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Phthalocyanines Containing Silicons in Their Peripheral Substituent Groups

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Some phthalonitriles and 1*H*-isoindole-1,3(2*H*)-diimines containing silicon(s) in their alkoxy substituent groups are prepared and used for phthalocyanine formation reactions. Silicon–carbon bonds often survive under the reaction conditions using K_2CO_3 in *N*,*N*-dimethylformamide (DMF), but are often broken in the presence of sodium hydride. Silicons in the alkoxy groups do not affect the electronic absorption spectra of phthalocyanines in solution significantly. The Q band of films of phthalocyanines (Pcs) with alkyl or alkoxy groups attached to benzene carbons furthest from the Pc core lies to the blue compared to the Pcs in solution, while films of Pcs with eight alkoxy groups closest to Pc core have a Q band shifted to the red.

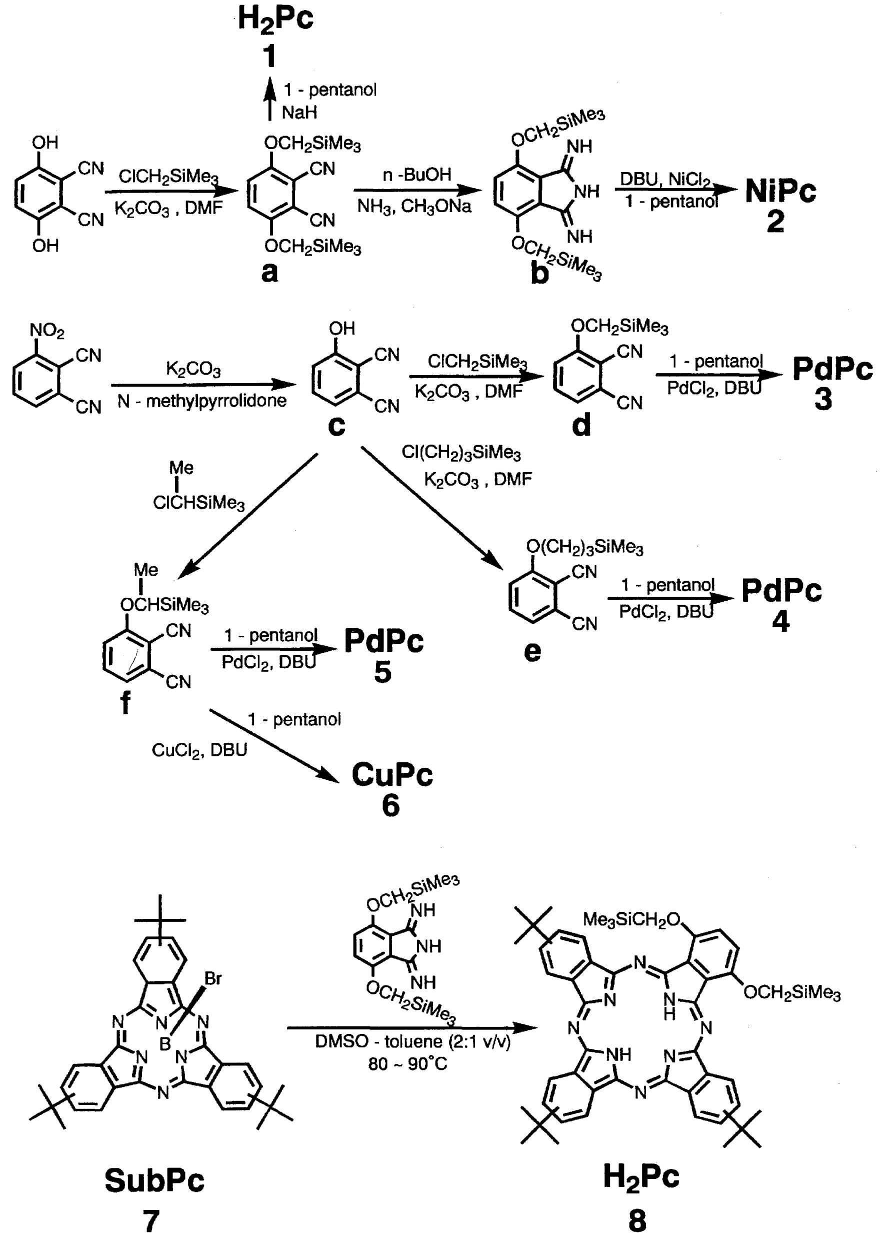
Ever since their unexpected fabrication in 1907,[1] phthalocyanines (Pcs) have been the subject of intensive study both in fundamental academic and practical fields.[2,3] However, Pcs containing silicons in their peripheral substituents are still rare,[4] although silicon is often used as a central metal. It is accepted that the Si–C bond is generally weaker than the C–C bond.[5] Accordingly, in order to examine whether a Si–C bond can survive under some Pc fabrication conditions, we decided to prepare phthalonitriles containing silicon(s) in their alkoxy groups, and used them in some metal-free and metal Pc formation reactions. Our second interest was the effect of silicon on their electronic absorption spectra. Carbon and silicon both belong to the IVB group in the periodic table. However, their properties are not necessarily close. For example, Si–Si double bonds are rare and no benzene-like compound made of silicons is known to date.[6] Accordingly, we wanted to know whether the replacement of carbons by silicons in the substituent groups affects the electronic absorption spectra or not. In addition to standard-type Pcs, we prepared a monosubstituted Pc by a ring-expansion reaction of a so-called "Subphthalocyanine" (SubPc).[7] In addition, the electronic absorption spectra of the films of these Pcs were measured and compared with those in solution.

Results and Discussion

Synthetic. The structures of and synthetic routes to phthalonitriles containing silicons(s) in their peripheral substituent groups are shown in Scheme 1, together with some abbreviated notations of phthalocyanines derived therefrom. In preparation of these phthalonitriles, we preferentially utilized the coupling reaction of 3,6-dihydroxy- and 3-hydroxyphthalonitriles with commercially available (chloroalkyl)trimethylsilanes. The reaction between 3,6-dihydroxyphthalonitrile and (chloromethyl)trimethylsilane proceeded smoothly in dry DMF and in the presence of K_2CO_3. However, the use of sodium hydride in place of K_2CO_3 often cleaved the bond between Si and C of the three methyl groups. This happened in the Pc formation reaction also, although alcohols were used as solvents in this step. Typically, for example, the bonds between Si and C of the three methyl groups of 3,6-bis[(trimethylsilyl)methoxy]phthalonitrile, **a**, were broken under the reaction condition to form H_2Pc **1**, and therefore CH_3 groups are not present in **1**.

Introduction of alkoxy groups containing silicon in the 3-position of phthalonitrile was carried out using 3-hydroxyphthalonitrile. We have succeeded in the preparation of 3-hydroxyphthalonitrile from 3-nitrophthalonitrile in ca. 50% by improving the conditions of the previously reported synthetic reaction of 4-hydroxyphthalonitrile from 4-nitrophthalonitrile.[8] As in the case of 3,6-dihydroxyphthalonitrile and (chloromethyl)trimethylsilane, the coupling between 3-hydroxyphthalonitrile and (chloromethyl)trimethylsilane (also (1-chloroethyl)trimethylsilane and (3-chloropropyl)trimethylsilane) proceeded smoothly in DMF in the presence of K_2CO_3 at temperature of around 80—90 °C. However, again, the use of sodium hydride in place of K_2CO_3 often led to a cleavage of the Si–C bond, even at ca. 40—50 °C. For example, in a reaction between 3-hydroxyphthalonitrile and (chloromethyl)trimethylsilane (at room temperature for 1 h and subsequently at 50 °C for 6 h), the desired product was obtained in only 2.7% yield, the main product being 3-methoxyphthalonitrile (ca, 50%, mp 177—178 °C).

The introduction of a trimethylsilylmethoxy group to the Pc ring by a ring-expansion reaction of a SubPc proceeded smoothly under well-known "standard" conditions[7a] for this reaction. The presence of $SiMe_3$ in the resultant H_2Pc was confirmed in both the IR spectra (1251 and 861 cm^{-1}) and the ^1H NMR spectra (0.53—0.57 ppm).



Scheme 1.

Electronic Absorption Spectra in Solution. Solution electronic absorption spectra of most of the Pcs in this study are quite similar in shape to those of general metal-free or metalloPcs.[9] They show a strong Q_{0-0} (or Q_{x0-0}) band at ca. 700—775 nm, which is shifted to a longer wavelength than that of unsubstituted Pcs (650—690 nm). As in the case of general alkyl or alkoxy-substituted Pcs,[10] the Q band shifts to a longer wavelength with increasing number of alkoxy groups attached to the benzene carbons closest to the Pc core.[11] Thus, eight alkoxy group-substituted H_2Pc **1** showed two main Q band peaks at 775 and 745 nm. The effect of silicon on the electronic absorption spectra then appears to be small, since, as mentioned above, the shift of the Q band is explained based on the general substituent effect, i.e. only by the number and positions of alkoxy groups.[11]

The unsplit broad Q band of H_2Pc **8** alone (Fig. 1) is different from that of others, and can be ascribed to its low molecular symmetry and the presence of isomers and different substituent groups. Since only one benzene ring out of four benzene rings contains two alkoxy groups at the 1,4-positions, a shift of the Q_{0-0} band to the red is not enough compared with, for example, that in H_2Pc **1**. Although, two weak shoulders are seen on both sides of the Q_{0-0} band (Fig. 1), this may be reasonably explained if we consider that the single peak is produced by the superimposition of the broad $Q_{x(0-0)}$ and $Q_{y(0-0)}$ bands lying closely in energy. Namely, two weak shoulders appear to be a part of the $Q_{x(0-0)}$ and $Q_{y(0-0)}$ bands.

The spectra of Pc films are shown in Fig. 2, together with those in solution. The films were obtained by slowly evaporating chloroform solutions of the phthalocyanines. As explicitly seen in the curves in this Fig. 2, the Q_{0-0} position of

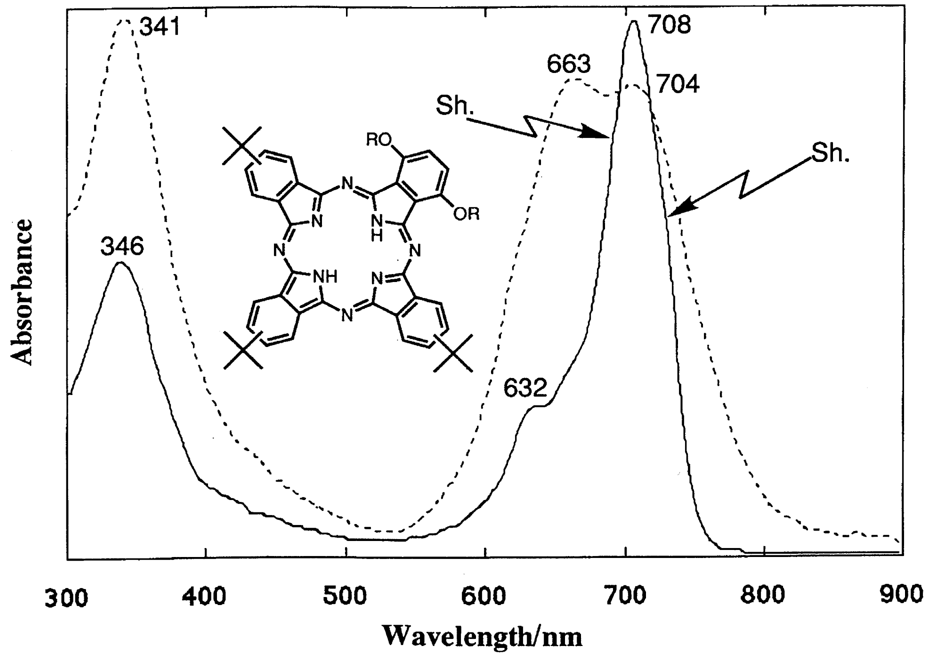


Fig. 1. The electronic spectra of H_2Pc **8** in chloroform (a solid line) and as a film (a broken line).

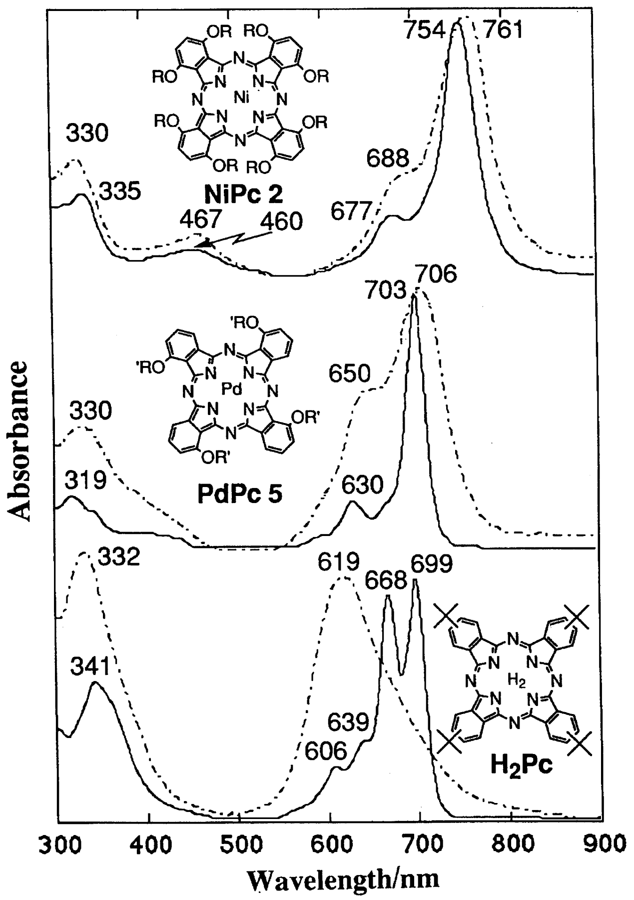


Fig. 2. The electornic spectra of several Pcs in solution (solid lines) and as films (broken lines). (a) NiPc **2**, (b) PdPc **5**, and (c) H_2Pc synthesized form 4-*t*-butylphthalonitrile.[13] $R = CH_2SiMe_3$, $R' = CH(Me)SiMe_3$.

films may appear on both sides of the solution Q_{0-0} band, depending on the number, kind, and positions of the substituent. In the case of alkoxy or alkyl groups, if these are attached to the benzene carbons closest to the core of the Pc, the Q_{0-0} band tends to appear at longer wavelengths in solution, which is due to the electron-releasing property of the substituents. When films are made, the Q_{0-0} band positions of films of H_2Pc **1** and NiPc **2** appear at longer wavelengths than those in solution by ca. 7—8 nm, while that of PdPc **5** appears at a closer wavelength (3 nm difference). Furthermore, in the case of H_2Pc **8**, which links three *t*-butyl groups at the benzene carbons furthest to the Pc core, and H_2Pc synthesized from 4-*t*-butylphthalonitrile, the Q_{0-0} band positions of the films emerge at shorter wavelengths than those in solution (see Fig. 1 and the bottom of Fig. 2). These shifts of the Q_{0-0} band positions of the films from those in solution are explained by the difference of aggregation. Namely, since long alkoxy chains attached to the carbons closest to the Pc core are known to be nearly normal to the Pc plane,[12] this may prevent the face-to-face type aggregation which causes a blue shift of the electronic spectra. On the other hand, such a phenomenon is not known for Pcs with long alkyl or alkoxy groups attached furthest to the Pc core. In such Pcs, the Q band of films shifts to shorter wavelengths from that in solution due to π–π stacking of Pc planes.

In conclusion, we have shown how to prepare silicon-containing 3-alkoxy and 3,6-dialkoxyphthalonitriles from 3-hydroxy- or 3,6-dihydroxyphthalonitriles and (chloroalkyl)-silanes. In addition, phthalocyaniens have been synthesized from the resultant phthalonitriles. In these processes, the use of sodium hydride as a base often leads to the cleavage of Si–C bonds, although K_2CO_3 was much safer to use. Alkoxy groups bearing silicon could servive under standard conditions of monosubstituted type phthalocyanine formation by the ring expansion of subphthalocyanines. It was found that the replacement of carbons by silicons in the substituent groups hardly affects the electronic absorption spectra of Pcs in solution. When films are prepared by evaporating a phthalocyanine solution, the Pc Q bands shift to the blue, remain unshifted, or are shifted to the red compared with the solution Q band, depending on the position and number of alkoxy substituents. Phthalocyanines with alkyl or alkoxy groups attached to benzene carbons furthest from the Pc core have a blue-shifted Q band, while inversely, Pcs with eight alkoxy groups closest to the Pc core have the band shifted to the red. Phthalocyanines with four alkoxy groups attached closest to the Pc core only change the Q band position to a lesser degree.

Experimental

Measurements. Electronic absorption spectra were recorded with a Shimadzu UV-250 spectrometer using chloroform as the solvent, and 400 MHz ^{1}H NMR spectra were obtained with a JEOL GX-400 spectrometer using $CDCl_3$ and DMSO-d_6 as solvents. IR spectra were recorded on a JEOL FT-IR 7000 spectrometer.

Synthesis. (A) Phthalonitriles and Isoindolediimines.

(a) 3,6-Bis[(trimethylsilyl)methoxy]phthalonitrile. 3,6-Dihydroxyphthalonitrile (30 g, 187.5 mmol) and dried K_2CO_3 (25.91 g, 187.5 mmol) were dissolved in dry DMF (200 ml) at 80—90 °C under nitrogen, and the mixture was cooled to ca. 40—45 °C. To this solution was added (chloromethyl)trimethylsilane (50.5 g, 187.5×2.2 mmol) a little at a time using a syringe; the temperature was then raised to 85—90 °C and reacted at the temperature for 24 h. After cooling, the solution was poured into dilute hydrochloric acid (300 ml). Chloroform-soluble products were extracted (1.2 L), and this layer was washed with water several times, dried by magnesium sulfate, and filtered. After removing chloroform under reduced pressure the residue was chromatographed using silicagel and toluene. Evaporation of the solvent, followed by recrystrallization from ether–hexane gave 46.6 g (74.9%) of white microcrystals of the desired compound. Mp 143—144 °C. Anal. Found: C, 57.20; H, 8.02; N, 8.18%. Calcd for $C_{16}H_{26}N_2O_2Si_2$: C, 57.44; H, 7.83; N, 8.37%. ^{1}H NMR ($CDCl_3$) δ = 7.27 (2H, s, arom), 3.66 (4H, s, OCH_2Si), and 0.19 (18H, s, $Si(CH_3)_3$); IR (KBr) 3096, 2964, 2232, 1576, 1487, 1429, 1317, 1265, 1216, 1191, 1045, 936, 864, 777, 704, 658, 605, 528, 463, 422 cm^{-1}.

(b) 4,7-Bis(trimethylsiliymethoxy)-1*H*-isoindole-1,3(2*H*)-diimine. Sodium methoxide (8.54 g, 63.25×2.5 mmol) and 3,6-bis[(trimethylsilyl)methoxy]phthalonitrile (21 g, 63.25 mmol) were dissolved in dry *n*-butanol (180 ml). Ammonia gas was bubbled through this solution for 1 h at room temperature and then for 3 h at 80 °C. After removing the solvent by an evaporator, the residue was dissolved in toluene, and this layer was washed several times with water. Removal of toluene left 20.7 g (93.8%) of the desired isoindolediimine, which decomposes at 205—215 °C. Anal. Found: C, 54.27; H, 8.61; N, 11.68%. Calcd for $C_{16}H_{29}N_3O_2Si_2$: C, 54.66; H, 8.31; N, 11.95%. IR (KBr) 2960, 1649, 1543, 1497, 1460, 1290, 1251, 1131, 1098, 1036, 948, 870, 704, 576, 503, 468, 416 cm^{-1}. This isoindolediimine was used without recrystallization.

(c) 3-Hydroxyphthalonitrile. 3-Nitrophthalonitrile (173.4 mmol) was dissolved in dry *N*-methylpyrrolidone (160 ml) and $NaNO_2$ (11.97 g, 173.4 mmol) was added. The solution was bubbled with nitrogen and the temperature was raised to 165—170 °C and reacted at this temperature for 40 min under a nitrogen atmosphere. After cooling to ca. 30 °C, potassium carbonate (16.78 g, 173.4 mmol) was added, and the solution was stirred at 150—160 °C for 45 min. The solution was cooled to ambient temperature and added dropwise to 0.6 M hydrochloric acid (1 M = 1 mol dm^{-3}) under stirring. After 2 h, the resultant precipitate was collected by filtration and washed with water until the filtrate become neutral. After drying, the solid was purified by silica-gel chromatography using acetone as the eluent and recrystallized from acetic acid, to give 13 g (52%) of a pale yellow solid. Mp 232—234 °C. Anal. Found: C, 66.23; H, 3.00; N, 19.19%. Calcd for $C_8H_4N_2O$: C, 66.67; H, 2.80; N, 19.44%. ^{1}H NMR (DMSO-d_6) δ = 7.63 (1H, t, atom), 7.40 (1H, d, arom), 7.29 (1H, d, arom), 2.96 (1H, s, OH); IR (KBr) 3242, 2234, 1586, 1568, 1466, 1354, 1319, 1272, 1173, 1021, 977, 919, 810, 733, 696, 607, 551, 462, 412 cm^{-1}.

(d) 3-(Trimethylsilylmethoxy)phthalonitrile. 3-Hydroxyphthalonitrile (5 g, 34.7 mmol) was dissolved in nitrogen-saturated dry DMF (50 ml), dry K_2CO_3 (2.64 g, 34.7×0.55 mmol) was added, and the solution stirred at 90 °C for 1.5 h. After cooling to ca. 40 °C, (chloromethyl)trimethylsilane (4.26 g, 34.7 mmol) was added through a syringe and the mixture was reacted at 80—90 °C for 26 h. To the mixture cooled to ambient temperature, dilute hydrochloric acid was added until the solution became slightly acidic, and the whole solution was washed with toluene. The toluene layer was then washed with water, dried with magnesium sulfate, and filtered. The toluene was removed by a rotary evaporator and the residue purified by silica-gel chromatography using toluene as the eluent. After removing the solvent, the residue was recrystallized from toluene to afford 4.72 g (59.1%) of white crystals. Mp 112—113 °C. Anal. Found: C, 62.40; H, 6.33; 11.90%. Calcd for $C_{12}H_{14}N_2OSi$: C, 62.57; H, 6.13; N, 12.16%. ^{1}H NMR ($CDCl_3$) δ = 7.64 (1H, t, arom), 7.32 (1H, d, arom), 3.74 (2H, s, OCH_2), 0.21 (9H, s, $Si(CH_3)_3$); IR (KBr) 2964, 2230, 1584, 1468, 1429, 1296, 1180, 1045, 884, 793, 708, 661, 611, 551, 458 cm^{-1}.

(e) 3-[3-(Trimethylsilyl)propoxy]phthalonitrile. 3-Hydroxyphthalonitrile (5 g, 34.7 mmol) was dissolved in nitrogen-saturated dry DMF (50 ml) and the solution was stirred at ca. 90 °C for 1.5—2 h. To the reaction mixture cooled to ca. 30—40 °C, (3-chloropropyl)trimethylsilane (5.23 g, 34.7 mmol) was added dropwise from a syringe, and the mixture was reacted at 85—90 °C for 17 h. K_2CO_3 (1.91 g, 34.7×0.4 mmol) was added to the mixture cooled to room temperature, and again the reaction was continued at 85—90 °C for 16 h. After cooling to room temperature, 0.6 M hydrochloric acid was poured into the mixture until the solution became slightly acidic. Organic solvent-soluble compounds were extracted into toluene (700 ml); this layer was washed with water several times, dried with magnesium sulfate, and filtered. Toluene was evaporated from the filtrate and the residue was imposed on a silica-gel column using toluene as the eluent. After removing the toluene, the residue was recrystallized from toluene–hexane (5 : 95 v/v) to afford 3.77 g (42.1%) of white crystals which melt at 80 °C. Anal. Found: C, 64.88; H, 7.24; N, 10.74%. Calcd for $C_{14}H_{18}N_2O$: C, 65.07; H, 7.02; N, 10.84%. ^{1}H NMR ($CDCl_3$) δ = 7.63 (1H, t, arom), 7.33 (1H, d, arom) 7.22 (1H, d, arom) 4.09 (2H, t, OCH_2), 1.87 (2H, tt, $CH_2CH_2CH_2$), 0.63 (2H, m, CH_2CH_2Si), 0.03 (9H, s, $Si(CH_3)_3$); IR (KBr) 3088, 2960, 2238, 1976, 1584, 1475, 1303, 1249, 1181, 1050, 861, 797, 756, 731, 692, 629, 609, 551, 460, 441, 422 cm^{-1}.

(f) 3-[1-(Trimethylsilyl)ethoxy]phthalonitrile. This compound was synthesized from 3-hydroxyphthalonitrile and (1-chloroethyl)trimethylsilane in a manner similar to the above 3-[3-(trimethylsilyl)propoxy]phthalonitrile. Recrystallization from hexane gave white crystals of the desired compound in 27% yield. Mp 67—68 °C. Anal. Found: C, 63.63; H, 6.85; N, 11.25%. Calcd for $C_{13}H_{16}N_2O$: C, 63.90; H, 6.60; N, 11.46%. ^{1}H NMR ($CDCl_3$) $\delta = 7.61$ (1H, t, arom), 7.29 (2H, d, arom), 4.24 (1H, q, C*H*), 1.39 (3H, d, CHCH_3), 0.16 (9H, s, Si(CH_3)$_3$); IR (KBr) 3088, 2962, 2230, 1582, 1470, 1377, 1286, 1251, 1187, 1102, 1044, 1007, 841, 658, 627, 609, 551, 460, 412 cm^{-1}.

(B) Phthalocyanines.

(a) H$_2$Pc 1. NaH (1.004 mmol) was first dissolved in dry 1-pentanol (10 ml) at 5—10 °C, and then 2 g (6.024 mmol) of 3, 6-bis[(trimethylsilyl)methoxy]phthalonitrile was added. The solution was heated under reflux with stirring for 2 h, allowed to cool to room temperature and poured into 80 ml of methanol. After leaving overnight, a green precipitate was collected by filtration, and the chloroform-soluble portion of the precipitate alone was imposed on a silica-gel column using chloroform–tetrahydrofuran (THF) (9 : 1 v/v) as eluent. Removal of the solvent under reduced pressure afforded 300 mg (18%) of the green solid. According to the following data, in the above reaction condition, all Si–C bonds between Si and Me were cut. Anal. Found: C, 47.98; H, 5.31; N, 10.92%. Calcd for $C_{40}H_{50}N_8O_8Si_8$: C, 48.26; H, 5.06; N, 11.25%. ^{1}H NMR ($CDCl_3$) $\delta = 7.60$ (8H, s, arom), 4.60 (16H, s, CH_2), 4.79 (1H, m, Si*H*), 2.41 (1H, m, Si*H*), 1.67 (1H, m, Si*H*), 0.19 (2H, s, N*H*); IR (KBr) 2944, 1605, 1510, 1460, 1260, 1193, 1064, 963, 880, 806, 759, 721, 592, 493, 468, 418 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 775 (4.67), 745 (4.64), 707 (4.14), 670 (4.08), 333 (4.38).

(b) NiPc 2. 4,7-Bis(trimethylsilylmethoxy)-1*H*-isoindole-1,3-diimine (2 g, 5.73 mmol) and 1,8-diazabicyclo[4.4.0]undec-7-ene, DBU (0.87 g, 5.73 mmol) in dry 1-pentanol (9 ml) were heated to ca. 120 °C with stirring under a nitrogen atmosphere; dried nickel chloride (0.185 g, 5.73/4 mmol) was then added and the mixture refluxed for 60 h in the dark. After cooling to room temperature, methanol 80 ml was added and left overnight in a refrigerator. The precipitate was collected by filtration, washed with a small amount of methanol, and chloroform-soluble portion alone was applied to silica-gel chromatography using chloroform–THF (9 : 1 v/v) as eluent. Recrystallization from ethyl acetate–hexane afforded 140 mg (8.4%) of green crystals of NiPc **2**. Anal. Found: C, 54.79; H, 7.72; N, 7.80%. Calcd for $C_{64}H_{104}N_8O_8Si_8Ni$: C, 55.03; H, 7.50; N, 8.02%. IR (KBr) 2960, 1603, 1497, 1421, 1288, 1251, 1096, 1058, 922, 857, 741, 530, 493, 460 418 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 753 (5.19), 676 (4.59), 464 (4.18), 332 (4.70), 309 (4.61).

(c) PdPc 3. To a stirred solution of 3-(trimethylsilylmethoxy)-phthalonitrile (2.5 g, 10.87 mmol) and DBU (1.16 g, 10.87×0.7 mmol) in dry 1-pentanol (10 ml) was added under a nitrogen atmosphere and at 110—120 °C, palladium chloride (0.49 g, 10.87/4 mmol); the reaction was continued for 24 h. The 1-pentanol was removed under reduced pressure, and the resultant solid was passed through a silica-gel column using toluene as the eluent. Evaporation of the solvent, followed by recrystallization from toluene–methanol, yielded 910 mg (32.6%) of green PdPc **3** as a mixture of isomers. Anal. Found: C, 55.74; H, 5.73; N, 10.67%. Calcd for $C_{48}H_{56}N_8O_4Si_4Pd$: C, 56.09; H, 5.49; N, 10.90%. IR (KBr) 2962, 1591, 1489, 1429, 1336, 1296, 1253, 1135, 1106, 1089, 1056, 938, 859, 797, 743, 704, 625, 551, 493, 460, 412 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 693 (5.36), 623 (4.65), 316 (4.66), 281 (4.56).

(d) PdPc 4. To 3-[3-(trimethylsilyl)propoxy]phthalonitrile 3 g (11.6 mmol) in 10 ml dry 1-pentanol were added, under nitrogen atmosphere and at 110—120 °C, palladium chloride (0.83 g, 11.6×0.4 mmol) and DBU (1.24 g, 11.6×0.7 mmol), and the reaction stirred in the dark under flowing nitrogen for 30 h. Upon cooling, 40—50 ml of toluene was added, and the insoluble products were filtered off. Solvents in the filtrate were removed by a rotary evaporator, and 50 ml of methanol was added to the residue. The residue was triturated and collected by filtration, then imposed on a silica-gel column using toluene–chloroform (1 : 1 v/v) as the eluent. Evaporation of the solvent left 1.262 g (38.1%) of a green product mixture. Anal. Found: C, 58.75; H, 6.59; N, 9.70%. Calcd for $C_{56}H_{72}N_8O_4Si_4Pd$: C, 59.00; H, 6.37; N, 9.83%. IR (KBr) 2954, 1593, 1495, 1334, 1249, 1135, 1108, 1071, 861, 741, 690, 605, 511, 493, 460, 412 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 692 (5.32), 621 (4.61), 314 (4.63), 281 (4.51).

(e) PdPc 5. To 3-[1-(trimethylsilyl)ethoxy]phthalonitrile (2 g, 8.2 mmol) in dry 1-pentanol (8 ml), DBU (8.2×0.7 mmol) and palladium chloride (0.58 g, 8.2×0.4 mmol) were added under nitrogen and at 110—120 °C; the solution was stirred for 30 hrs in the dark. Upon cooling, 40 ml of toluene was added and the insoluble materials were filtered off. Solvents in the filtrate were removed under reduced pressure, and finally passed through a silica-gel column using toluene–hexane as the eluent. Removal of the solvent left 408 mg (19.4%) of green product mixture. Anal. Found: C, 57.39; H, 6.22; N, 10.08%. Calcd for $C_{52}H_{64}N_8O_4Si_4Pd$: C, 57.62; H, 5.95; N, 10.34%. IR (KBr) 2962, 1589, 1487, 1332, 1255, 1135, 1106, 1046, 841, 745, 627, 511, 493, 460, 412 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 698 (5.38), 628 (4.68), 317 (4.69), 281 (4.59).

(f) CuPc 6. To 3-[1-(trimethylsilyl)ethoxy]phthalonitrile (1.5 g, 6.1 mmol) in dry 1-pentanol (6 ml), DBU (0.65 g, 6.1 mmol) and $CuCl_2$ (0.202 g, 6.1×0.33 mmol) were added under nitrogen and at 110—120 °C, and the reaction was continued for 42 h in the dark. After cooling to room temperature, the solution was poured into 100 ml toluene, and the insoluble materials were filtered off. Solvents in the filtrate were removed under reduced pressure, and the resultant residue was triturated with 50 ml methanol, and left in a refrigerator overnight. The precipitate was collected, applied to a silica-gel column using toluene as the eluent, and recrystallized from toluene–methanol, to afford, as a mixture of four isomers, CuPc **6** as a blue-green solid, 0.48 g (29.4%). Anal. Found: C, 59.76; H, 6.49; N, 10.47%. Calcd for $C_{52}H_{64}N_8O_4Si_4Cu$: C, 60.00; H, 6.20; N, 10.76%. IR (KBr) of most abundant isomer (the 3rd flowing isomer on TLC) 2962, 1589, 1487, 1338, 1257, 1139, 1091, 1046, 841, 745, 625, 551, 460, 427, 412 cm^{-1}; UV/vis ($CDCl_3$) λ_{max} (log ε) 716 (5.28), 643 (4.57), 333 (4.71).

(g) 2,9(or 10),16(or 17)-Tri-*t*-butyl-22,25-bis(trimethylsilylmethoxy)phthalocyanine (H$_2$Pc 8). To tri-*t*-butylated subphthalocyanine **7** (2.3 g, 3.58 mmol) in dry dimethyl sulfoxide–toluene (2 : 1 v/v) (80 ml), was added 4,7-bis(trimethylsilylmethoxy)-1*H*-isoindole-1,3(2*H*)-diimine (5 g, 3.58×4 mmol), and the solution was stirred for 33 h at 80—90 °C under a nitrogen atmosphere. Upon cooling to room temperature, toluene was evaporated under reduced pressure, and the remaining solution was poured into 300 ml of chloroform. The resultant solution was washed with warm water (300 ml×5), and the organic layer was dried with anhydrous magnesium sulfate and filtered. The solvents in the filtrate were removed under reduced pressure, and the residue was applied to a silica-gel column using toluene–hexane (4 : 1 v/v) as the eluent, and recrystallized from toluene–methanol to give a blue solid (0.27 g, 8.5%). Anal. Found: C, 69.88; H, 7.46; N, 12.33%. Calcd for $C_{52}H_{64}N_8O_2Si_2$: C, 70.23; H, 7.25; N, 12.60%. ^{1}H NMR ($CDCl_3$) $\delta = 9.35$—9.62 (5H, m, arom), 8.15—8.43 (3H, m, arom), 7.70—7.94 (3H, m, arom), 4.26—4.43 (4H, m, OCH_2), 1.72—1.80 (27H, m, (CH_3)$_3$), 0.53—0.57 (18H, m, Si(CH_3)$_3$), 0.27—0.28 (2H, br, N*H*); IR (KBr) 2962, 1603, 1499, 1251, 1116, 1046, 1007, 861, 758, 721, 667, 600, 518, 460, 420 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε) 712 (4.98), 645 (4.41), 344 (4.71), 298 (4.46).

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