Commun.*, 1134 (1987). (b) B.A. Gregg, M.A. Fox, and A.J. Bard, *J. Am. Chem., Soc.*, **111,** 3024 (1989).

[8] (a) Q.M. Wang, and D.W. Bruce, *Chem. Commun.*, 2505 (1996). (b) Q.M. Wang, and D.W. Bruce, *Angew. Chem. Int. Ed. Engl.*, **36,** 150, (1997).

[9] Y. Shimizu, J. Matsuno, M. Miya and A. Nagata, *J. Chem. Soc., Chem. Commun.*, 2411 (1994).

[10] J.W. Buchler, L. Puppe, K. Rohbock and H.H. Schneehage, *Chem. Ber.*, 2710 (1973).

[11] B. Heinrich, K. Praefcke and D. Guillon, *J. Mater. Chem.*, **7,** 1368 (1997).

[12] Y. Shimizu, M. Miya, A. Nagata, K. Ohta, I. Yamamoto and S. Kusabayashi, *Liq. Cryst.*, **14,** 795 (1993).

[13] A. Nagata, Y. Shimizu, H. Nagamoto and M. Miya, *Inorg. Chim. Acta,* **238,** 169 (1995).

[14] Yo. Shimizu, A. Ishikawa, S. Kusabayashi, M. Miya and A. Nagata, *J. Chem. Soc., Chem. Commun.*, 656 (1993).