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Synthesis, structural and conformational analysis and chemical properties of phthalocyaninatometal complexes

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Abstract

Syntheses of the phthalocyaninatometal complexes were performed and the crystal and molecular structures were determined by single-crystal X-ray diffraction analysis. The general formulas of these Pc dye compounds are $-[Si(Pc)OSiR^1_2R^2SiR^1_2O]_n-$ and $Si(Pc)(OSiR^1R^2R^3)_2$: $-[Si(Pc)OSi(CH_3)_2(CH_2)_7Si(CH_3)_2O]_n-$ (**1**), $Si(Pc)[OSi(C_6H_{13})_3]_2$ (**2**) $Si(Pc)[OSiC_8H_{17}(CH_3)_2]_2$ (**3**) and $Si(Pc)[OSiCH_3C_{12}H_{25}CH_3]_2$ (**4**). These Pc dye derivatives were prepared by refluxing a mixture of $Si(Pc)(OH)_2$ and $SiR^1R^2R^3Cl$ in pyridine, followed by cooling the mixture slowly and then drying the resulting precipitates. For **1**–**3**, the Pc skeleton and the oxo-bridged substituentes are coplanar. The dihedral angle between the mean planes of the Pc skeleton and two single-atom Si_{me} [Si_{me}–O–Si_{pc}–O–Si_{me}] is nearly at right angles. The Si_{pc}–O bonds are shorter than the Si_{pc}–N bonds and the Si_{me}–O bonds are shorter than the Si_{pc}–O bonds. For **1**, the Pc microcyclic rings are related by a center of symmetry at the center of the O_1–Si_1–O_2 bonds. The chemical formula of a mononer is $C_{43}H_{42}N_8O_2Si_3$ ($C_{25}H_{28}N_5O_2Si_3$ in crystallographic symmetry) and the polymer is built up by the addition polymerization of the monomers. The polymer chain is constructed at the siloxy group along the a axis. Two hexyl groups of two siloxy side groups for **2** have the same direction, but one hexyl extends in the opposite direction. For **3**, two methyl groups and one octyl group extend in the opposite direction. We applied Pc dyes **2**–**4**, mixed with a polymer for the control of the aggregation state to CD-R and DVD-R recording systems. The aggregation state of the recording layer is controlled by choosing the set of axial substituents R^1–R^3. The interactions of Pc dyes with polymers are dependant upon the length of axial substituents. We achieved the best writing contrast and the highest stability with the mixed PC dye **4**. The conformation of axial substituents is very important for the ability of the dye aggregation and the capability to control the aggregation state. © 1998 Elsevier Science B.V.

Keywords: Crystal structures; Optical disk; Polymers; Phthalocyaninatometal complexes

1. Introduction

Since phthalocyanine (Pc) was synthesized in 1907 [1], it has been used widely in ballpoint pen ink, coloring for metal surfaces and plastics, chemical sensors, electronic display devices, medical applications and optical computer read/write devices. There are two Pc structures: metal-free phthalocyanines (without metals) and metal phthalocyanine complexes. The latter is classified into single atom bridged dimers and phthalocyaninatometal complexes. The general

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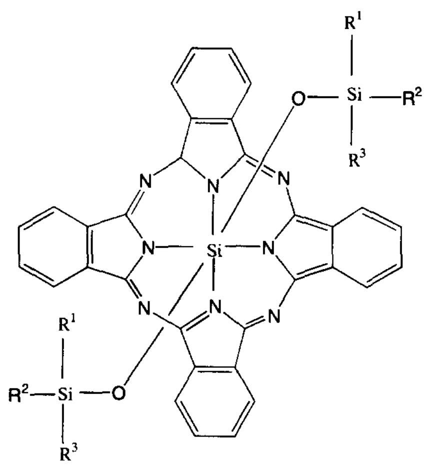


	1	**2**	**3**	**4**
R^1 =	CH_3	C_6H_{13}	CH_3	CH_3
R^2 =	$-(CH_2)_7-$	C_6H_{13}	C_8H_{17}	$C_{12}H_{25}$
R^3 =	CH_3	C_6H_{13}	CH_3	CH_3

Scheme 1. Phthalocyanine (Pc) dye derivatives.

formulas of the single atom bridged dimers are $[M(Pc)]_2X$ or $M(Pc)X_2$, where M is a metal (Si, Sn, Fe, Co, Mn, Zn) and X is a light atom (O, N, C). The general formulas of the phthalocyaninatometal complexes are $-[M(Pc)X]_n-$ for polymeric bridged phthalocyaninatometal complexes and $M(Pc)X_2$ for phthalocyaninatometal isocyanide complexes. The X is a functional ligand such as O, $OSiR^1R^2R^3$, OCOR and so on.

The Pc dye compounds (Scheme 1) are especially used for computer optical mass storage. The development of the optical disk using organic dye films for recording layers has been carried out. Extensive studies have already been developed for some write-once type optical disks [2] and reported for a few re-writable disks [3]. The recording mechanisms of these optical disks are based on a photo-thermal process that induces an ablation or an expansion of the recording layer by laser irradiation.

In this paper, we describe synthesis of the phthalocyaninatometal dye complexes. Detailed stereochemical studies by X-ray diffraction and a thermal-motion analysis were undertaken. Furthermore, we applied these Pc dye derivatives to optical disks. Our interest focused on the stereochemistry and the refractivity of these compounds on CR-R and DVD-R recording systems.

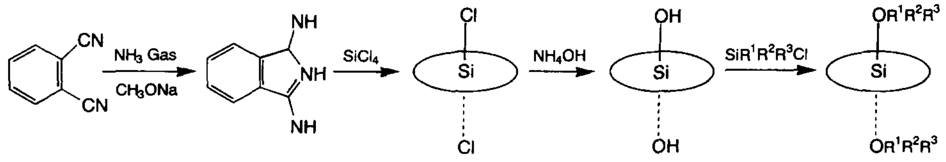
2. Experimental

2.1. Synthesis

Four Pc dye derivatives are synthesized as shown in Scheme 2. *n*-Butyldimethylchlorosilane, tri-*n*-hexylchlorosilane and *n*-octyldimethylchlorosilane were obtained from the Shin-Etsu Chemical Co. Ltd. *o*-Phthalonitrile, silicon tetrachloride and other chemicals were obtained from the Kanto Chemical Industry Co. Ltd. These were of reagent grade and were used without further purification. Pyridine was distilled from BaO, $CHCl_3$ and CH_2Cl_2, benzene and methanol under nitrogen.

2.1.1. Synthesis of 1,3-di-iminoisoindoline

1,3-Di-iminoisoindoline was prepared from *o*-phthalonitrile by a modification of the Kenney group [4–7]. Dry NH_3 was slowly bubbled through a stirred mixture of *o*-phthalonitrile (25 g) and CH_3ONa (5.1 g) and dry methanol (306 mL) for 1 h. With continued NH_3 introduction, the mixture was refluxed for 3 h. After the resultant had cooled, the product was collected by filtration, washed and air dried (25.5 g, 90%): IR (KBr) 3285, 3200, 3080, 1700, 1640, 1545, 1520 cm^{-1} NMR [300 MHz, $(CD_3)_2SO$] δ8.31 (s, 1,4-H), 8.08 (m, 5,8-H), 7.68 (m, 6,7-H). From batch to batch, the product ranged



Scheme 2. Synthesis of Pc Derivatives **1**, **2**, **3** and **4**.

Table 1
Crystal data, experimental conditions and refinement details

	1	**2**	**3**
Chemical formula	$C_{43}H_{42}N_8O_2Si_3$	$C_{68}H_{94}N_8O_2Si_3$	$C_{52}H_{62}N_8O_2Si_3$
Formula weight	787.12	1139.80	915.37
Melting point (°C)	242.6–246.1	169.0–172.3	171.8–176.0
Crystal system	Orthorhombic	Triclinic	Triclinic
Space group	*Pbcm*	$P\bar{1}$	$P\bar{1}$
Z	8	2	2
a (Å)	9.704(2)	10.062(7)	9.758(1)
b (Å)	20.042(2)	12.419(4)	9.974(2)
c (Å)	21.491(4)	13.788(6)	13.562(1)
α (°)		92.86(3)	78.85(1)
β (°)		107.29(4)	73.69(1)
γ (°)		94.75(4)	78.88(1)
V (Å^3)	4179.5(12)	1634.4(15)	1229.4(2)
D_o (g cm^{-3})	1.253(10)	1.154(2)	1.234(2)
D_x (g cm^{-3})	1.251	1.158	1.236
Diffractometer	Mac MXC3	Mac MXC3	Mac MXC3
Radiation	Cu Kα	Cu Kα	Cu Kα
λ (Å)	1.54178	1.54178	1.54178
μ(Cu Kα) (cm^{-1})	14.07	10.30	12.58
F(000)	1656	616	488
Color of crystal	Blue	Blue	Blue
Shape of crystal	Plate	Plate	Plate
Crystal dimensions (mm^3)	0.03 × 0.23 × 0.33	0.03 × 0.25 × 0.38	0.03 × 0.13 × 0.43
Laue group	*mmm*	$\bar{1}$	$\bar{1}$
Number and range of 2θ for cell parameters	$20(57 < 2\theta < 60)$	$20(42 < 2\theta < 60)$	$18(54 < 2\theta < 60)$
T (K)	295	295	295
$2\theta_{\max}$ (°)	55	55	55
Range of h, k and l	$-11 \leq h \leq 0; 0 \leq k \leq 23; 0 \leq l \leq 25$	$-11 \leq h \leq 0; -14 \leq k \leq 14; -15 \leq l \leq 16$	$-10 \leq h \leq 0; -11 \leq k \leq 11; -15 \leq l \leq 14$
Scan technique	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
Scan width (°)	$1.46 + 0.20 \tan \theta$	$2.39 + 0.20 \tan \theta$	$1.21 + 0.20 \tan \theta$
Sacn rate (°) (θ) min^{-1}	8	8	8
Number of unique reflections	3593	5362	3858
Number of observed reflections	2018 $[I > \sigma(I)]$	4373 $[I > \sigma(I)]$	3622 $[I > \sigma(I)]$
Number of parameters refined	404	1103	831
R	0.066	0.066	0.047
ωR	0.089	0.091	0.062
S	0.36(1)	0.284(4)	0.183(3)
$(\Delta/\sigma)_{\max}$	0.26	0.29	0.28
$\Delta\rho/e$ (Å^{-3})	−0.09, 0.23	−0.06, 0.19	−0.18, 0.15

from yellow to green in color. It failed to purify by recrystallization and sublimation. The product is sufficiently pure for use as a phthalocyanine precursor.

2.1.2. Synthesis of Si(Pc)Cl_2

(Phthalocyaninato)silicon dichloride was prepared by a modification of the Kenney group [5]. A mixture of 1,3-di-iminoisoindoline (4.3 g), silicon tetrachloride (5.4 ml), dry tetrahydronaphthalene (40 ml) and dry tri-*n*-butylamine (20 ml) was refluxed for 3 h. The resultant was allowed to cool and then methanol (30 mL) was added. The product was filtered off, washed and air dried (4.1 g, 90%): IR (KBr) 475 (m, Si–Cl) cm^{-1}. The product was quite impure, containing as much as 30%–50% impurities. It was dark green and had a very low solubility in a variety of

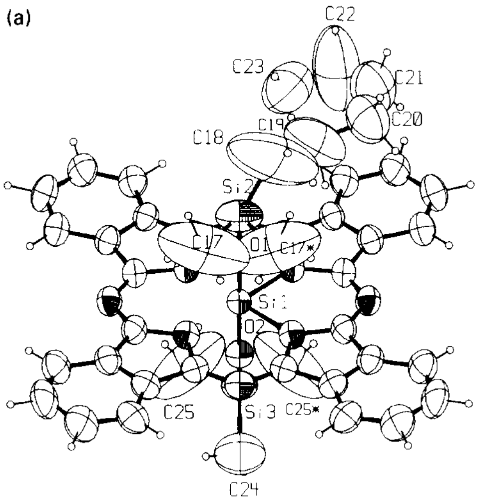


Fig. 1. ORTEP drawing [11, 32]. (a) Looking down the *b* axis for **1**; (b) looking down the *b* axis for **2**; (c) looking down the *b* axis for **3**. Octant-shaded ellipsoids are chlorine, oxygen and nitrogen atoms. Thermal ellipsoids of the C, O and Cl atoms are drawn at 50% probability level. H atoms are shown with arbitrary radii.

organic solvents; it had little volatility. Attempts made to purify it failed.

2.1.3. Synthesis of Si(Pc)(OH)$_2$

(Phthalocyaninato)silicon dihydroxide was prepared via the route of Davidson and Wynne [8]. A mixture of Si(Pc)Cl$_2$ and concentrated H_2SO_4 (150 ml) was stirred for 2 h and then poured over ice. The solid was filtered off and washed with water and an acetone–water solution. A mixture of this solid (4.4 g) and concentrated NH_4OH (150 ml) was refluxed for 1 h and allowed to cool. The resulting solid was filtered off and vacuum dried. Part of it was extracted with pyridine in a Soxhlet extractor, washed and vacuum dried (2.05 g, 49.5%). A mixture of water (5 ml), 1,2-dimethoxyethane (50 ml) and concentrated HCl (0.05 ml) was refluxed for 5 h. The resulting suspension was allowed to cool and the solid was collected by filtration, washed and vaccum dried (25 mg, 50%): IR (KBr) 3435 (O–H), 840 (Si–O) cm^{-1}. The compound was green. It was only slightly soluble in a variety of organic solvents.

2.1.4. Synthesis of Si(Pc)(OR)$_2$

A synthetic procedure similar to that described by the Kenney group [6,7,24] was followed. Each mixture of Si(Pc)(OH)$_2$ (0.75 g), *n*-butyldimethylchlorosilane (5 ml) for poly{[1,7-(*n*-butyl)bis(dimethylsiloxy)]silicon-phthalocyanine} (**1**), tri-*n*-hexylchlorosilane (5 ml) for bis(trihexylsiloxy)silicon–phthalocyanine (**2**), *n*-octyldimethylchlorosilane (5 ml) for bis(*n*-octyldimethylsiloxy)silicon–phthalocyanine (**3**), *n*-dodecanedimethylchlorosilane (5 ml) for bis(*n*-dodecanedimethylsiloxy)silicon–phthalocyanine (**4**) and dry pyridine (75 ml) was refluxed for 5 h. After the solution obtained was allowed to cool, it was filtered (no residue) and concentrated under vacuum. The resulting oil was mixed with pentane (10 ml) and the slurry formed was filtered. The solid was washed with pentane (10 ml) and an acetone–water solution and vacuum dried. To recover additional products, the pentane filtrates were combined, concentrated and filtered. The solid was washed, vacuum dried (0.21 g for **1**, 0.48 g for **2** and 0.31 g for **3**). For **1**, m.p. 242.6–246.1°C. IR (KBr) 1251w (Si–CH$_2$), 1040s (Si–O–Si) cm^{-1}. Anal. found: C, 65.66; H, 5.60; N, 13.55; O, 3.55. Calcd. for $C_{43}H_{42}N_8O_2Si_3$: C, 65.62; H, 5.38; N14.24; O, 4.07, Si, 10.71%. For **2**, m.p. 169.0–172.3°C. IR (KBr) 1247w (Si–CH$_2$), 1056s (Si–O–Si) cm^{-1}. Anal. found: C, 71.24; H, 8.08; N, 9.63; O, 2.80. Calcd. for $C_{68}H_{94}N_8O_2Si_3$: C, 71.66; H, 8.31; N, 9.83; O, 2.81, Si, 7.39%. For **3**, m.p. 171.8–176.0°C. IR (KBr) 1251w (Si–CH$_2$), 1062s (Si–O–Si) cm^{-1}. Anal. found: C, 67.85; H, 5.96; N, 12.40; O, 3.49. Calcd. for $C_{52}H_{62}N_8O_2Si_3$: C, 68.23; H, 6.83; N, 12.24 O, 3.50, Si, 9.20%.

2.2. Materials

Crystals of $C_{43}H_{42}N_8O_2Si_3$ ($C_{25}H_{28}N_5O_2Si_3$ in crystallographically) (**1**), $C_{68}H_{94}N_8O_2Si_3$ (**2**) and $C_{52}H_{62}N_8O_2Si_3$ (**3**) were recrystallized as blue plates from a chloroform solution by slow evaporation. The crystal data and experimental details are summarized in Table 1. Cell parameters of **1** were obtained by least-squares refinement of the setting angles for 20 reflections by the LQPARM3 program [9,10]. Three standard reflections were monitored every 100 reflections and showed little variation. No decay corrections were performed.

2.3. Structure analysis and refinement

The structures of **1**, **2** and **3** were solved by the

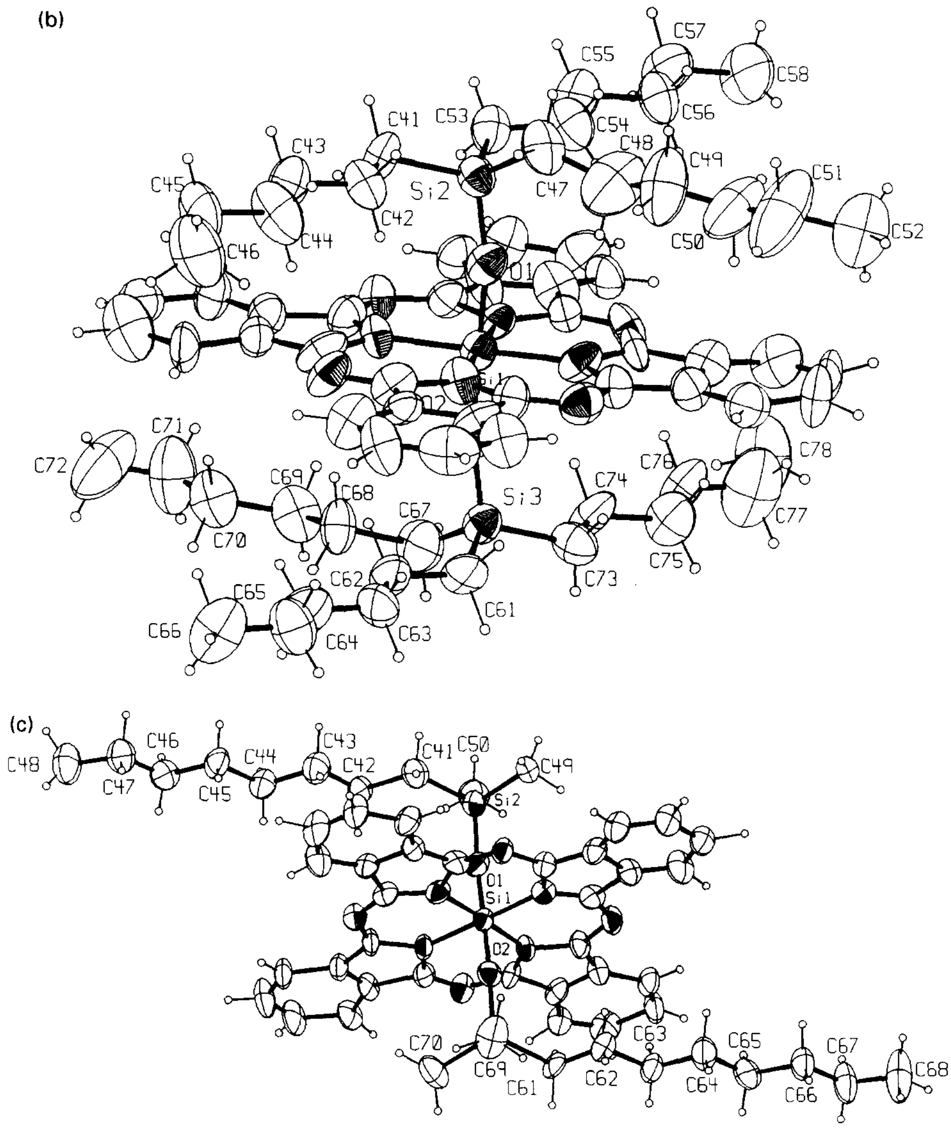


Fig. 1. (*continued.*)

application of direct methods. The DIRECTER3 program [11,12] yielded the positions for 28/35, 55/68 and 65/65 nonhydrogen atoms, respectively. The other atoms were obtained from the SEARCHER3 program [12,13]. Eight atoms of **1** were located on the special position ($z=1/4$), then these coordinates z and the coefficients β_{13} and β_{23} were fixed for least-squares. The approximate coordinates were refined by full-matrix least-squares to minimized $\Sigma w[|F_o(\mathbf{h})| - |F_c(\mathbf{h})|]^2$ with the weight of Cruickshank [14] $w = 1/(a+|F_o(h)|+c|F_o(\mathbf{h})|^2)$, where $a = 7.75$ and $c=0.005$ for **1**; $a = 1.98$ and $c = 0.006$ for **2**; and $a=2.01$ and $c = 0.011$ for **3**, respectively. All hydro gen atoms were located on difference-Fourier synthesis and refined isotropically. Atomic scattering factors used in all calculations were taken from the *International Tables for Crystallography* [15]. All X-ray diffraction computations were performed on an Compaq Deskpro 5100/5 personal computer with a DS*SYSTEM3 [9].

2.4. Thermal-motion analysis

To confirm the dynamic or static disorder, a thermal-motion analysis of the anisotropic displacement parameters (ADPs) was carried out in terms of the **LST** rigid-body approximation according to Schomaker and Trueblood [16] as well as Trueblood [17] and also considering the correlations in the internal and overall motions according to Dunitz and White [18] using the THMA3 program [9,19].

2.5. Preparation of Pc thin films mixed with polymers

On Pc dyes **1–3** and **4**, several thin films are prepared on the quartz substrate that changed the ratio of polymer versus dye by the spin-coating method from a chloroform solution. We selected the following polymers that have the long substituents R^1 and R^2 in $(CH_2CR^1R^2)_n$ form: polystyrene, poly(4-*tert*-butylstyrene), poly(4-methylstyrene), poly(α-methylstyrene), poly(methyl methacrylate), poly(ethyl methacrylate), poly(isopropyl methacrylate), poly(butyl methacrylate), poly(isobutyl methacrylate), poly(cyclohexyl methacrylate), poly(2-vinylnaphthalene) and poly(4-vinylbiphenyl). We also measured UV absorption spectra for these thin films at room temperature (20°C), 70°C and 150°C.

3. Result and discussion

X-ray crystallographic works for Pc compounds have not been numerously reported. The following Pc compounds such as $M(Pc)X_2$ or $[M(Pc)]_2X$ were determined: M is Fe [20], Mn [21], Sn [22], Zn [23] or Si [24–27]. For M = Si, only one Pc dimer was determined by X-ray crystallography [24] and two polymeric phthalocyaninatosilicon complexes are observed in high-resolution electron microscopy [26,27]. The Si atom in Pc skeleton (Si_{pc}) is normally centered and has six coordinates. According to the synthesis described in Section 2, the polymer **1** is built up by the addition polymerization of the monomer. Two reactants R^2 [*n*-butyl groups] of the $Si_{pc}(Pc)(OSi_{me}R^1)_2R^2$ add together to form a single new *n*-heptyl group and this group mediates two Pcs. The chemical formula of the polymer is $-[Si(Pc)O\,Si(CH_3)_2(CH_2)_7Si(CH_3)_2O]_n-$. The difference between **2** and **3** is only the side substituent groups R^1 to R^3.

The molecular structures and the conformations with the numbering of the atoms are shown in Fig. 1. Selected bond distances, angles and stacking intervals are given in Table 2.[1] The maximum deviations and the dihedral angles between the mean planes of the macrocyclic rings skeleton are shown in Table 3.

3.1. Conformation of a polymeric Pc (1)

The Pc microcycle ring is related by a center of symmetry at the center atom Si_1 of the O_1–Si_1–O_2 bonds. The chemical formula of mononers is $C_{43}H_{42}N_8O_2Si_3$ [$C_{25}H_{28}N_5O_2Si_3$ in crystallographic symmetry (*Pbcm*)] and for the polymer $-[Si(Pc)O\text{-}Si(CH_3)_2(CH_2)_7Si(CH_3)_2O]_n-$ is built up by the addition polymerization of the monomers. Eight atoms [Si_1–Si_3, O_1, O_2, N_1, N_5, C_{24}] are located on the mirror plane passing $z = 1/4$. Each benzopyrrole group is planar within a maximum deviation of 0.032(4) Å. The Pc skeleton [Si_1, N_2–N_5, C_1–C_{16}, plane A] and the mean plane defined by five atoms [Si_1–Si_3, O_1, O_2, plane B] of [Si_{me}–O–Si_{pc}–O–Si_{me}] indicate good planarities. The Si_{pc}–N bonds [Si_1–N 1.920(4) and 1.922(3) Å] are apparently extended from the normal Si–N length (1.711 Å) [28]. The Si_{me}–O bonds and the Si_{me}–C bonds are a little short compared with the normal Si–O length (1.622–1.680 Å) and Si–C length (1.857–1.888 Å), respectively. The Si_{pc}–O bonds are shorter than the Si_{pc}–N bonds and the Si_{me}–O bonds are shorter than the Si_{pc}–O bonds. This is the same tendency observed in $Si(Pc)[OSi(CH_3)_3]_2$ [24]. The distances of $Si_{pc}\cdots Si_{me}$ are shorter than the previously reported 3.244 Å (M = Ni) and 3.33 Å (M = Si) [29]. The bond angles O–M_{pc}–O [179.7(12)°] is practically linear and the same as reported previously (178° for

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[1] Lists of atomic coordinates, equivalent isotropic thermal parameters, anisotropic thermal parameters, H-atom coordinates, remaining bond lengths, intermolecular distances, best least-squares planes and structure factors have been deposited with the B.L.L.D. as Supplementary Publication No. SUP26602 (108 pages).

Table 2
Bond distances (Å), angles (°) and stacking intervals (Å) with esds in parentheses

	1	**2**	**3**		**1**	**2**	**3**
Si_1-N_2	1.922(3)	1.923(14)	1.933(7)	Si_1-N_6		1.942(12)	1.919(7)
Si_1-N_4	1.920(4)	1.907(11)	1.938(8)	Si_1-N_8		1.944(10)	1.915(7)
Si_1-O_1	1.674(5)	1.674(8)	1.689(8)	Si_2-O_1	1.580(5)	1.623(10)	1.595(9)
Si_1-O_2	1.678(4)	1.683(8)	1.661(8)	Si_3-O_2	1.602(4)	1.610(10)	1.619(9)

1			
Si_2-C_{17}	1.803(26)	Si_3-C_{24}	1.777(19)
Si_2-C_{18}	1.696(27)	Si_3-C_{25}	1.773(22)
2			
Si_2-C_{41}	1.893(18)	Si_3-C_{61}	1.901(17)
Si_2-C_{47}	1.886(14)	Si_3-C_{67}	1.824(19)
Si_2-C_{53}	1.831(16)	Si_3-C_{73}	1.843(18)
3			
$Si_2\ C_{41}$	1.825(11)	Si_3-C_{61}	1.908(9)
Si_2-C_{49}	1.817(12)	Si_3-C_{69}	1.879(13)
Si_2-C_{50}	1.838(13)	Si_3-C_{70}	1.931(1)

	1	**2**	**3**		**1**	**2**	**3**
$O_1-Si_1-O_2$	179.7(12)	178.5(7)	179.7(15)	$Si_1-N_4-C_9$	126.9(3)	127.7(9)	123.1(6)
$O_1-Si_1-N_2$	90.5(2)	87.9(5)	90.6(3)	$Si_1-N_4-C_{16}$	126.2(3)	127.6(9)	126.1(6)
$O_1-Si_1-N_4$	89.1(2)	90.0(4)	91.1(4)	$N_2-Si_1-N_4$	89.8(1)	89.4(5)	92.2(3)
$O_1-Si_1-N_6$		90.9(5)	88.8(4)	$Si_1-N_6-C_{24}$		126.4(9)	125.4(6)
$O_1-Si_1-N_8$		90.1(4)	89.3(3)	$Si_1-N_6-C_{25}$		123.3(9)	128.4(6)
$O_2-Si_1-N_2$	89.3(2)	90.7(5)	89.1(3)	$Si_1-N_8-C_{32}$		125.3(10)	127.4(6)
$O_2-Si_1-N_4$	91.2(2)	89.6(4)	89.0(4)	$N_2-Si_1-N_6$		178.2(5)	178.8(5)
$O_1-Si_1-N_6$		90.5(5)	91.5(4)	$N_2-Si_1-N_8$		89.8(5)	90.2(3)
$O_1-Si_1-N_8$		90.4(4)	90.7(3)	$N_4-Si_1-N_6$		89.4(5)	88.9(3)
$Si_1-N_2-C_1$	125.9(3)	126.8(9)	126.3(6)	$N_4-Si_1-N_8$		179.2(5)	177.6(4)
$Si_1-N_2-C_8$	126.5(3)	126.1(9)	126.4(6)	$N_6-Si_1-N_8$		91.4(5)	88.8(3)
$Si_1-O_1-Si_2$	161.2(3)	164.5(8)	160.5(4)	$Si_1-O_2-Si_3$	157.3(3)	165.6(7)	160.4(4)

1			
$O_1\ Si_2-C_{17}$	110.7(7)	$C_{24}-Si_3-C_{25}$	112.8(9)
$O_1-Si_2-C_{18}$	112.3(11)	$C_{24}-Si_3-O_2$	109.5(7)
2			
$O_1-Si_2\ C_{41}$	110.1(6)	$O_2-Si_3-C_{61}$	109.9(6)
$O_1-Si_2-C_{47}$	107.5(7)	$O_2-Si_3-C_{67}$	104.4(8)
$O_1-Si_2-C_{53}$	109.1(6)	$O_2-Si_3-C_{73}$	109.7(6)
3			
$O_1\ Si_2-C_{41}$	110.9(6)	$O_2-Si_3-C_{61}$	109.6(5)
$O_1-Si_2\ C_{49}$	109.2(5)	$O_2-Si_3-C_{69}$	104.8(6)
$O_1\ Si_2-C_{50}$	110.1(5)	$O_2-Si_3-C_{70}$	110.0(5)

	1	**2**	**3**
$Si_1\cdots Si_2$	3.220(3)	3.246(6)	3.202(4)
$Si_1\cdots Si_3$	3.136(3)	3.258(6)	3.207(4)

M = Mn [21] and 177.4(1)° for M = Si [24]). The Si_{pc}–O–Si_{me} bond systems are nearly 160° [161.2(3)° for $Si_1-O_1-Si_2$ and 157.3(3)° for $Si_1-O_2-Si_3$] and are the same as 157°–158° in $Si(Pc)[OSi(CH_3)_3]_2$ [24].

The large temperature factors for the siloxy carbons [$C_{18}-C_{24}$, B_{eq} = 11.6(13)–31.9(37) Å^2], the two methyl groups [B_{eq} = 27.6(28) Å^2 for C_{17} and 24.8(17) Å^2 for C_{25}], the C–C bond distance ranging

Table 3
The maximum deviations (Å) and the dihedral angles (°) of the mean planes of Pc with esds in parentheses

(a) The maximum deviations (Å)

	Plane	Deviation	At
1	A: $Si_1,N_2–N_5,C_1–C_{16}$	− 0.063(5)	C_{13}
	B: $Si_2–O_1–Si_1–O_2–Si_3)$	+ 0.000(3)	Si_1
2	A: $Si_1,N1–N_8,C_1–C_{32}$	+ 0.073(14)	C_2
	B; $Si_2–O_1–Si_1–O_2–Si_3)$	− 0.010(15)	Si_1
	C: $C_{41}–C_{58}$	− 0.510(24)	C_{47}
	D: $C_{61}–C_{78}$	− 0.389(23)	C_{67}
3	A: $Si_1,N1–N_8,C_1–C_{32})$	+ 0.068(10)	C_{21}
	B: $Si_2–O_1–Si_1–O_2–Si_3$	+ 0.003(4)	Si_1
	C: $C_{41}–C_{50}$	+ 0.050(12)	C_{43}
	D: $C_{61}–C_{70}$	− 0.094(11)	C_{68}

(b) The dihedral angles (°)

Planes	**1**	**2**	**3**
A/B	87.8(1)	89.3(1)	88.9(1)
A/C		1.5(1)	4.2(3)
A/D		1.1(1)	5.4(3)
B/C		88.8(1)	85.0(1)
B/D		88.9(1)	84.3(1)
C/D		0.4(2)	2.2(5)

from 1.273(38) to 1.698(39) Å, the C–C–C bond angles from 120.7(33)° to 150.1(18)° and the maximum distance from the mean plane defined by seven carbons $[C_{18}–C_{23}$ and $C_{24}\ (-1 + x, y, z)] + 0.219(23)$ Å at C_{19} suggest disorder or incomplete occupancy of their positions. These tendencies are also observed in $[Mn(Pc)Py]_2O$ [21] and in $Si(Pc)[OSi(CH_3)_3]_2$ derivatives [24]. In the difference map, there is no significant peak around the siloxy groups. The distorted angle 82.7(11)° of $Si_2–C_{24}–C_{23}$ $(1 + x, y, z)$ seems to be the reason why the atoms Si_2 and C_{24} are located at special positions. The polymeric Pc is constructed along the *a* axis by the translation of $(1 + x, y, z)$ symmetry. The minimum distance of the siloxy groups from the mean plane of the Pc skeleton is 4.484(22) Å at C_{24}. The intermolecular distance between the Pc skeletons is 7.452(4) Å.

3.2. Conformation of a Pc dye (2)

The chemical formula is $Si(Pc)[OSi(C_6H_{13})_3]_2$. This oxo Pc $Si_{pc}(Pc)(OSi_{me}R_3)_2$ is a molecule in which two Si_{me} atoms are substituted with hexyl groups. Each benzopyrrole group is planar within a maximum deviation of 0.042(4) Å. The Pc skeleton (plane A) and the mean plane defined by $Si_{me}–O–Si_{pc}–O–Si_{me}$ (plane B) indicate good planarities. Two mean planes of alkyl substituents on the Si_2 and Si_3 (planes C and D) are considerably uneven. The dihedral angles between plane B and other planes are nearly at right angles. The other dihedral angles (A/C, A/D, B/C, B/D and C/D) are almost parallel to each other. The tendencies of the bond lengths, angles and the stacking intervals around Si_{pc} and Si_{me} are the same as **1**. For alkyl carbons having comparative large temperature factors $(C_{46}$, $C_{50}–C_{52}$, C_{58}, $C_{71}–C_{72}$ and $C_{77}–C_{78}]$, bond distance ranging from 1.285(40) to 1.635(25) Å and bond angles from 108.1(8)° to 135.1(25)° seem to be normal values and indicate large vibrations at these side chain positions. The distance between the mean planes of the siloxy alkyl groups on Si_2 and Si_3 is 6.937(5) Å. Fig. 2 shows two projections, perpendicular and parallel to the Pc skeleton. Looking down from the $Si_2–O_1–Si_1–O_2–Si_3$ direction, two hexyl groups $(C_{41}–C_{48}/C_{61}–C_{68}$ and $C_{53}–C_{58}/C_{73}–C_{78})$ of two siloxy side groups have the same direction, but one hexyl group $(C_{47}–C_{52})$ on Si_2 extends to the opposite direction from the one on Si_3 $(C_{67}–C_{72})$ with respect to the facing axis.

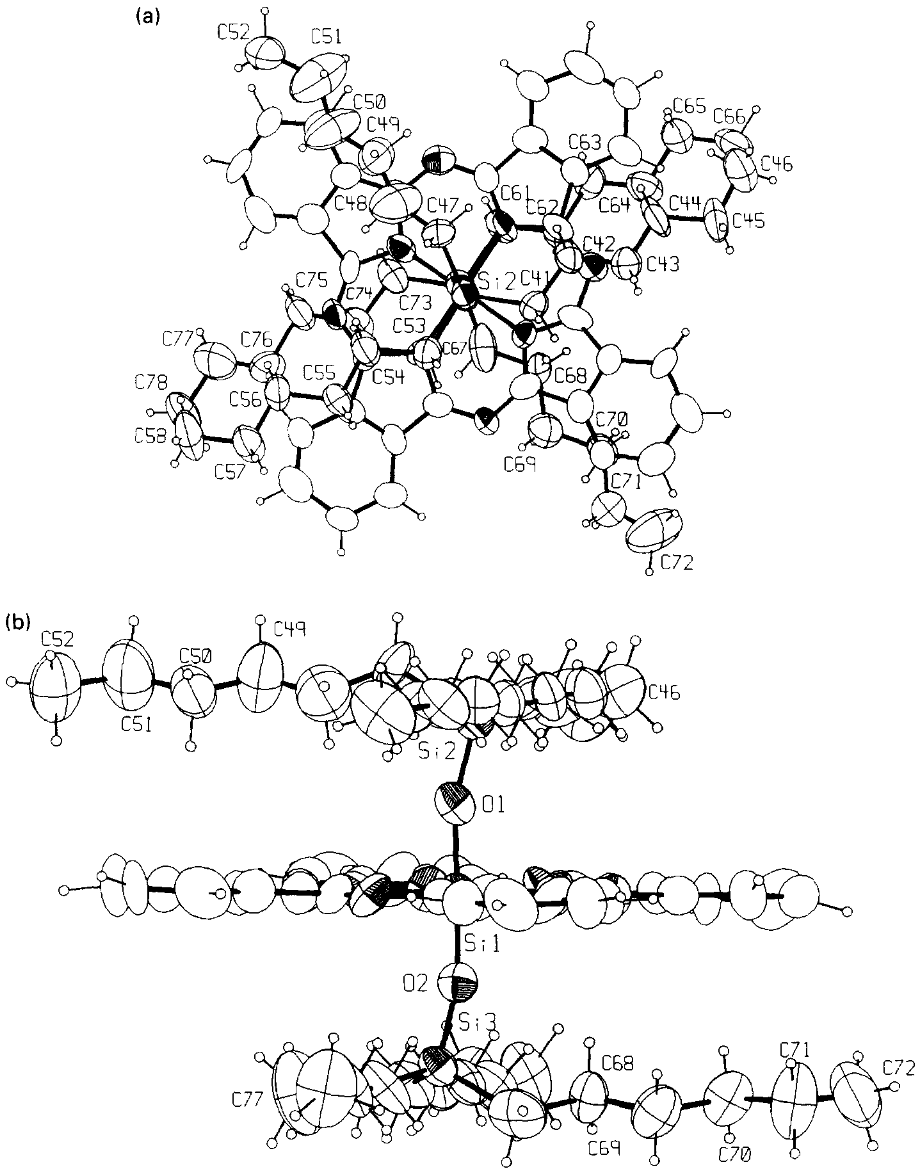

Fig. 2. ORTEP drawing for **2**. (a) Perpendicular to the Pc skeleton; (b) parallel to the Pc skeleton.

3.3. *Conformation of a Pc dye* (**3**)

The chemical formula is $Si(Pc)[OSiC_8H_{17}(CH_3)_2]_2$. This oxo Pc $Si_{pc}(Pc)(OSi_{me}R)_2$ is a molecule that substitutes siloxy groups by one octyl group and two methyl groups. The bond lengths, angles, stacking intervals, torsion angles and the planarities of the Pc skeleton are essentially the same as those in **1** and **2**. The planes B–D are good planarities and the dihedral angles between these planes are almost the same as those in **2**. Fig. 3 shows two projections [perpendicular and parallel] to the Pc skeleton. Looking down from the Si_2–O_1–Si_1–O_2–Si_3 direction, two methyl groups [C_{49} and C_{50}] and one octyl group [C_{41}–C_{48}] on Si_2 extend in opposite directions from those on Si_3 (C_{70}, C_{69} and C_{61}–C_{68}) with respect to the facing axis.

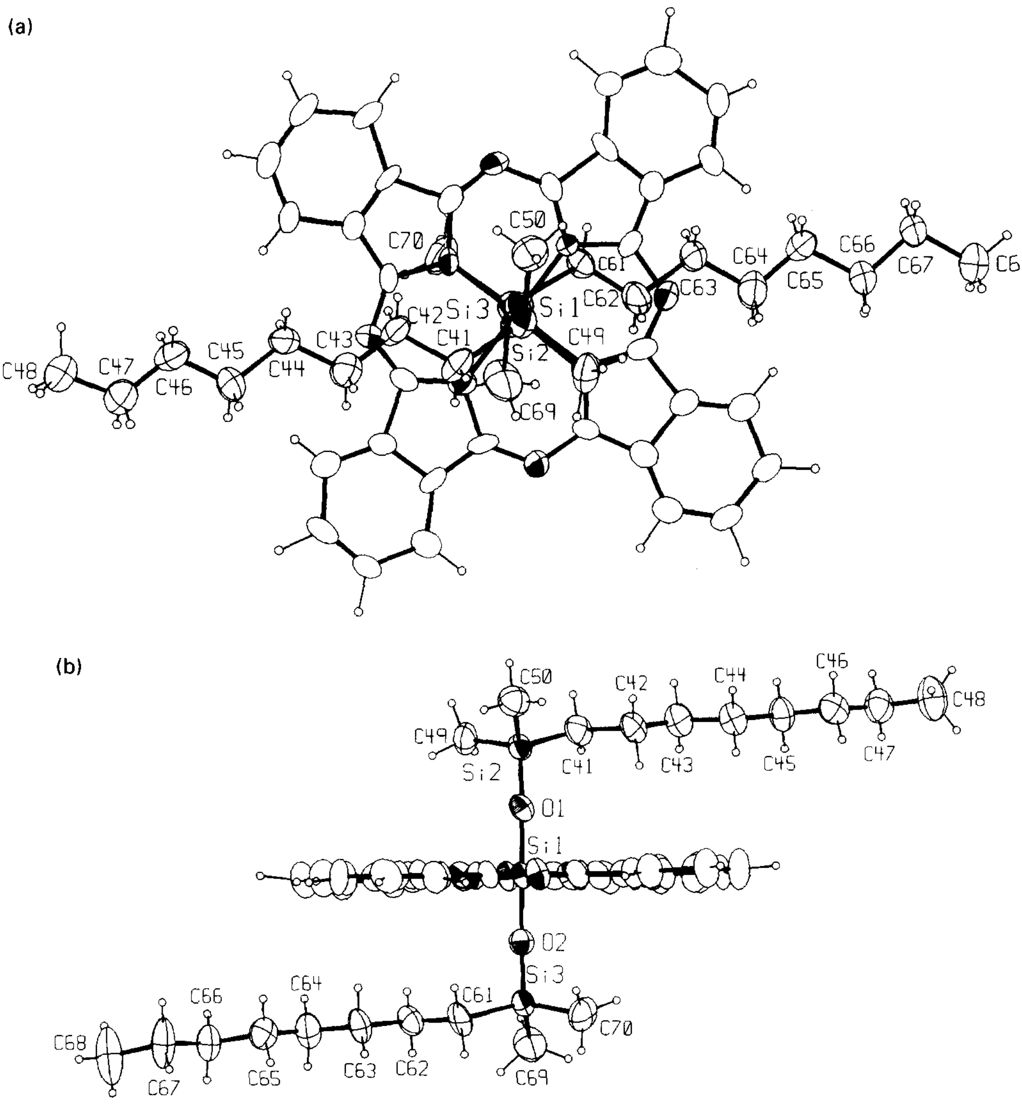

Fig. 3. ORTEP drawing for **3**. (a) Perpendicular to the Pc skeleton; (b) parallel to the Pc skeleton.

3.4. Thermal motions

Table 4 and Table 5 list the ADPs for the attached rigid groups (ARGs). The analysis is complicated by the large agreement indices R_{wU} and strong correlation at room temperature. For **1**, the ADP of seven carbons [C_{18}–C_{24}] has a large $\langle\phi^2\rangle$ value. The mean-square libration amplitudes $\langle\phi^2\rangle$ are large, meaning that thermal motions vary freely. An inspection of Fig. 1 suggests that disorders should be considered around each butyl group, although no significant peaks appear in the difference map. For **2**, the ADPs of six siloxy groups are small $\langle\phi^2\rangle$ values except for one hexyl group [C_{47}–C_{52}] and for **3**, the $\langle\phi^2\rangle$ values of two octyl groups are small.

3.5. Crystal packing

The packing diagrams of the compounds **1**–**3** are illustrated in Fig. 4. Hydrogen bonds and intermolecular C–H···X contacts such as those reported by Taylor and Kennard [30] are shown in Table 6. Eight atoms

Table 4

Analysis of the anisotropic displacement parameters (ADPS) in terms of LST rigid-body and internal motions. Agreement index $R^{a}_{\omega U}$ and goodness of fit[b]

Motion	**1**		**2**		**3**	
	Rigid body	Internal	Rigid body	Internal	Rigid body	Internal
Na[c]	35		81		65	
No[d]	210		486		390	
Np[e]	6		20		2	
$R_{\omega U}$ (All)	0.327	0.327	0.356	0.332	0.297	0.294
(Diagonal)	0.280	0.280	0.302	0.1278	0.229	0.229
Goodness of fit	5.93	6.01	2.48	2.39	2.51	2.52

[a] $R_{\omega U} = [\sum \omega(\Delta U)^2 / \sum \omega(U_{obs})^2]^{1/2}$, where $\Delta U = U_{ij}(obs) - U_{ij}(calc)$, ω = reciprocal of $\sigma(U_{ij}(obs))^2$.

[b] Goodness of fit = $[\sum\omega(\Delta U)^2/(No - Np)]^{1/2}$.

[c] Na = number of atoms determining thermal motion parameters.

[d] No = number of independent observations.

[e] Np = number of parameters.

Table 5

Mean-square libration amplitudes $\langle \phi^2 \rangle$ (deg^2) correlated to overall and internal motions with esds

Libration		1		2		3	
Group	Along	Rigid body	Internal	Rigid body	Internal	Rigid body	Internal
C_{18}–C_{24}	O_1–Si_2	19(6)	19(4)				
C_{41}–C_{46}	O_1–Si_2			1(1)	5(4)		
C_{47}–C_{52}	O_1–Si_2			1(1)	− 20(18)		
C_{53}–C_{58}	O_1–Si_2			2(1)	5(4)		
C_{61}–C_{66}	O_2–Si_3			− 3(1)	− 5(4)		
C_{67}–C_{72}	O_2–Si_3			− 2(1)	4(7)		
C_{73}–C_{78}	O_2–Si_3			1(2)	− 4(6)		
C_{41}–C_{48}	O_2–Si_2					− 2(1)	0(2)
C_{63}–C_{68}	O_2–Si_3					0(1)	0(9)

Table 6

Hydrogen-bonding parameters (Å, °) and C–H···X contacts with esds in parentheses

Donor–H···acceptor	D–H	D···A	H–A	∠D–H···A
1				
C_{11}–H_{11}···N_3^{i}	0.98(4)	3.652(6)	2.68(4)	172(3)
2				
C_{11}–H_{11}···N_3^{ii}	0.99(9)	3.128(18)	2.70(8)	106(5)
C_{48}–H_{48a}···O_1^{ii}	0.98(7)	3.212(29)	2.62(4)	119(6)
3				
C_{42}–H_{42b}···N_5^{ii}	1.09(11)	3.703(17)	2.75(12)	145(7)
C_{69}–H_{69b}···O_2^{ii}	1.09(9)	2.776(17)	2.70(8)	82(4)

Symmetry codes: (i) x, $1/2-y$, $1+z$; (ii) x, y, z.

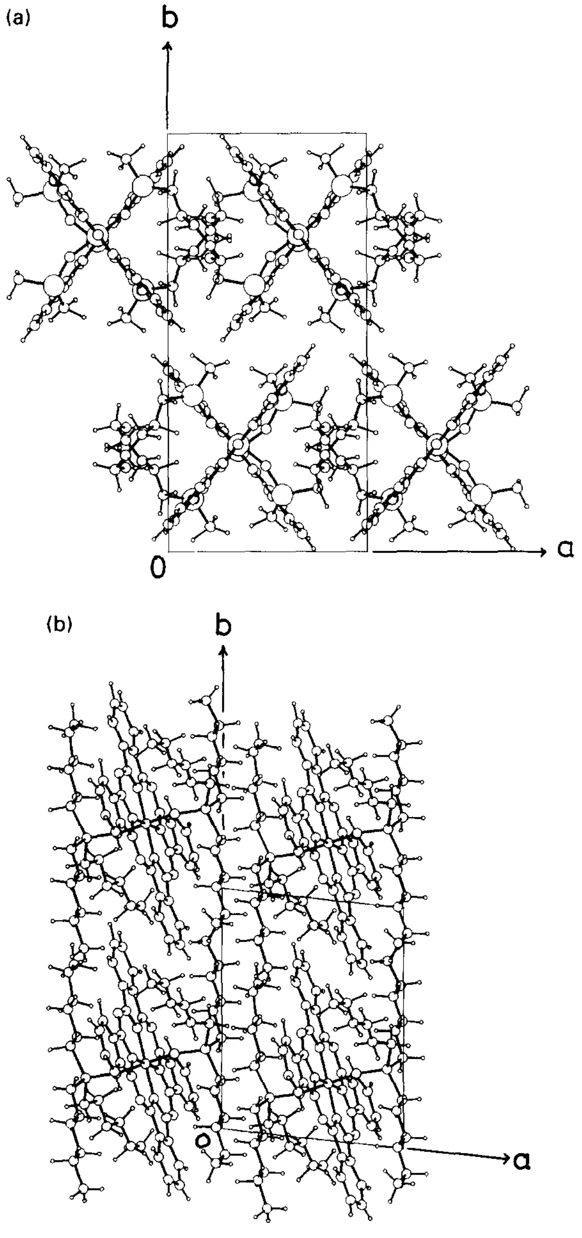

Fig. 4. Molecular packing diagram. (a) Looking down the *c* axis for **1**; (b) looking down the *c* axis for **2**; (c) looking down the *b* axis for **3**.

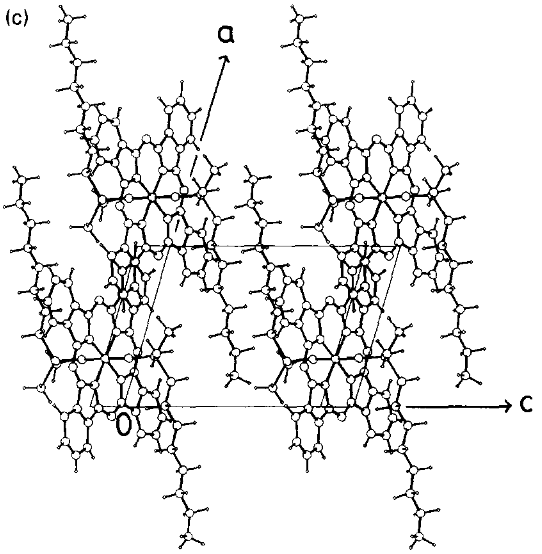

Fig. 4. Continued.

(Si_1–Si_3, O_1, O_2, N_1, N_2 and C_{24}) of **1** are located at a special position (x, y, $1/4$). The *n*-heptyl portion of the molecule is lipophobic; thus, we cannot find an intermolecular contact less than 3.5 Å except for a C_{11}–$H_{11}\cdots N_3$ (x, $1/2-y$, $1+z$) contact. The polymer chain is constructed at the siloxy group [Si_2–C_{18}–C_{23}–C_{24} ($-1+x$, y, z)–Si_3 ($-1+x$, y, z)] along the *a* axis (Fig. 5). The Pc skeleton and the mean plain of the *n*-heptyl portion [C_{18}–C_{23}, C_{24} ($-1+x$, y, z)] are almost parallel [the dihedral angle is 9.0(4)°]. In addition, a $-Si_{pc}$–O–Si_{me}–alkyl groups–Si_{me}–O–Si_{pc}– chain is built. Meanwhile, another polymeric Pc chain related by two-fold rotation axis (x, $1/2-y$, $1/2+z$) is constructed in the same direction. The Pc skeleton has a mosaic feature, is positioned at an angle of 40° from the *b* axis and stacks to the *a* axis [Fig. 4(a)]. This Pc skeleton is also related to the two-fold rotation axis perpendicular to the *b* axis passing $y = 1/4$ and 3/4. Looking down the *c* axis, the Pc skeleton performs an angle of 40° from the *a* axis. Namely the polymer axis is the *a* axis and the staggering angle is zero [Fig. 5(b)]. The stacking interval between the Pc skeleton and the Si_1 ($1+x$, y, z) of the next Pc skeleton is 7.449(4) Å.

The Pc skeletons of **2** and **3** are packed vertically in a unit cell looking down the *a* axis, respectively. For **2**, the siloxy groups stack cofacially to each other along the *a* axis. Two weak intramolecular C–H···X contacts within a molecule exist. The stacking interval between the Pc skeleton and the Si_1 ($1+x$, y, z) of the next Pc skeleton is 7.536(17) Å. For **3**, the Pc skeleton inclines 55° to the *b* axis. One intramolecular C_{69}–$H_{69a}\cdots O_2$ contact within a molecule exists. No

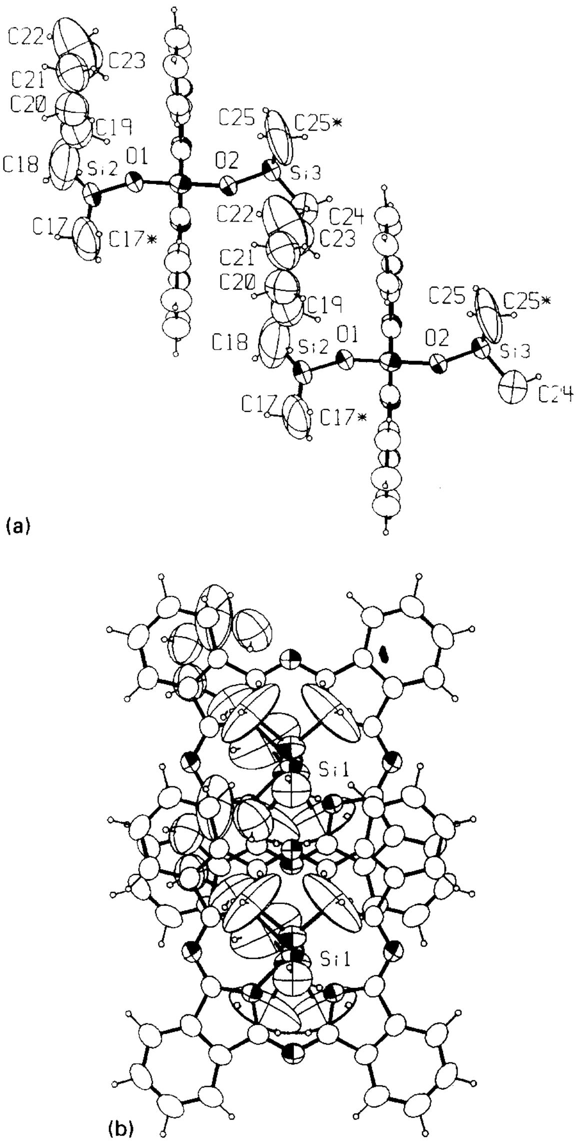

Fig. 5. ORTEP drawing of polymeric chain for **1**. (a) Looking down the *c* axis; (b) looking down the *a* axis.

intermolecular contacts less than 3.5 Å are found in **2** and **3**. The stacking interval between the Pc skeleton and the Si1 (x, $1+y$, z) of the next Pc skeleton is 7.046(17) Å and this length is shorter than the values of **1** and **2**.

4. Application

A re-writable and a write-once optical disk system (CD-R and DVD-R) has recording materials that comprise of a Pc dye or the Pc dye mixed with a polymer such as poly(*t*-butyl styrene). The structure of the optical disk has three layers that are the substrate, recording layer and reflective layer. The recording layer consists of the Pc dye dispersed in the polymer. The reflective layer is sputtered gold. The dye indicates a strong aggregation state in an unrecorded state (dispersion in polymer) and a weak aggregation state in a recorded state (line-up in polymer). The recording mechanisms are based on photo-thermal processes that induce ablation or expansion of the recording material by laser-pulsed irradiation. The complex refractive index N ($N = n - ik$, where n and k are the real and imaginary parts) of the recording material changes reversibly depending upon the aggregation state of the dye which is induced by the interaction between the dye and the polymer. The temperature of the recording layer is risen by a laser-pulsed irradiation. As a result, main chain conformation of the polymer changes from rod- to coil-like. Since the temperature of the recording layer is cooled down in a moment, the changed interaction state is retained. The imaginary part k of the refractive index is increased or decreased by the aggregation state of the Pc.

We applied Pc dyes **2–4** mixed with a polymer for the control of the aggregation state. For making the medium interaction of dye molecules, the axial substituents R^1–R^3 of the Pc dye derivatives gave considerable ability to control the aggregation state on the laser irradiation compared with a nonsubstituted Pc or a ring substituted Pc dye derivative. The interaction between the dye and the polymer is mainly determined by what kind of substituents are chosen and by the construction of axial substituents R^1–R^3 (how axial substituents are spread over the Pc ring). In the laser irradiation, the nonsubstituted or ring substituted Pc have too strong an interaction of the dye to change the aggregation state. In the recorded state, the spectra were quite different depending on the set of axial substituents. If the Pc dye derivative **1** was a polymer, then **1** did not mix at all with the polymer in chloroform and toluene solvent; Pc dye **2** did not mix well with the polymer; and Pc dyes **3** and **4** mixed well with the polymer. The recording films using **3** and **4** were homogeneous at unrecording and recording states. We found that the aggregation state was

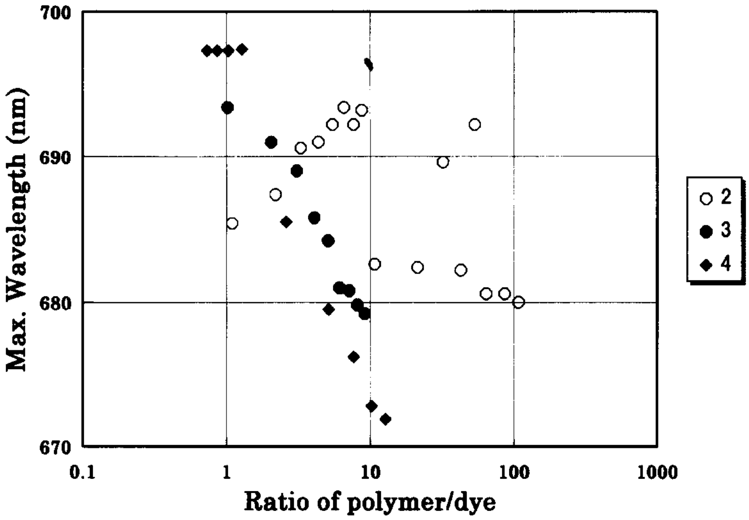

Fig. 6. The aggregation state changes by metal ligand substitutes R^1–R^2 in $(CH_2CR^1R^2)_n$ form at room temperature (20°C). The vertical axis is the mixed ratio of a polymer (mol) versus a dye (mol). The horizontal axis is the maximum wavelength (nm) that the mixture indicates.

controlled by metal ligand substituents as shown in Fig. 6. Pc dye **4** mixed with a polymer showed an absorption wavelength in a wide range compared with dyes **2** and **3**. Namely, the aggregation state of the recording layer is controlled by choosing the set of axial substituents R^1–R^3. The detailed UV spectra of the mixed Pc dye **4** are shown in Fig. 7. The value 1.03 of the ratio compared with other ratios indicates that the hypsochromic shift (blue shift) occurs at the high temperature (λ_{max} = 685.7 nm) and this shift range is wider rather than others. This material applied to CD-R and DVD-R recording systems is easily able to satisfy the standard [31] (a high refractivity of more than 65% and a large signal modulation of more than 0.60) with respect to refractivity and contrast. We achieved the best writing contrast and the highest stability with this material. The conformation of axial substituents is very important for the ability of the dye aggregation and the capability to control the aggregation state. This material indicates several features, i.e. the wavelength dependence of the refractivity is less than the organic dye of a conventional method. It is very important to note that the interactional mechanism of dyes and the interaction with a polymer depend upon the length of axial substituents. It also makes the parallel conformation to the Pc skeleton.

5. Conclusion

The crystal and molecular structures of three phthalocyanine dye derivatives, polymer $-[Si(Pc)O-Si(CH_3)_2(CH_2)_7Si(CH_3)_2O]_n-$ for **1**, $Si(Pc)[O-Si(C_6H_{13})_3]_2$ for **2** and $Si(Pc)[OSiC_8H_{17}(CH_3)_2]_2$ for **3** were determined by X-ray crystal structure analysis.

The Pc macrocyclic rings of both compounds are related by a center of symmetry at the center of the O_1–Si_1–O_2 bonds. The mean planes of the macrocyclic rings skeleton and two single-atom oxo-bridged substitutes (Si_{me}–O–Si_{pc}–O–Si_{me}) are coplanar. The dihedral angle between the mean planes of the macrocycle rings and the two single-atom substitutes is nearly at right angles [87.8(1)° for **1**, 89.3(1)° for **2** and 88.9(1)° for **3**]. For **1**, the polymeric Pc is constructed along the *a* axis by the translation of $(1 + x, y, z)$. The distance between the mean planes of the Pc skeleton is 7.452(4) Å. For **2**, the distance between the mean planes of the siloxy groups is 6.937(5) Å. Two hexanyl groups of two siloxy side groups have the same direction, but one hexane extends in the opposite direction against the facing axis. For **3**, the distance between the mean planes of two octyl groups is 6.613(6) Å. Two siloxy side groups (two methyl groups and one octyl group) extend just to the opposite direction.

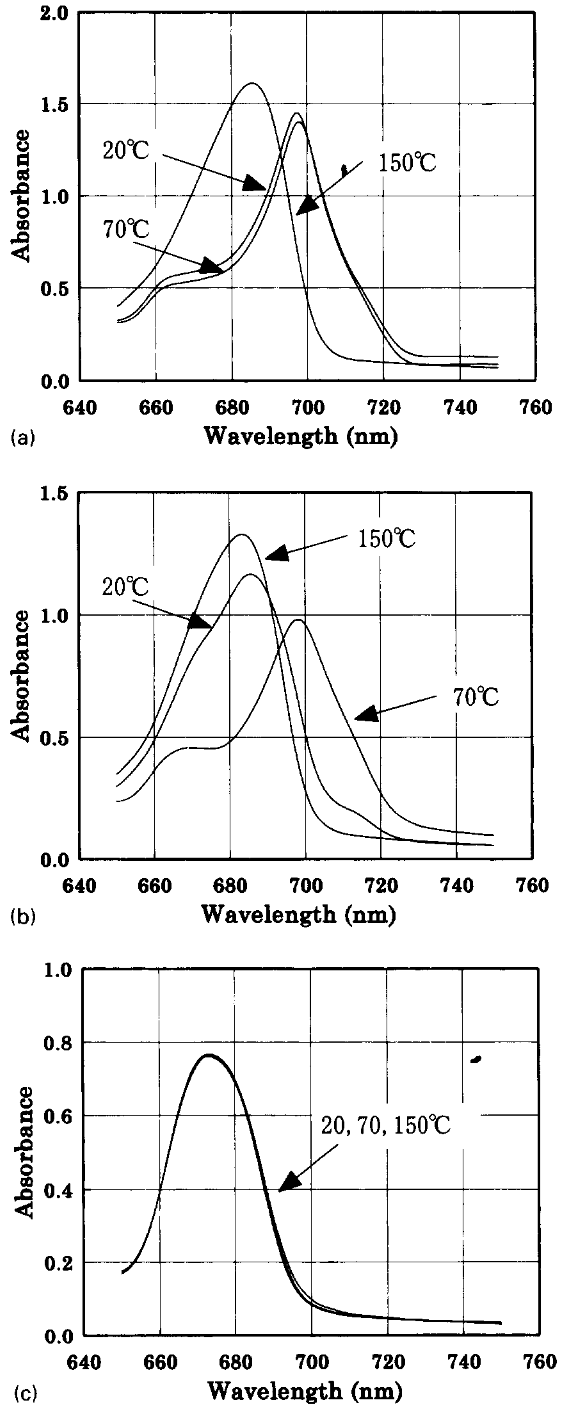

Fig. 7. UV absorption spectra of the Pc dye **4** mixed with a poly(4-*tert*-butylstyrene) at room temperature (20°C), 70°C and 150°C. Mixed ratios of a polymer versus Pc dye **4** are (a) 1.03; (b) 2.57; and (c) 10.26.

Compounds **3** and **4** mixed well with polymers homogeneously, but **2** did not; **1** did not mix at all with polymers. Alkyl groups with less than six carbons do not go out from the Pc skeleton plane. Larger numbers than eight carbons in the alkyl group are required for the axial substituents (R^1–R^3) to mix with polymers. The interaction of dye with a polymer depends upon the length of axial substituents. We found the interactions of Pc dyes with polymers are dependant upon the length of axial substituents for CD-R and DVD-R recording systems. We could achieve high contrasts because it was easy to change the aggregation state of dyes **3** and **4**, which have a long substitute. It is easy to control spectra with less optimum laser power rather than the other CD-R recording system.

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