Novel Silicon Naphthalocyanines: Synthesis and Molecular Arrangement in Thin Films

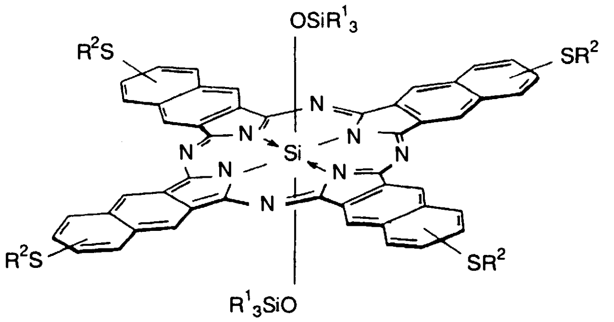
Mitsuo Katayose, Seiji Tai,* Koichi Kamijima, Hideo Hagiwara and Nobuyuki Hayashi
Ibaraki Research Laboratory, Hitachi Chemical Co. Ltd., 13–1, 4-Chome, Higashi-cho, Hitachi 317, Japan

A series of highly organic-soluble [bis(trialkylsiloxy)]silicon tetrakis(alkylthio)-2,3-naphthalocyanines [$(R^1{}_3SiO)_2SiNc(SR^2)_4$] have been synthesized, and their ^1H NMR, electronic absorption and fluorescence spectra measured. These spectra indicate that $(R^1{}_3SiO)_2SiNc(SR^2)_4$ are monomeric in solution (10^{-2}–10^{-7} mol dm^{-3}). In their solid films, all Q-band absorption maxima of $(R^1{}_3SiO)_2SiNc(SR^2)_4$ are red-shifted from their monomeric Q-band maximum. The extent of shift significantly increases with decreasing R^1 length of the axial substituents, but the effect is far less with ring substituents, R^2. These observations are clearly explained using the exiton model. Our results indicated that novel naphthalocyanine $(R^1{}_3SiO)_2SiNc(SR^2)_4$ molecules have a J-type molecular arrangement in thin solid films.

Physical and chemical properties of naphthalocyanines [Nc] have recently attracted much attention from material chemists because of their potential use in semiconducting materials,[1] nonlinear optics[2] and other optical devices. Nc is one of the most suitable compounds for optical devices such as optical recording materials[3] and organic photoconductors,[4] since it effectively absorbs semiconductor laser light that is used in these devices.

In particular, organic-soluble Ncs have advantages for these applications because they are easily purified by column chromatography and/or recrystallization. However, as is well known, Nc has a high tendency to form molecular aggregates such as dimers, trimers and oligomers, even in dilute solution.[5] In optical devices using Nc, the influence of their aggregation cannot be neglected because monomers, dimers, trimers and oligomers all have different photophysicochemical characteristics. Generally, derivatives of Nc having only ring substituents tend to form H-aggregates in solution,[5] whereas those with two axial substituents bound to a central metal show monomeric properties.[6] Although many Ncs have been reported or patented for use in optical devices, the substrates of their fundamental research were limited to Ncs with some substituents on the central metal[6] or on the naphthalocyanine ring.[7] Organic-soluble Ncs bearing two axial substituents bound to a central metal and four ring substituents have not yet been reported.

Here we report syntheses of a series of highly organic-soluble Ncs [$(R^1{}_3SiO)_2SiNc(SR^2)_4$, **1**] (Fig. 1) which have two bulky axial substituents and four ring substituents, as well as their physical and chemical molecular properties in solution and in thin solid films.



Me10 $R^1 = CH_3$, $R^2 = C_{10}H_{21}$
Et10 $R^1 = C_2H_5$, $R^2 = C_{10}H_{21}$
Pr10 $R^1 = C_3H_7$, $R^2 = C_{10}H_{21}$
BU10 $R^1 = C_4H_9$, $R^2 = C_{10}H_{21}$
HE10 $R^1 = C_6H_{13}$, $R^2 = C_{10}H_{21}$
PR6 $R^1 = C_3H_7$, $R^2 = C_6H_{13}$
PR14 $R^1 = C_3H_7$, $R^2 = C_{14}H_{29}$
PR16 $R^1 = C_3H_7$, $R^2 = C_{16}H_{31}$
ETMC $R^1 = C_2H_5$, R^2 = 4-methylcyclohexyl
PRMC $R^1 = C_3H_7$, R^2 = 4-methylcyclohexyl
BUMC $R^1 = C_4H_9$, R^2 = 4-methylcyclohexyl
ME4 $R^1 = CH_3$, $R^2 = C_4H_9$
ET4 $R^1 = C_2H_5$, $R^2 = C_4H_9$
PR4 $R^1 = C_3H_7$, $R^2 = C_4H_9$
BU4 $R^1 = C_4H_9$, $R^2 = C_4H_9$
HE4 $R^1 = C_6H_{13}$, $R^2 = C_4H_9$
BU12 $R^1 = C_4H_9$, $R^2 = C_{12}H_{25}$
ET16 $R^1 = C_2H_5$, $R^2 = C_{16}H_{33}$

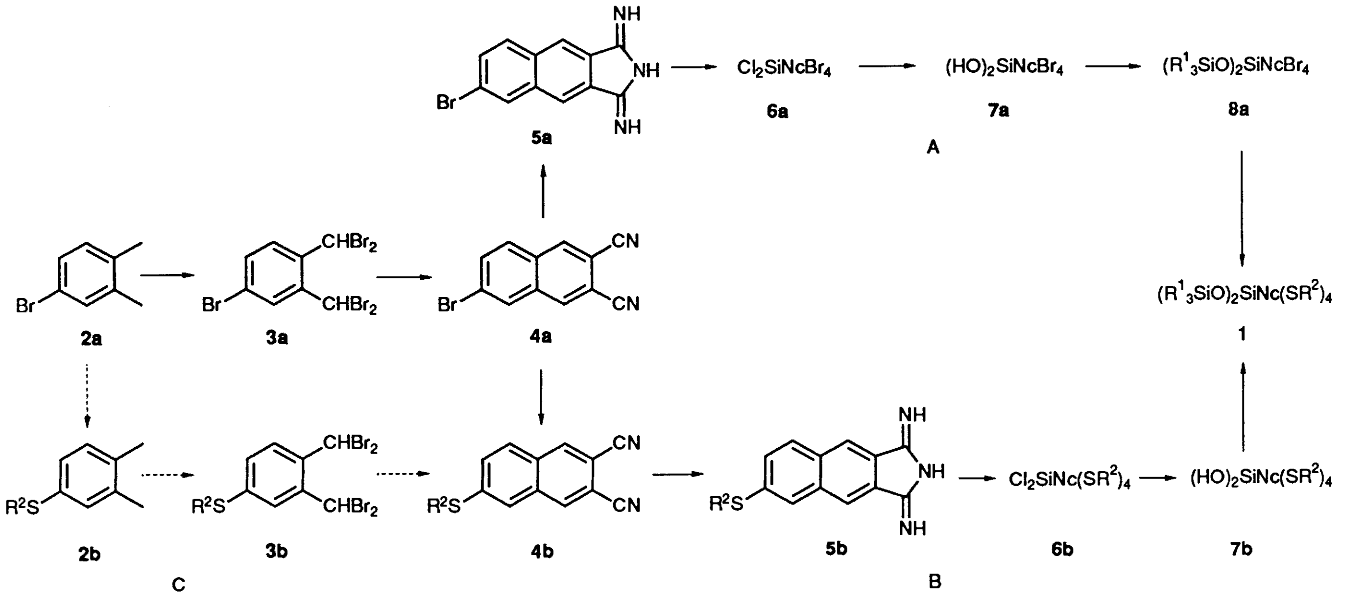
Fig. 1 Molecular structure of $(R^1{}_3SiO)_2SiNc(SR^2)_4$ **1**

Results and Discussion

All naphthalocyanines **1** shown in Fig. 1 were synthesized *via* two routes (A and B) (Scheme 1). Another possible method for synthesis of 6-alkylthio-2,3-dicyanonaphthalene (route C) was unsuitable, because the long alkyl groups (R^2) of 4-alkylthio-1,2-dimethylbenzene prevented bromination of methyl groups to give **3b** and/or the subsequent cyclization reaction with fumaronitrile leading to **4b**. In fact, isolation of **4b** from the reaction mixture was difficult because of formation of many by-products. Similar findings were also obtained during synthesis of 6-alkoxycarbonyl-2,3-dicyanonaphthalene.[8] Route A can be used for synthesizing **1** with various ring substituents. However, since the reaction mixture in the final step (from **8** to **1**) involved several minor products such as $(R^1{}_3SiO)_2SiNcBr_{(4-n)}(SR^2)_n$ (n = 1–3) which were not completely converted into **1** even by further heating, careful purification of the products by column chromatography followed by recrystallization was necessary. On the other hand, route B is most suitable for preparing compounds **1** with a variety of axial substituents. In the final step of route B (from **7b** to **1**), isolation of the products from the reaction mixture was easier than that in the final step of route A because the above mentioned minor products were not formed.

All compounds **1** obtained by these synthetic methods are highly organic-soluble so that we can evaluate the physicochemical properties of **1** not only in solution but also in thin solid films prepared by coating.

Electronic absorption and fluorescence emission spectra of **ME10** (*ca.* 10^{-6} mol dm^{-3}) are shown in Fig. 2. The strongest Q-band absorption, assigned to the $S_0(0)$–$S_1(0)$ transition,[6] was observed at 785 nm in CH_2Cl_2. The fluorescence emission



Scheme 1 Synthetic routes toward $(R^1{}_3SiO)_2SiNc(SR^2)_4$ **1**

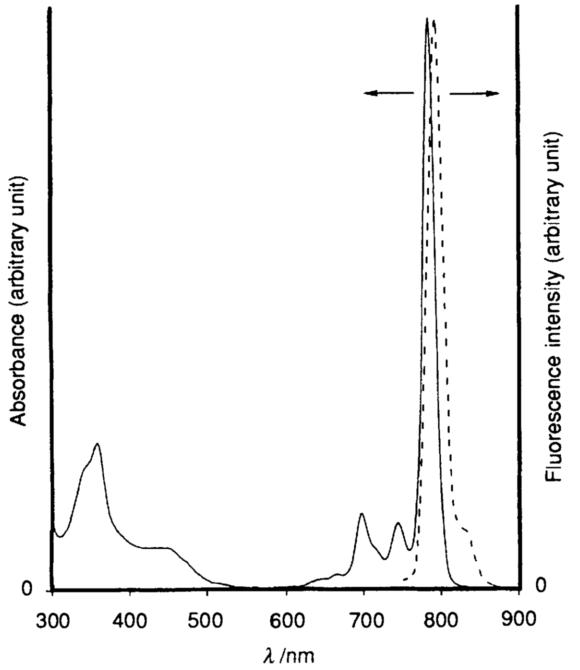


Fig. 2 Electronic absorption (——) and fluorescence emission ( ) (excited at 700 nm) spectra of **ME10** in CH_2Cl_2 solution

maximum from the corresponding transition was observed at 791 nm. These absorptions and fluorescence emission spectra have good mirror image correlation. Q-band absorption spectra in solutions of various concentrations obeyed the Beer–Lambert law. Other **1** also showed similar electronic absorption and fluorescence emission spectra. All **1** revealed sharp ^1H NMR signals which were easily assignable. These results indicate that all **1** are monomeric in solution. The Q-band maximum observed at 785 nm is typical for the monomeric state of **1**.

In contrast, all Q-band absorption maxima of **1** in solid films showed red shifts from the monomeric Q-band maximum (785 nm). The red-shift values ($\Delta\lambda$/nm) are shown in Fig. 3. Generally, the $\Delta\lambda$ values became larger with decreasing R^1 chain length. It seems that the steric bulkiness of the axial trialkylsiloxy group ($R^1{}_3SiO$) determines the extent of intermolecular interactions between molecules of **1** in thin films. A similar red shift was observed in adjacent weak Q-bands.*

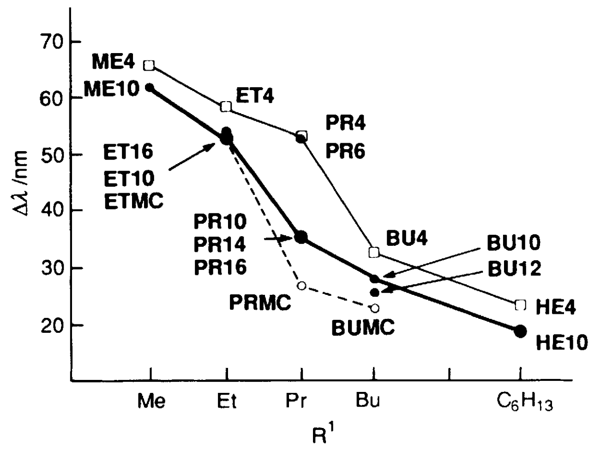


Fig. 3 Red shift values ($\Delta\lambda$) for $(R^1{}_3SiO)_2SiNc(SR^2)_4$ in thin films

According to the exiton model,[9] the spectral shift value ($\Delta\nu$) of coplanar molecules such as Ncs is given by eqn. (1), where N

$$\Delta\nu = (N - 1)\cdot N^{-1}\cdot h^{-1}\cdot|M|^2\cdot(1 - 3\cos^2\theta)\cdot r^{-3} \quad (1)$$

is the degree of aggregation, h is Planck's constant, M is the transition dipole moment of the monomer, r is the centre-to-centre distance between molecules, and θ is the tilt angle between the polarization axis of a unit molecule and the line connecting the molecular centres. In the region $90° > \theta > 54.7°$, $\Delta\nu$ has a positive value which means blue shifts of absorption spectra. The blue shifts of Nc induced by formation of H-aggregates are discussed elsewhere.[5] In the situation $54.7° > \theta > 0$, $\Delta\nu$ has a negative value which represents red shifts of spectra. Our observation of red shifts suggests that all **1** have slipped J-type molecular arrangement in thin solid films as shown in Fig. 4.

To discuss the dependence of $\Delta\lambda$ on the chain length of R^1 in detail, the absorption spectra of a series of $(R^1{}_3SiO)_2SiNc(SC_{10}H_{21})_4$ in solid films are shown in Fig. 5. The red-shift

---

* It is well known that J aggregates exhibit spectral red shifts (probably 'J' for Jelley, one of the first workers to investigate these shifts), whereas the blue-shifted aggregates are designated as 'H' aggregates (H for hypsochromic).

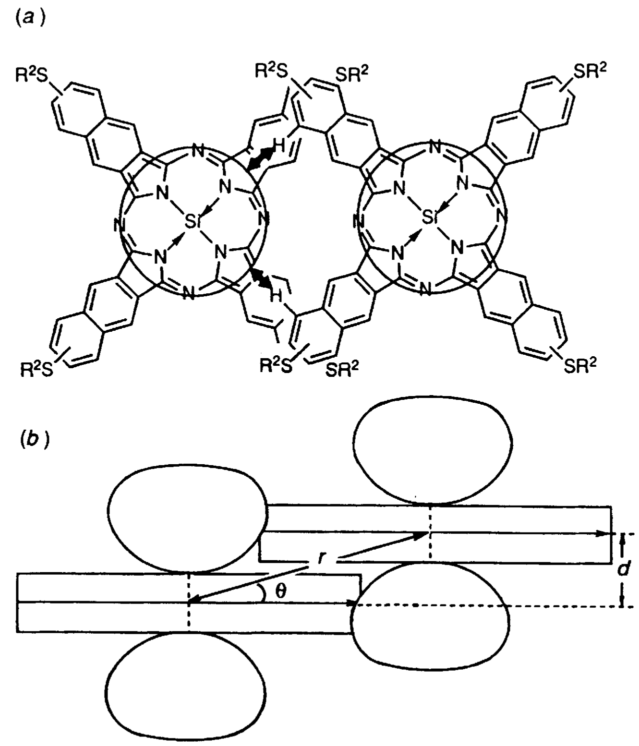


Fig. 4 Schematic diagram of presumed J-type slipped molecular arrangement of [$(R^1{}_3SiO)_2SiNc(SR^2)_4$] aggregate in thin film: (*a*) top view; (*b*) side view

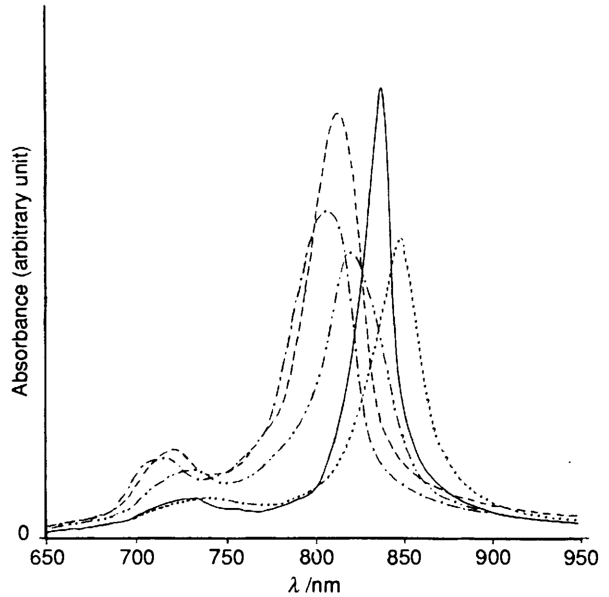


Fig. 5 Q-band absorption spectra of **ME10–HE10** in thin films: **ME10**, (- - - -); **ET10**, (——); **PR10**, (— - - —); **BU10**, (· - - -); **HE10**, (— - —)

values from the monomeric Q-band absorption in $\Delta\lambda$/nm and $\Delta\nu$/cm^{-1} are summarized in Table 1.

As shown in Fig. 4, the increase in R^1 chain length should induce steric repulsion between a $R^1{}_3SiO$ group of one Nc and two naphthalene rings of another. The dependence of $\Delta\nu$ on R^1 chain length can be explained using the exiton model. Interplanar spacing (*d*) is given by eqn. (2). Here, *d* for

$$d = r \cdot \sin\theta \qquad (2)$$

$(R^1{}_3SiO)_2SiNc(SR_{10}H_{21})_4$ is assumed to be 4.0 Å based on *d* values described in the literature.[10] Since *N* is considered to be sufficiently large in thin films, eqn. (1) was simplified to eqn. (3).

Table 1 The red-shift value of $(R^1{}_3SiO)_2SiNc(SC_{10}H_{21})_4$ in thin films from the monomeric Q-band absorption

Compound	$\Delta\lambda$/nm	$\Delta\nu$/cm^{-1}
ME10	62	940
ET10	52	780
PR10	35	540
BU10	28	440
HE10	18	280

Table 2 Tilt angle (θ), estimated centre-to-centre intermolecular distance (*r*) and the related value ($1 - 3\cos^2\theta$) and r^{-3} estimated at the interplanar spacing of 4.0 Å

Compound	θ/°	$1 - 3\cos^2\theta$	r/Å	$r^{-3}/10^{20}$ cm^{-3}
ME10	20.3	−1.64	12.0	5.79
ET10	18.0	−1.71	13.2	4.35
PR10	16.0	−1.77	14.5	3.27
BU10	14.9	−1.80	15.6	2.63
HE10	12.7	−1.86	18.1	1.69

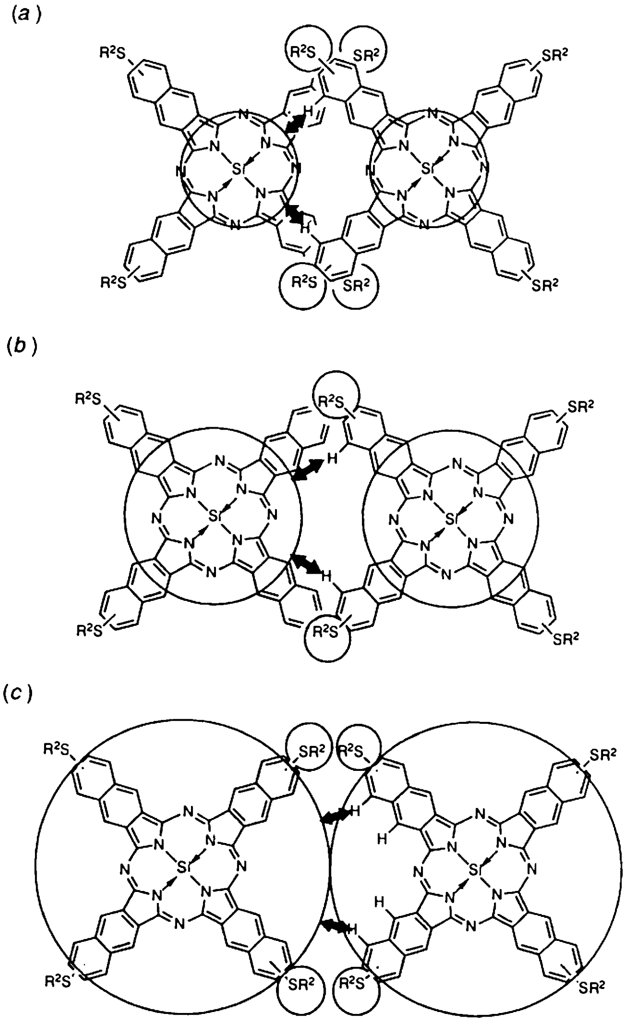


Fig. 6 Schematic diagram of presumed J-type slipped molecular arrangement of $(R^1{}_3SiO)_2SiNc(SR^2)_4$ aggregate in thin film. (*a*): R^1 = Me, Et (*b*): R^1 = Pr, (c): R^1 = C_6H_{13}.

$$\Delta\nu = h^{-1} \cdot |M|^2 \cdot (1 - 3\cos^2\theta) \cdot r^{-3} \qquad (3)$$

Then, *M* can be determined experimentally from the integrated absorption coefficient of the Q-band. The average *M* value for

Table 3 Details of reaction conditions for preparation of **1**

Condition	**ME10**	**ET10**	**PR10**	**BU10**	**HE10**
7b (g mmol^{-1})	0.8/0.6	9.3/6.4	21/14.5	15.5/10.6	1/0.7
Reagent	Me_3SiOH	Et_3SiOH	Pr_3SiCl	Bu_3SiOH	$(C_6H_{13})_3SiCl$
(g mmol^{-1})	0.8/9	13.8/105	18.5/96	21/80	0.9/2.7
Additive	none	none	Bu_3N (56 cm^3)	none	none
Solvent	quinoline	PhCl	quinoline	PhCl	pyridine
(cm^3)	40	615	700	500	80
Temp/°C	180	reflux	150	reflux	reflux
Time/h	2	5.5	1.5	10.5	1

Condition	**ME4**	**ET4**	**PR4**	**BU4**	**HE4**
7b (g mmol^{-1})	8/7.1	8/7.1	8/7.1	16/14.2	8/7.1
Reagent	Me_3SiOH	Et_3SiOH	Pr_3SiCl	Bu_3SiOH	$(C_6H_{13})_3SiCl$
(g mol^{-1})	5/56	4.4/34	4.4/23	59/234	5/16
Additive	none	none	Bu_3N (25 cm^3)	none	none
Solvent	quinoline	quinoline	quinoline	quinoline	quinoline
(cm^3)	200	200	200	960	200
Temp/°C	180	180	150	reflux	150
Time/h	2	2	1.5	3.5	2

Condition	**ET16**	**PR6**	**ETMC**	**PRMC**	**BUMC**
7b (g mol^{-1})	13.9/7.7	10/8.1	1.7/1.3	1.7/1.3	1.7/1.3
Reagent	Et_3SiOH	Pr_3SiCl	Et_3SiOH	Pr_3SiCl	Bu_3SiOH
(g mol^{-1})	17.2/131	8.8/46	2.2/16	2.6/14	3.1/12
Additive	none	Bu_3N (25 cm^3)	none	Bu_3N (56 cm^3)	none
Solvent	PhCl	quinoline	quinoline	quinoline	quinoline
(cm^3)	500	300	70	100	70
Temp./°C	reflux	150	180	150	200
Time/h	24	2	2	2	2

1 was 21.5 D. From $\Delta\nu$, d, and the average M value, θ and r were estimated by using eqns. (2) and (3) as summarized in Table 2, together with values of $(1 - 3\cos^2\theta)$ and r^{-3}. These estimated θ and r are considered to be averaged values for **1** of various J-type arrangements in thin solid films, and enabled us to estimate the average arrangement favoured by each compound **1**. With increasing R^1 chain length of the axial substituent ($R^1{}_3SiO$) r increases and θ decreases. The values of the $(1 - 3\cos^2\theta)$ term, however, changed only slightly when R^1 chain length increased from methyl to hexyl (**ME10–HE10**), although there were significant changes in $\Delta\nu$, almost proportional to the r^{-3} value. Consequently, it was concluded that the red-shift value ($\Delta\nu$) is mainly dependent on centre-to-centre distance (r), which is controlled by the chain length of R^1.

As seen from Fig. 3, $\Delta\lambda$ decreased with an increase in the length of the ring substituents, R^2. An increase in the steric bulkiness of the R^2 group could increase the interplanar spacing (d), which naturally increases r and θ. An increase of both r and θ should decrease $\Delta\nu$ according to eqn. (3). In particular, $\Delta\lambda$ values of $(Pr_3SiO)_2SiNc(SR^2)_4$ were highly sensitive to R^2 bulkiness compared with those of other **1** [R^1 = Me, Et, Bu, C_6H_{13}].

These findings can be interpreted by the schematic representations of three types of molecular arrangements for **1** in thin films as shown in Fig. 6. In $(Me_3SiO)_2SiNc(SR^2)_4$ and $(Et_3SiO)_2SiNc(SR^2)_4$, the steric requirement of the R^2 group would not be large enough to create a large dependence on $\Delta\lambda$ because two R^2 groups of one Nc molecule would not be located close to those of another molecule due to the small steric bulkiness of their $R^1{}_3SiO$ group as shown in Fig. 6(*a*). In $[(C_6H_{13})_3SiO]_2SiNc(SR^2)_4$, the dependence of $\Delta\lambda$ on the R^2 group is also small because molecules are located distinctly far from each other as shown in Fig. 6(*c*), due to the high steric requirement of the $(C_6H_{13})_3SiO$ group. In contrast, in thin films of $(Pr_3SiO)_2SiNc(SR^2)_4$, alkylthio groups (SR^2) are located close to each other, as shown in Fig. 6(*b*), owing to the steric repulsion between the naphthalene ring and the Pr_3SiO groups of intermediate bulkiness, so that $\Delta\lambda$ of $(Pr_3SiO)_2SiNc(SR^2)_4$ is highly sensitive to the bulkiness of R^2. As we would expect, a sterically more hindered R^2 group, such as the 4-methylcyclohexyl derivative of $(Pr_3SiO)_2SiNc(SR^2)_4$, resulted in a significant decrease of $\Delta\lambda$ as shown in Fig. 3. This observation supports the fact that $(Pr_3SiO)_2SiNc(SR^2)_4$ molecules in thin films are located as represented in Fig. 6(*b*). The findings from a series of $(Bu_3SiO)_2SiNc(SR^2)_4$ should have intermediate properties between $(Pr_3SiO)_2SiNc(SR^2)_4$ and $[(C_6H_{13})_3SiO]_2SiNc(SR^2)_4$.

On the other hand, no significant shifts were observed in Soret bands of the spectra of **1**. Although these results still remain to be clarified, they may have resulted from the various properties of the transition dipole moments, such as different directions of the dipole between S_0–S_1 (Q-band) and S_0–S_2 (Soret-band).

Conclusions

It is suggested that Ncs which have two axial substituents ($R^1{}_3SiO$) on the central metal as well as four ring substituents (SR^2) have a J-type molecular arrangement in solid films, exhibiting a red shift of Q-band absorption, whereas monomeric spectra were observed in solution. The intermolecular centre-to-centre distance of Nc molecules in solid films could be dependent mainly on steric repulsion between an $R^1{}_3SiO$ groups of one Nc and two naphthalene rings of an adjacent Nc molecule. The size of the SR^2 groups has some effect on the molecular arrangement when the SR^2 groups of one Nc are located close to the SR^2 groups of the other, as in $(Pr_3SiO)_2SiNc(SR^2)_4$.

Experimental

Apparatus.—All melting points were determined with a

Table 4 Physical properties of **1**

	ME10	**HE10**	**ME4**	**ET4**	**PR4**	**BU4**
Yield (%)	45	28	27	32	29	26
M.p./°C	273–275	43–46	>300	>300	297–299	233–234
Molecular formula	$C_{94}H_{122}N_8Si_3O_2S_4$	$C_{124}H_{182}N_8Si_3O_2S_4$	$C_{70}H_{74}N_8Si_3O_2S_4$	$C_{76}H_{86}N_8Si_3O_2S_4$	$C_{82}H_{98}N_8Si_3O_2S_4$	$C_{88}H_{110}N_8Si_3O_2S_4$
Found (%)	C, 69.7; H, 7.7; N, 7.0; S, 8.0	C, 73.05; H, 9.2; N, 5.7; S. 6.0	C, 66.2; H, 6.0; N, 8.85; S, 9.9	C, 66.9; H, 6.4; N, 7.95; S, 9.3	C, 68.5; H, 6.6; N, 7.7; S, 8.9	C, 69.2; H, 7.35; N, 7.2; S, 8.2
Requires (%)	C, 70.2; H, 7.65; N, 6.8; S, 8.0	C, 73.4; H, 9.0; N, 5.3; S, 6.3	C, 66.1; H, 5.9; N, 8.8; S, 10.1	C, 67.3; H, 6.4; N, 8.3; S, 9.5	C, 68.4; H, 6.9; N, 7.8; S, 8.9	C, 69.3; H, 7.3; N, 7.35; S, 8.4
ν_{max}(KBr)/cm^{-1}	1360, 1080	1355, 1080	1360, 1080	1355, 1080	1355, 1080	1340, 1070
λ_{max}(CH_2Cl_2)/nm (log ε)	784 (5.7), 744 (4.8), 697 (4.8), 357 (5.1)	784 (5.7), 743 (4.8) 697 (4.8), 358 (5.1)	784 (5.7), 744 (4.8), 697 (4.8), 357 (5.1)	784 (5.7), 743 (4.8), 697 (4.8), 358 (5.1)	784 (5.7), 744 (4.8), 697 (4.8), 357 (5.1)	784 (5.7), 744 (4.8), 697 (4.8), 357 (5.1)
δ_H (250 MHz; $CDCl_3$)	−2.44 (18 H, s, Me_3SiO), 0.89 (12 H, m, SC_9H_{18}-CH_3), 1.32 (48 H, m, SC_3H_6-$\mathit{C}_6\mathit{H}_{12}$-$CH_3$), 1.62 (8 H, m, SC_2H_4-CH_2-C_7H_{15}), 1.92 (8 H, quintet, *J* 7.32, SCH_2-CH_2-C_8H_{17}), 3.29 (8 H, t, *J* 7.32, S-CH_2-C_9H_{19}), 7.80 (4 H, dd, *J* 8.54, 1.22, Ar-7-H), 8.41 (4 H, brs, Ar-5-H), 8.50 (4 H, d, *J* 8.54, Ar-8-H), 9.93 (4 H, brs, Ar-1-H), 10.0 (4 H, brs, Ar-4-H).	−2.08 [12 H, m, (C_5H_{11}-CH_2)$_3$SiO], −1.00 [12 H, m, (C_4H_9-CH_2-CH_2)$_3$SiO), 0.06 [12 H, m, (C_3H_7-CH_2-C_2H_4)$_3$SiO], 0.23 [12 H, m, (C_2H_5-CH_2-C_3H_6)$_3$SiO], 0.43 [18 H, t, *J* 7.32, (CH_3-C_5H_{10})$_3$SiO], 0.62 [12 H, m, (CH_3-CH_2-C_4H_8)$_3$ SiO], 0.90 (12 H, m), 1.33 (48 H, m), 1.63 (8 H, m), 1.92 (8 H, quintet, *J* 7.32), 3.28 (8 H, t, *J* 7.32), 7.80 (4 H, dd, *J* 8.54, 1.22), 8.46 (4 H, brs), 8.52 (4 H, d, *J* 8.54), 9.95 (4 H, brs), 10.00 (4 H, brs).	−2.44 (18 H, s), 1.08 (12 H, t, SC_3H_6-CH_3), 1.65 (8 H, sextet, *J* 7.32, SC_2H_4-CH_2-CH_3), 1.92 (8 H, quintet, *J* 7.32, SCH_2-CH_2-C_2H_5), 3.29 (8 H, t, *J* 7.32, S-CH_2-C_9H_{19}), 7.80 (4 H, dd, *J* 8.54, 1.83), 8.45 (4 H, brs), 8.50 (4 H, d, *J* 8.54), 9.93 (4 H, brs), 10.00 (4 H, brs).	−2.09 (12 H, q, *J* 7.32), −1.02 (8 H, t, *J* 7.32), 1.09 (12 H, t, *J* 7.32), 1.69 (8 H, sextet, *J* 7.32), 1.93 (8 H, quintet, *J* 7.32), 3.31 (8 H, t, *J* 7.32), 7.81 (4 H, dd, *J* 8.54, 1.83), 8.45 (4 H, brs), 8.53 (4 H, d, *J* 8.54), 9.97 (4 H, brs), 10.02 (4 H, brs).	−2.06 (12 H, m), −0.84 (12 H, m), −0.27 (18 H, t, *J* 7.32), 1.09 (12 H, t, *J* 7.32), 1.69 (8 H, sextet, *J* 7.32), 1.93 (8 H, quintet, *J* 7.32), 3.31 (8 H, t, *J* 7.32), 7.80 (4 H, dd, *J* 8.54, 1.83), 8.45 (4 H, brs), 8.54 (4 H, d, *J* 8.54), 9.96 (4 H, brs), 10.00 (4 H, brs)	−2.03 (12 H, m), −0.97 (12 H, m), 0.00 (30 H, m), 1.08 (12 H, t, *J* 7.32), 1.65 (8 H, sextet, *J* 7.32), 1.92 (8 H, quintet *J* 7.32), 3.31 (8 H, t, *J* 7.32), 7.80 (4 H, dd, *J* 8.54, 1.83), 8.45 (4 H, brs), 8.52 (4 H, d, *J* 8.54), 9.95 (4 H, brs), 10.00 (4 H brs)

Yanagimoto micro melting point apparatus and were uncorrected. The electronic absorption, fluorescence emission and IR spectra were obtained using a Hitachi U-3410 spectrometer, a Hitachi 850 fluorescence spectrometer, and a Hitachi 260–30 or a JEOL JIR-100 spectrometer, respectively. ^{1}H NMR spectra were measured with a Hitachi R-250 spectrometer and chemical shifts were recorded in ppm downfield from tetramethylsilane as an internal standard (δ scale). Coupling constants are in Hz. Elemental analyses were performed at the microanalytical laboratory of the Sagamihara Chemical Research Centre. Flash column chromatography was performed using Merck 60H silica gel.

Materials.—The synthetic procedure of route A has been fully described elsewhere.[11] That of route B was as follows.

Table 4 (*continued*)

	HE4	**ET16**
	45	29
	164–165	238.5–239.5
	$C_{100}H_{134}N_8Si_3O_2S_4$	$C_{124}H_{182}N_8Si_3O_2S_4$
	C, 70.7; H, 7.7; N, 7.0; S, 8.0	C, 73.3; H, 9.1; N, 5.6; S, 6.0
	C, 71.0; H, 8.0; N, 6.6; S, 7.6	C, 73.4; H, 9.0; N, 5.5; S, 6.3
	1360, 1080	1345, 1075
	784 (5.7), 744 (4.8), 697 (4.8), 357 (5.1)	784 (5.7), 743 (4.8), 697 (4.8), 358 (5.1)
	−2.08 (12 H, m), −1.00 (12 H, m), 0.06 (12 H, m), 0.23 (12 H, m), 0.43 (18 H, m), 0.62 (12 H, m), 1.08 (12 H, t, *J* 7.32), 1.65 (8 H, sextet, *J* 7.32), 1.92 (8 H, quintet, *J* 7.32), 3.29 (8 H, t, *J* 7.32), 7.80 (4 H, dd, *J* 8.54, 1.83), 8.46 (4 H, brs), 8.52 (4 H, d, *J* 8.54), 9.95 (4 H, brs), 10.00 (4 H, brs).	−2.05 (12 H, q, *J* 7.94), −1.01 (18 H, t, *J* 7.94), 0.86 (12 H, m), 1.25 (96 H, m), 1.64 (8 H, m), 1.93 (8 H, quintet, *J* 7.32), 3.29 (8 H, t, *J* 7.32), 7.81 (4 H, dd, *J* 8.85, 1.83), 8.44 (4 H, brs), 8.53 (4 H, d, *J* 8.85), 9.96 (4 H, brs), 10.02 (4 H, brs)
	PR6	**ETMC**
	31	33
	243–246	>300
	$C_{90}H_{114}N_8Si_3O_2S_4$	$C_{88}H_{102}N_8Si_3O_2S_4$
	C, 69.45; H, 7.5; N, 7.2; S, 8.0	C, 69.6; H, 6.9; N, 7.2; S, 8.35
	C, 69.6; H, 7.4; N, 7.2; S, 8.3	C, 69.7; H, 6.8; N, 7.4; S, 8.5
	1360, 1080	1350, 1080
	784 (5.7), 744 (4.8), 697 (4.8), 357 (5.1)	784 (5.7), 743 (4.8), 697 (4.8), 358 (5.1)
	−2.06 (12 H, m), −0.84 (12 H, m), −0.27 (18 H, t, *J* 7.32), 0.98 (12 H, m), 1.45 (16 H, m), 1.65 (8 H, t, *J* 7.32), 1.94 (8 H, quintet, *J* 7.32), 3.30 (8 H, t, *J* 7.32), 7.80 (4 H, dd, *J* 8.85, 1.52), 8.45 (4 H, brs), 8.53 (4 H, d, *J* 8.85), 9.96 (4 H, brs), 10.01 (4 H, brs).	−2.07 (12 H, q, *J* 7.94), −1.01 (18 H, t, *J* 7.94), 0.98–2.35 (48 H, m), 3.96–4.09 (4 H, m), 7.86 (4 H, dd, *J* 8.85, 1.84), 8.53 (4 H, d, *J* 8.85), 8.55 (4 H, brs), 9.98 (4 H, brs), 10.03 (4 H, brs)
	PRMC	**BUMC**
	77	34
	>300	260–263
	$C_{94}H_{114}N_8Si_3O_2S_4$	$C_{100}H_{126}N_8Si_3O_2S_4$
	C, 70.4; H, 7.2; N, 6.95; S, 8.1	C, 71.6; H, 7.65; N, 6.6; S, 7.3
	C, 70.5; H, 7.2; N, 7.0; S, 8.0	C, 71.3; H, 7.5; N, 6.7; S, 7.6
	1350, 1080	1350, 1080
	784 (5.7), 744 (4.8), 697 (4.8), 357 (5.1)	784 (5.7), 743 (4.8), 697 (4.8), 358 (5.1)
	−2.06 (12 H, m), −0.85 (12 H, m), −0.26 (18 H, t, *J* 7.32), 0.98–2.35 (48 H, m), 3.96–4.10 (4 H, m), 7.86 (4 H, d, *J* 8.85), 8.53 (4 H, d, *J* 8.85), 8.55 (4 H, brs), 9.98 (4 H, brs), 10.03 (4 H, brs)	−2.02 (12 H, m), −0.96 (12 H, m), 0.00 (30 H, m), 0.99–2.16 (48 H, m), 3.99–4.11 (4 H, m), 7.86 (4 H, dd, *J* 8.85, 1.53), 8.54 (4 H, d, *J* 8.85), 8.56 (4 H, brs), 9.97 (4 H, brs), 10.01 (4 H, brs)

General Procedure for Preparation of 6-*Alkylthio*-2,3-*dicyanonaphthalene* **4b**.—A mixture of cuprous alkylthiolate (160 mmol) synthesized according to the known procedure[12] and 6-bromo-2,3-dicyanonaphthalene[13] (78 mmol) in quinoline (400 cm^3) and pyridine (130 cm^3) was heated under reflux for 6 h. The reaction mixture was allowed to cool and then poured into a mixture of water (750 cm^3) and methanol (750 cm^3). The reddish brown solid was purified by chromatography on silica gel with toluene–chloroform solution as the eluent followed by recrystallization from toluene–hexane to obtain the *title compound* **4b** as a colourless powder.

Physical properties of 6-*alkylthio*-2,3-*dicyanonaphthalene* **4b**. 6-Decylthio-2,3-dicyanonaphthalene. Yield 53%, m.p. 117–118 °C (Found: C, 74.4; H, 7.5; N, 8.0; S, 9.15. $C_{22}H_{26}N_2S$ requires: C, 74.6; H, 7.3; N, 7.9; S, 9.1%); ν_{max}(KBr)/cm^{-1} 2200 (CN); δ_H(250 MHz; CDCl$_3$) 0.88 (3 H, t, *J* 6.7, SC$_9$H$_{18}$-*CH*$_3$), 1.27 (12 H, brs, SC$_3$H$_6$-*C*$_6$*H*$_{12}$-CH$_3$), 1.50 (2 H, m, SC$_2$H$_4$-*CH*$_2$-C$_7$H$_{15}$), 1.76 (2 H, quintet, *J* 7.32, SCH$_2$-*CH*$_2$-C$_8$H$_{17}$), 3.09 (2 H, t, *J* 7.32, S-*CH*$_2$-C$_9$H$_{19}$), 7.63 (1 H, dd, *J* 8.55, 1.83, Ar-7-H), 7.65 (1 H, brs, Ar-5-H), 7.82 (1 H, d, *J* 8.54, Ar-8-H), 8.19 (1 H, s, Ar-1-H) and 8.25 (1 H, s, Ar-4-H).

6-*Hexylthio*-2,3-*dicyanonaphthalene*. Yield 52%, m.p. 141–142.5 °C (Found: C, 73.9; H, 6.2; N, 9.3; S, 10.5. $C_{18}H_{18}N_2S$ requires: C, 73.4; H, 6.2; N, 9.5; S, 10.9%); ν_{max}(KBr)/cm^{-1} 2230 (CN); δ_H(250 MHz; CDCl$_3$) 0.91 (3 H, t, *J* 7.32, SC$_5$H$_{10}$-*CH*$_3$), 1.3–1.4 (4 H, m, SC$_3$H$_6$-*C*$_2$*H*$_4$-CH$_3$), 1.43–1.57 (2 H, m, SC$_2$H$_4$-*CH*$_2$-C$_3$H$_7$), 1.76 (2 H, quintet, *J* 7.32, SCH$_2$-*CH*$_2$-C$_4$H$_9$), 3.09 (2 H, t, *J* 7.32, S-*CH*$_2$-C$_5$H$_{11}$), 7.60 (1 H, dd, *J* 8.54, 1.52), 7.64 (1 H, brs), 7.82 (1 H, d, *J* 8.54), 8.19 (1 H, s) and 8.25 (1 H, s).

6-*Butylthio*-2,3-*dicyanonaphthalene*. Yield 70%, m.p. 134.5–136 °C (Found: C, 72.05; H, 5.2; N, 10.5; S, 12.1. $C_{16}H_{14}N_2S$

requires: C, 72.1; H, 5.3; N, 10.5; S, 12.0%); ν_{max}(KBr)/cm^{-1} 2210 (CN); δ_H(250 MHz; CDCl$_3$) 0.98 (3 H, t, *J* 7.32, SC_3H_6-CH_3), 1.53 (2 H, sextet, *J* 7.32, SC_2H_4-CH_2-CH_3), 1.76 (2 H, quintet, *J* 7.32, SCH_2-CH_2-C_2H_5), 3.10 (2 H, t, *J* 7.32, S-CH_2-C_3H_7), 7.62 (1 H, dd, *J* 8.54, 1.83), 7.64 (1 H, brs), 7.82 (1 H, d, *J* 8.54), 8.19 (1 H, s) and 8.25 (1 H, s).

6-*Hexadecylthio*-2,3-*dicyanonaphthalene*. Yield 58%, m.p. 120–121 °C (Found: 77.45; H, 8.9; N, 6.4; S, 7.5. $C_{28}H_{38}N_2S$ requires: C,77.4; H, 8.8; N, 6.4; S, 7.4%); ν_{max}(KBr)/cm^{-1} 2200 (CN); δ_H(250 MHz; CDCl$_3$) 0.88 (3 H, t, *J* 6.7, $SC_{15}H_{30}$-CH_3), 1.25 (24 H, brs, SC_3H_6-$C_{12}H_{24}$-CH_3), 1.50 (2 H, m, SC_2H_4-CH_2-$C_{13}H_{27}$), 1.76 (2 H, quintet, *J* 7.32, SCH_2-CH_2-$C_{14}H_{29}$), 3.09 (2 H, t, *J* 7.32, S-CH_2-$C_{15}H_{31}$), 7.62 (1 H, dd, *J* 8.55, 1.83), 7.64 (1 H, brs), 7.82 (1 H, d, *J* 8.55), 8.19 (1 H, s) and 8.25 (1 H, s).

6-(4-*Methylcyclohexyl*)*thio*-2,3-*dicyanonaphthalene*. Yield 46%, m.p. 129–131 °C (Found: C, 74.3; H, 6.0; N, 9.0; S, 10.4. $C_{19}H_{18}N_2S$ requires: C, 74.5; H, 5.9; N, 9.1; S, 10.5%); ν_{max}(KBr)/cm^{-1} 2220 (CN); δ_H(250 MHz; CDCl$_3$) 0.95 (3 H, m, $SCH(C_2H_4)_2CH(CH_3)$, 1.08 (1 H, m, $SCH(C_2H_4)_2CH$-Me), 1.3–2.1 (8 H, m, $SCH(C_2H_4)_2CH$-Me), 3.79–3.92 (1 H, m, S-$CH(C_2H_4)_2CH$-CH_3), 7.65 (1 H, d, *J* 8.54), 7.73 (1 H, brs), 7.83 (1 H, d, *J* 8.54), 8.19 (1 H, s) and 8.25 (1 H, s).

General Procedure for Preparation of Dihydroxysilicon Naphthalocyanine Derivatives **7b**.—*Preparation of* 6-*alkylthio*-1,3-*diiminobenz*[f]*isoindoline* **5b**. Compound **4b** (34 mmol) was added to a methanol solution of sodium methoxide prepared by dissolving sodium (74 mmol) in absolute methanol (70 cm^3). The mixture was heated under reflux for 2 h with bubbling of anhydrous NH_3 and then allowed to cool. The solid precipitated was filtered, washed with ethanol and then hexane, and dried *in vacuo* to obtain a yellow solid (yield > 85%). The yellow solid was confirmed to consist of mainly the *title compound* **5b** by its IR spectrum [ν_{max}(KBr)/cm^{-1} 3200 (NH), 3350 (NH) and 1470 (–C=N–)] and was used for the subsequent reaction without further purification.

Preparation of $Cl_2SiNc(SR^2)_4$ **6b**. A mixture of compound **5b** (27.2 mmol) and $SiCl_4$ (130 mmol) in dry quinoline (100 cm^3) was heated at 220 °C for 3 h and then allowed to cool. The reaction mixture was poured into methanol (500 cm^3). The precipitated solid was filtered, washed with ethanol, and dried *in vacuo* to obtain a green solid (yield > 88%). The green solid was confirmed to consist of mainly the *title compound* **6b** by its electronic absorption spectrum [λ_{max}(THF)/nm 835] and was used for the subsequent reaction without further purification.

Preparation of $(HO)_2SiNc(SR^2)_4$ **7b**. A mixture of compound **6b** (6.69 mmol), ethanol (200 cm^3) and concentrated aqueous ammonia (200 cm^3) was heated under reflux for 3 h and then allowed to cool. The solid was filtered, washed with ethanol and dried *in vacuo* to obtain a dark green solid (yield quantitative). The dark green solid was confirmed to consist of mainly the *title compound* **7b** by its electronic absorption spectrum [λ_{max}(THF)/nm 784] and was used for subsequent reaction without further purification.

General Procedure for Preparation of $(R^1{}_3SiO)_2SiNc(SR^2)_4$ **1**.—A mixture of $(HO)_2SiNc(SR^2)_4$ **7b**, reagents and additives in the solvents described in Table 3 was heated. After cooling, the reaction mixture was poured into methanol. The precipitated green solid was filtered, washed with methanol and dried *in vacuo*. The solid was purified by column chromatography on silica gel followed by recrystallization to obtain the *title compound* **1** as a green powder. Detailed reaction conditions are summarized in Table 3. The physical properties of **1** are summarized in Table 4. The physical properties of **ET10, PR10, PR12, PR14, PR16, BU10** and **BU12** are fully described elsewhere.[11]

Preparation of Thin Solid Films.—Solutions (1.0 wt%, 0.5 cm^3) of **1** in tetrahydrofuran were dropped onto a pyrex glass plate of 1.2 mm thickness and then spin-coated using an ABLE ASS-300 spinner (1st, 1000 rpm × 10 s; 2nd, 2000 rpm × 10 s) at 20 °C. The thickness of the films were confirmed to be in the range 700–1000 Å using a Sloan Dektak 3030 surface profiler.

References

1 (*a*) M. Hanack, G. Rentz, J. Strahre and S. Schmid, *Chem. Ber.*, 1988, **121**, 1479; (*b*) M. Hanack, S. Deger, U. Keppeler, A. Lange, A. Leverenz and M. Rein, *Conducting Polymers*, 1987, 173; (*c*) M. Hanack, A. Lange, M. Rein, R. Behnisch, G. Renz and A. Leverenz, *Synthetic Metals*, 1989, **29**, F1.

2 (*a*) N. Q. Wang, Y. M. Cai, J. R. Hefflin and A. F. Garito, *Mol. Cryst. Liq. Cryst.*, 1990, **189**, 39; (*b*) A. F. Garito and J. W. Wu, *Proc. SPIE*, 1989, **1147**, 2.

3 D. E. Nikeles, K. Chiang, H. A. Goldberg, R. S. Kohn and F. J. Onorato, *Proc. SPIE*, 1990, **1248**, 65.

4 L. Q. Minh, T. Chot, N. N. Dinh, N. N. Xuan, N. T. Binh, D. M. Phuoc and N. T. Binh, *Phys. Stat. Sol.*, 1987, **101**, K143.

5 S. Tai and N. Hayashi, *J. Chem. Soc., Perkin Trans. 2*, 1991, 1275.

6 B. L. Wheeler, G. Nagasubramanian, A. J. Bard, L. A. Schechtman, D. R. Dininny and M. E. Kenny, *J. Am. Chem. Soc.*, 1984, **106**, 7404.

7 M. J. Cook, A. J. Dunn, S. D. Howe, A. J. Thomson and K. J. Harrison, *J. Chem. Soc., Perkin Trans. 1*, 1988, 2453.

8 S. Tai, S. Hayashida and N. Hayashi, USP 4 833 264, 1989 (*Chem. Abstr.*, 1989, **110**, 97173j).

9 (*a*) M. Kasha, M. A. El-bayoumi and W. Rhodes, *J. Chem. Phys.*, 1961, **58**, 916; (*b*) M. Kasha, H. R. Rawls and M. A. El-bayoumi, *Pure Appl. Chem.*, 1965, **11**, 371; (*c*) M. Kasha, *Radiation Research*, 1963, **20**, 55.

10 (*a*) S. Hyashida and N. Hayashi, *Chem. Lett.*, 1990, 2137–2140; (*b*) H. Yamagi, M. Ashida, J. Elbe and D. Wohrle, *J. Phys. Chem.*, 1990, **94**, 7056.

11 S. Tai, S. Hayashida, N. Hayashi, H. Hagiwara, M. Katayose, K. Kamijima, T. Akimoto, S. Era, S. Kobayashi and A. Mukoh. U. S. Pat. 5 034 309, 1991 (*Chem. Abstr.*, 1989, **111**, 105880a).

12 R. Adams, W. Reifschneider and A. Ferretti, *Org. Synth.*, Coll. Vol. 5, 1973, 107.

13 E. I. Kovshev, V. A. Puchnova and E. A. Luk'yanets, *Zh. Org. Khim.*, 1971, **7**, 369.

Paper 1/05266G
Received 16*th October* 1991
Accepted 20*th November* 1991