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Effect of Axial Substituents on the Aggregate of Silicon Naphthalocyanine in the Vacuum Deposited Thin Films

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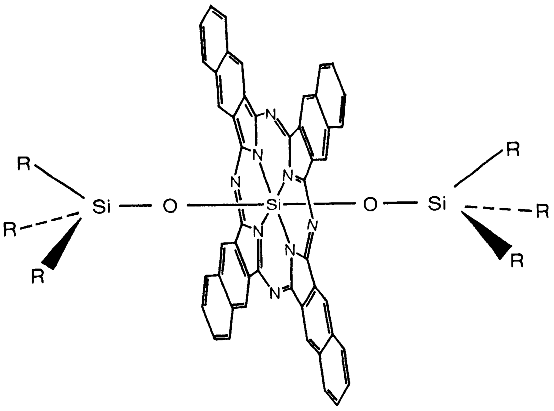
Studies on the electronic and FTIR spectra of bis(tri-n-alkylsiloxy)2,3-naphthalocyaninatosilicon complexes in the form of vacuum deposited thin films show an unambiguous stacking of naphthalocyanine molecules along the axial directions of the complexes with distances dependent on the bulkiness of alkyl substituents.

The optical and electrical properties of phthalocyanines (Pcs) relevant to their molecular structures have been studied extensively because of the widespread utility of Pcs in the field of material science. Metal-free and metal-ligated Pcs tend to be self-assembled into reasonably sized aggregates by weak van der Waals forces and/or weak electrostatic forces.[1,2] Then the orientation of molecules in the aggregates should have influence on their physical properties. In fact, Armstrong and co-workers have recently shown that trivalent and tetravalent metal Pcs in vacuum deposited thin films leads to red-shift of Q band when associated in a slipped arrangement.[3] On the other hand, naphthalocyanines (Ncs) which have greater conjugation rather than Pcs leads to a absorption maximum of Q-band in the near-infrared region. The wavelength of Q-band absorption of Ncs corresponds to that of diode laser, which is a useful light source for the application of electronic devices.

In this paper, we report the correlation between the electronic and FTIR spectra of silicon naphthalocyanines (SiNcs) in the vacuum deposited thin films and molecular structure with the help of differential scanning calorimetry and X-ray diffraction.

SiNcs were synthesized according to the procedure of Kenney[4] (Scheme 1). Each SiNc was evaporated from a Mo crucible onto an appropriate substrate kept at ambient temperature under the pressure of 4 x 10^{-4} Pa. The crucible temperature was kept at 470 °C for **1**, 410 °C for **2**, 370 °C for **3**, and 350 °C



1 ; R = C_2H_5
2 ; R = n-C_3H_7
3 ; R = n-C_4H_9
4 ; R = n-C_6H_{13}

Scheme 1.

for **4**. The thickness of films was about 200 nm for the measurement of electronic spectra and 500 nm for the measurement of FTIR spectra and differential scanning calorimetry.

The wavelength of maximum absorbance of four SiNcs, Q-band, in methylene chloride solution is 772 nm and independent of the length of alkyl chain in the axial substituents. The wavelength of maximum absorbance of each SiNc in the vacuum deposited thin film is considerably red shifted from the absorbance peak in solution; 820 nm for **1**, 810 nm for **2**, 807 nm for **3**, 779 nm for **4**.5) The magnitude of red-shift depends on the axial substituents. This result suggests that the spectral change arises from the difference in the distance between adjacent chromophores of the aggregate which is determined by an intermolecular interaction.

The thermogram obtained from the powder of **2** shows an endothermic peak at 399 °C, which corresponds to the melting point of this complex. On the other hand, the thermogram of **2** in the thin film which was prepared by vacuum deposition on the Au cell, shows a large exothermic peak in the corresponding temperature region. The endothermic peak observed with the powder is no longer visible in the thin film. Furthermore, the thermogram of the powder which was obtained by scratching off the vacuum deposited film is similar to the sum of the above two thermograms. The large exothermic peak observed in the vacuum deposited thin film appears to be due to the phase transition which may be attributed to the collapse of a stacking arrangement of silicon naphthalocyanine molecules.

The FTIR spectra of the KBr pellet and the thin film of **2** are given in Fig.1. The thin film was prepared by vacuum deposition on thallium substrate. We have assigned the three peaks in the region of 800 - 1050 cm^{-1} to Si-C stretching, CH_3 rock, and Si-O stretching modes based on the data of silicon phthalocyanines and **4**.4,6) The two peaks appeared in 700 - 800

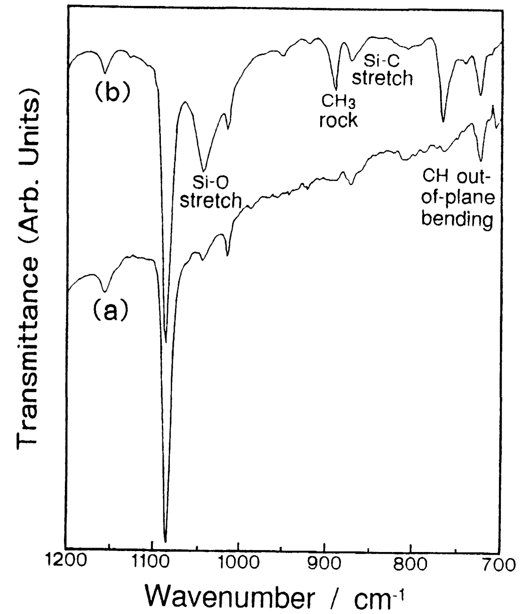


Fig.1. FTIR spectra of **2**.
(a) thin film deposited on thallium substrate and (b) KBr pellet.

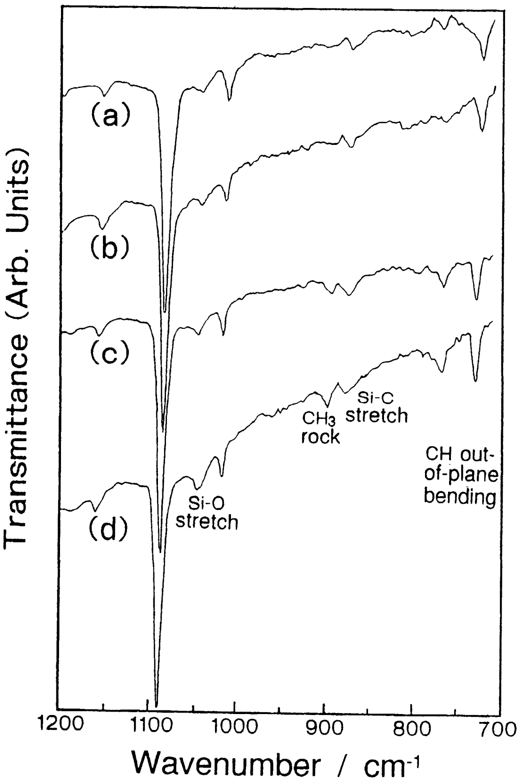


Fig.2. FTIR spectra of (a) **1**, (b) **2**, (c) **3**, and (d) **4** for thin films deposited on thallium substrate.

cm^{-1} may be assigned to C-H out-of-plane bending mode by reference to various phthalocyanines.7) The comparison of spectra shows that the bands due to Si-O stretching, CH_3 rock and one of C-H out-of-plane bending modes considerably collapse in the vacuum deposited thin film. This result clearly indicates that silicon naphthalocyanine molecules stack along the axial direction in the vacuum deposited thin film.

Fig.2 shows the FTIR spectra of **1**, **2**, **3**, and **4** in the vacuum deposited thin films. The intensities of three bands at 1043, 889, and 766 cm^{-1} similarly decrease with decreasing the length of alkyl chain in the axial substituents. As discussed above these bands can be assigned to Si-O stretching, CH_3 rock and C-H out-of-plane bending modes, respectively. These results suggest that there is an unambiguous stacking arrangement of silicon naphthalocyanine molecules in the vacuum deposited thin films in spite of the difference in the steric effect of the axial direction.

Table 1 shows the d-spacing of SiNcs obtained from X-ray diffraction of the thin films. Many phthalocyanines show strong reflection in the region corresponding to interplanar spacing of 3.3 to 3.7 Å.$^{1)}$ Therefore, we tentatively assigned the interplanar spacing of SiNcs to 3.49 Å for **1**, 3.50 Å for **2**, 3.54 Å for **3**, 3.63 Å for **4**. The result of X-ray diffraction seems to indicate that naphthalocyanine molecules are packed in an orderly fashion in the thin films.

Table 1. d-spacing of SiNcs obtained from X-ray diffraction in the thin films (Å)

1	10.83	8.70	4.43	4.11	3.86	3.49
2	11.07	8.55	4.38	4.13	3.85	3.50
3	10.62	9.80	4.41	4.03		3.54
4	10.20		4.32	4.14	3.86	3.63

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References

1) R. S. Nohr, P. M. Kuznesof, M. E. Kenney, and P. G. Siebenmann, *J. Am. Chem. Soc.*, **103**, 4371 (1981).

2) R. Aroca, *Spectrochim. Acta, Part A*, **41**, 1095 (1985).

3) T. D. Sims, J. E. Pemberton, P. Lee, and N. R. Armstrong, *Chem. Mater.*,**1**, 26 (1989).

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

5) The each solution obtained by dissolving the corresponding vacuum deposited film shows the same spectrum as the solution of the original SiNc. Therefore, we confirmed that the chemical and physical reaction such as elimination of the axial substituents dose not occur during the vacuum deposition.

6) R. Rafaeloff, F. J. Kohl, P. C. Krueger, and M. E. Kenney, *J. Inorg. Nucl. Chem.*, **28**, 899 (1966).

7) C. W. Dirk, T. Inabe, K. F. Schoch, Jr., and T. J. Marks, *J. Am. Chem. Soc.*, **105**, 1539 (1983); J. H. Sharp, and M. Abkowitz, *J. Phys. Chem.*, **77**, 477 (1973).

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