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Synthesis and Spectroscopic Properties of Germanium Naphthalocyanines

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Synopsis. Two novel naphthalocyanines, naphthalocyaninatobis(triethylsiloxy)germanium $GeNc[OSi(C_2H_5)_3]_2$ and naphthalocyaninatobis(tributylsiloxy)germanium $GeNc[OSi(n\text{-}C_4H_9)_3]_2$ were synthesized. These compounds had a strong absorption peak in the near-infrared; the absorption maximum of their evaporated films shifted to the long-wavelength side from the position in solution.

Naphthalocyanine compounds are receiving much interest because of their strong absorption bands in the near-infrared.[1] However, the naphthalocyanines that do not have a suitable substituent attached to the metal or to the naphthalocyanine ring are hardly soluble in any kind of organic solvent and can not be purified by recrystallization. Tetravalent metal naphthalocyanines are soluble in organic solvents if the trans groups attached to the metal are of a suitable kind. For example, the silicon naphthlocyanine, where the trans groups are trialkylsiloxy groups, is soluble in dichloromethane.[2,3] In this study we synthesized two novel naphthalocyanines, $GeNc[OSi(C_2H_5)]_2$ (**1**) and $GeNc[OSi(n\text{-}C_4H_9)_3]_2$ (**2**) (Fig. 1), and measured some of their spectroscopic properties.

Experimental

Compound **1** was prepared from 1*H*-benz(*f*)isoindole-1,3(2*H*)-diimine (**3**) by a modification of the published method[2] (Scheme 1). A mixture of **3** (10 g), germanium tetrachloride (10 ml), tri-*n*-butylamine (34 ml) and tetrahydronaphthalene (67 ml) was refluxed for 3 h. The product was washed repeatedly with methanol to give crude dichloro (naphtalocyaninato)germanium, $GeNcCl_2$ (**4**) (5.0 g). Compound **4** (5.0 g) was stirred with concentrated sulfuric acid for 3 h. The mixture was poured over crushed ice (500 g), and a green solid was filtered off and washed with water. This solid was heated with concentrated ammonia (180 ml) for 1.5 h at 100 °C to obtain dihydroxo(naphthalocyaninato) germanium $GeNc(OH)_2$ (**5**) (4.0 g). A mixture of **5** (0.4 g), triethylsilanol (0.2 ml) and chlorobenzene (20 ml) was refluxed for 1.5 h. The solid was filtered off and washed over methanol. Recrystallization of the product from chloroform gave **1** (0.17 g).[4] Compound **2** was synthesized in the same way.[5]

Results and Discussion

The color of **1**, **2**, **4**, and **5** is dark green. While **4** and **5** have very low solubilities in organic solvents, **1** and **2** have moderate solubilities. These properties can be understood in terms of the influence of trialkylsiloxy groups. Compounds **1** and **2** can be purified by means of recrystallization, allowing a clear absorption spectrum. The absorbtion spectrum of **1** in dichloromethane is shown in Fig. 2(a). Compound **1** has an absorbtion maximum at 779 nm (ε=317000). Thus, compound **1** has strong absorption bands in the near-infrared due to the widely spread π-electrons. The absorption

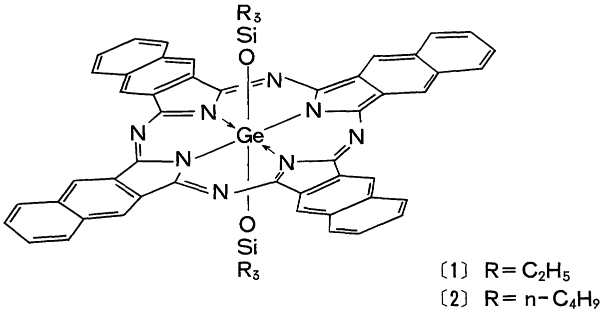
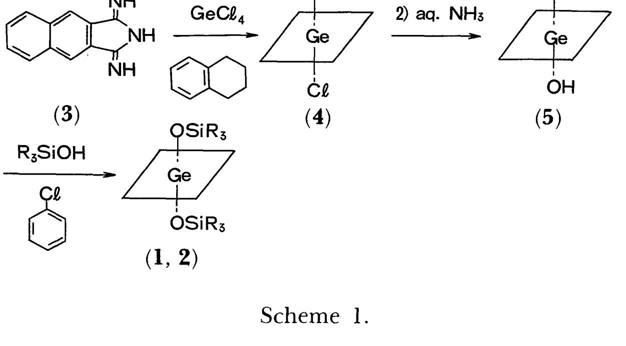


Fig. 1. Structure of germanium naphthalocyanine.



Scheme 1.

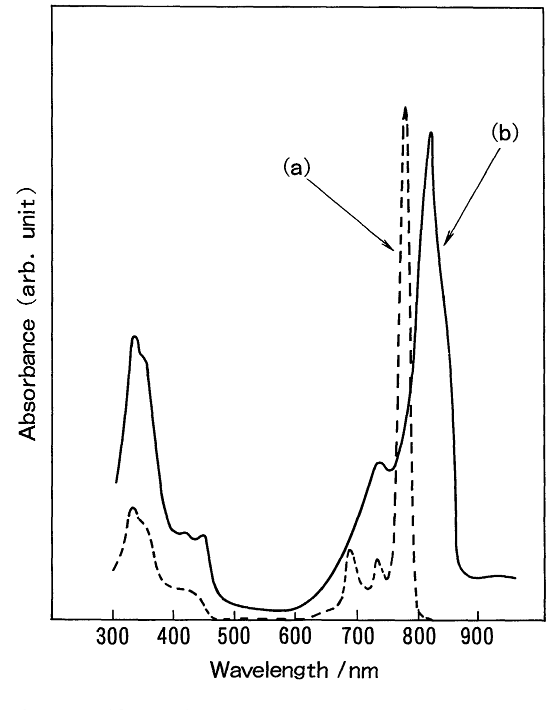


Fig. 2. Absorption spectrum of (a) $GeNc[OSi(C_2H_5)_3]_2$ in dichloromethane and (b) its evaporated film.

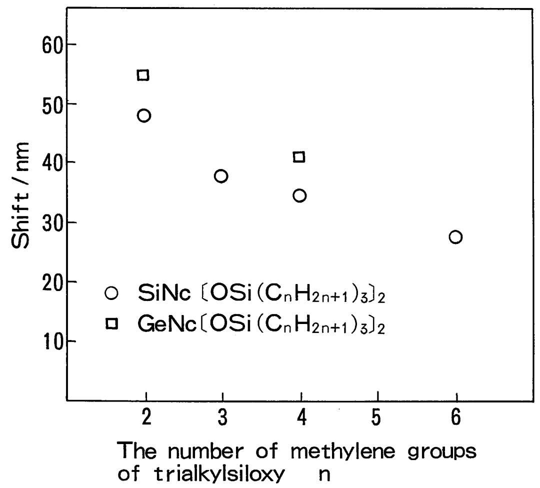


Fig. 3. The change of shift from the near-infrared absorption maximum of naphthalocyanine in solution to that of its evaporation film according to the number of carbon atoms of trialkylsiloxy groups.

maximum of **2** in dichloromethane is similar to that of **1** in dichloromethane. This absorption in the Q-band region appears to be composed of transitions from the ground state to two excited states.[2] Since the absorption maximum of **1** and **2** are equal, the transition does not depend on the size of the alkyl parts of the trialkylsiloxyl groups. On the other hand, the absorption spectrum depends on the species of the central metal. The absorption maximum of **1** and **2** shifts to the long-wavelength side (7 nm) relative to that of the corresponding silicon naphthalocyanine.[3] It is considered that decreasing the electronegativity of the central metal causes a shift of the charge onto the ring and increases the energy of the $a_{2u}(\pi)$HOMO.[6]

A film of **1**, about 100 nm thick on a glass slide, was prepared by vacuum evaporation at a pressure of 10^{-3} Pa. The absorption spectrum of a thin evaporated film of **1** is shown in Fig. 2.(b). This film exhibits a abroad near-infrared absorption peak at 834 nm and the absorption maximum is shifted to the long-wavelength side (55 nm) from that of **1** in solution. Similarly, the absorption maximum of **2** shifts to the long-wavelength side (41 nm) compared to that of **2** in solution. The same tendency was reported for silicon naphthalocyanine having trialkylsiloxy groups attached to the silicon atom.[3] This is shown in Fig. 3. The smaller the size of the alkyl parts of trialkylsioxy groups, the larger is the red-shift of the absorption maximum.

In the case of phthalocyanine, the absorption maximum shifts to the long-wavelength side with increasing pressure, and it is interpreted as being a van der Waal's (dispersion) interaction between neighboring molecules.[7] Similarly, in the case of naphthalocyanine, it is considered that smaller the size of the alkyl parts of the trialkylsiloxy groups, the larger is the intermolecular interaction between naphthalocyanine rings and the larger is the red-shift of the absorption maximum. The absorption maximum of a germanium naphthalocyanine film shifts even more to the long-wavelength side than does that of a silicon naphthalocyanine film when the trans groups attached to the metal are the same.

In conclusion, we have confirmed that germanium naphthalocyanines with trialkysiloxy groups have a strong absorption peak in the near-infrared and that the absorption maximum of their evaporated film shifts to the long-wavelength side from the position in solution. This shift depends on the size of the alkyl parts of the trialkylsiloxy groups and the central metal species.

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References

1) M. L. Kaplan, A. J. Lovinger, W. D. Reents, Jr., and P. H. Schmidt, *Mol. Cryst. Liq. Cryst.*, **112**, 345 (1984).

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

3) S. Hayashida, S. Tai, and N. Hayashi, 53th Autumn Meeting of the Chemical Society of Japan, October 1986, Abstr., No. 3X02.

4) **1**, Calcd for $C_{60}H_{54}N_8O_2Si_2Ge$: C, 68.77; H, 5.19; N, 10.69%. Found; C, 67.07; H, 4.90; N, 10.58%. ^1H NMR (200 MHz, $CDCl_3$) $\delta=-2.02$ (CH_2, 12H, q, $J=7.93$ Hz), -1.00 (CH_3, 18H, t, $J=7.93$Hz), 7.94 (6,7-Nc, 8H, dd, $J=6.10$, 3.05 Hz), 8.71 (5,8-Nc, 8H, dd, $J=6.10$, 3.05 Hz), 10.14 (1,4-Nc, 8H, s).

5) **2**, Calcd for $C_{72}H_{78}N_8O_2Si_2Ge$: C, 71.10; H, 6.46; N, 9.21%. Found: C, 71.03; H, 6.41; N, 9.41%. ^1H NMR (200 MHz, $CDCl_3$) $\delta=-1.99$ ($-CH_2$, 12H, t, $J=7.63$ Hz), -0.89 ($-CH_2$, 12H, q, $J=7.63$ Hz), -0.1—0.1 ($-CH_2$, CH_3, 30H, m), 7.94 (6,7-Nc, 8H, dd, $J=6.10$, 3.35 Hz), 8.68 (5,8-Nc, 8H, dd, $J=6.10$, 3.35 Hz), 10.12 (1,4-Nc, 8H, s).

6) C. W. Dirk T. Inabe, K. F. Schoch, Jr., and T. J. Marks, *J. Am. Chem. Soc.*, **105**, 1539 (1983).

7) B. M. Riggleman and H. G. Drickamer, *J. Chem. Phys.*, **35**, 1343 (1961).