Synthesis and Spectroscopic Properties of Symmetrically Tetrasubstituted Phthalocyanines with Four Alkyl or Aryl Chains or Porphyrin, Adamantane, Crown, or Quinone Units Attached[1]

Nagao Kobayashi,[*,†] Toshie Ohya,[‡] Mitsuo Sato,[‡] and Shin-ichiro Nakajima[§]

Pharmaceutical Institute, Tohoku University, Aobayama, Sendai 980, Japan, Biophysics Division,
Faculty of Pharmaceutical Sciences, Teikyo University, Sagamiko, Kanagawa 199-01, Japan, and
R & D Center, Ricoh Corporation, Shinei-cho, Kohoku-ku, Yokohama 223, Japan

Received September 15, 1992

Symmetrically tetrasubstituted phthalocyanines (Pcs) with four alkyl or aryl chains or adamantane, quinone, porphyrin, or crown units attached have been synthesized, and some of their spectroscopic properties are reported. These Pcs have been synthesized from the tetraanhydrides of metalated or nonmetalated 2,3,9,10,16,17,23,24-octacarboxyPcs and primary amines by one-step reaction in *N*-methyl-2-pyrrolidone. Differing from previously reported tetrasubstituted Pcs, the resultant Pcs do not generally contain positional isomers. They have a very high tendency toward aggregation, and as a result, their absorption spectra are unique in that the intensity of the Q band is extraordinally weak and its tail stretches to ca. 800 (Mt = Cu), 900 (Mt = H_2), 1000 (Mt = Fe), or 1200 (Mt = Co) nm. Some interaction between the substituent groups and Pc moiety was confirmed spectroscopically in quinone and porphyrin attached Pcs. A zinc complex showed S_2 emission in addition to S_1 emission.

Introduction

Tetrasubstituted Pcs are generally prepared from monosubstituted phthalonitrile, phthalic acid, phthalic anhydride, or isoindoline[2] and are mixtures of at least four positional isomers. Separation of the isomers is extremely difficult, and accordingly only a few pure tetrasubstituted isomers have been isolated hitherto.[3] For example, Gaspard and Maillard[3d] succeeded in preparing a Pc with C_{2v} symmetry, while Leznoff's group[3e] and Hanack's group[3f] obtained Pc derivatives with C_{4h} symmetry. However, high-symmetry such as D_{4h} symmetry is sometimes required, especially in theoretical fields, such as spectroscopy, and in the preparation of well-ordered discotic crystals.[4] In view of this, we present here the preparation of symmetrically tetrasubstituted Pcs by a completely new concept, in that substituent groups are linked to a presynthesized Pc skeleton. This Pc precursor is the tetraanhydride of 2,3,9,10,16,17,23,24-octacarboxyPc (OCPc). As will be shown below, any substituent groups which contain amino group(s) can be attached to it in a simple one-step high-yield reaction to produce symmetrical Pcs which do not generally contain positional isomers (in the present system, compound **9** alone may contain several isomers because of restricted rotation of the attached unit). Some spectroscopic properties of these compounds are also reported. By the introduction of various intriguing substituent groups, we have confirmed that some interaction does exist between the substituent

groups and Pc moiety. The most notable characteristic common to all compounds synthesized is that they are prone to aggregation in many organic solvents, mostly in a cofacial fasion.

Experimental Section

(i) Measurements. Absorption spectra were measured using a Shimadzu UV-360 spectrophotometer. Emission and excitation spectra were obtained with a Shimadzu RF-500 spectrofluorometer with appropriate filters to eliminate scattered light. Fluorescence quantum yields (ϕ_F) were determined by the use of quinine bisulfate in 1 N H_2SO_4 (ϕ_F = 0.55 at 296 K)[5a,b] or free base Pc (ϕ_F = 0.60) in 1-chloronaphthalene.[5c] Data were obtained by a comparative calibration method with use of the same excitation wavelength and absorbance for the imide Pcs and the calibrants and the same emission energies. Fluorescence decay curves were obtained at 20 °C by a Horiba NAES-550 series, using combinations of glass filters and a monochrometer for monitoring the emission. The fluorescence lifetimes were determined from the decay curves by the use of the least-squares method. Sample solutions for fluorescence measurements were purged with argon before measurement. Magnetic circular dichroism (MCD) spectra were recorded with a JASCO J-500 spectropolarimeter equipped with a JASCO electromagnet to produce longitudinal magnetic fields of up to 1.2 T. Electron spin resonance (ESR) measurements were obtained with a Varian E4 spectrometer calibrated with diphenyl-picrylhydrazyl (DPPH). In the above methods, solution spectra were quite often recorded in mixed-solvent systems because of low solubility of the compounds in single solvents. Infrared (IR) spectra were recorded with a JASCO A-302 spectrometer. ^{1}H nuclear magnetic resonance (NMR) spectra were recorded with a Jeol GX-500 spectrometer using tetramethyl-silane as an internal standard. Solvents for measurements were either distilled or Spectrograde.

Mössbauer spectra were measured with an Elscint AME-30A spectrometer with a ^{57}Co(Rh) source and calibrated with ^{57}Fe foil. Spectra were fitted to Lorenzian components by least-squares techniques. Estimated error limits on δ and ΔE_Q are ±0.01 mm s^{-1}. An Air Products LT-3-110 Heli-Tran liquid-transfer refrigeration system was employed for measurements at temperatures in the liquid-helium region, and a precalibrated thermocouple of Au (0.07% Fe) vs Chromel was used as the temperature sensor.

(ii) Synthesis. Nonmetalated (1) and Metalated (2–4) Tetraanhydrides of OCPcs. Finely ground H_2OCPc and MtOCPc (Mt = Cu, Fe, Co) were refluxed in a benzene–acetyl chloride (1:1 v/v) mixture for about 1 day, and after removal of the solvent, the residue was washed with dry

† Tohoku University.
‡ Teikyo University.
§ Ricoh Corp.
(1) Some preliminary results have been published: Kobayashi, N.; Nishiyama, Y.; Ohya, T.; Sato, M. *J. Chem. Soc., Chem. Commun.* **1987**, 390.
(2) Lever, A. B. P. *Adv. Inorg. Chem. Radiochem.* **1965**, *7*, 27. Moser, F. H.; Thomas, A. L. *The Phthalocyanines*; CRC Press Inc.: Boca Raton, FL, 1983; Vols. 1 and 2. Leznoff, C. C. In *Phthalocyanines-Properties and Applications*; Leznoff, C. C., Lever, A. B. P., Eds.; VCH: New York, 1989; Chapter 1.
(3) (a) Leznoff, C. C.; Marcuccio, S. M.; Greenberg, S.; Lever, A. B. P.; Tomer, K. B. *Can. J. Chem.* **1985**, *63*, 623. (b) Leznoff, C. C.; Marcuccio, S. M.; Svirskaya, P. I.; Greenberg, S.; Lever, A. B. P.; Tomer, K. B. *Ibid.* **1985**, *63*, 3057. (c) Wohrle, D.; Gitzel, J.; Okura, I.; Aono, S. *J. Chem. Soc., Perkin Trans. 2* **1985**, *2*, 1171. (d) Gaspard, S.; Maillard, P. *Tetrahedron* **1987**, *43*, 1083. (e) Greenberg, S.; Lever, A. B. P.; Leznoff, C. C. *Can. J. Chem.* **1988**, *66*, 1059. (f) Hanack, M.; Renz, G.; Strahle, J.; Schmid, S. *J. Org. Chem.* **1991**, *66*, 3501.
(4) Simon, J.; Engel, M. K.; Soulié, C. *New J. Chem.* **1992**, *16*, 287. Simon, J. In *Phthalocyanines*; Leznoff, C. C., Lever, A. B. P., Eds.; VCH: New York, 1992; Vol. II.

(5) (a) Melhuish, W. H. *J. Phys. Chem.* **1960**, *64*, 762. (b) Demas, J. N.; Crosby, G. A. *Ibid.* **1971**, *75*, 991. (c) Seybold, P. G.; Gouterman, M. *J. Mol. Spectrosc.* **1969**, *31*, 1.
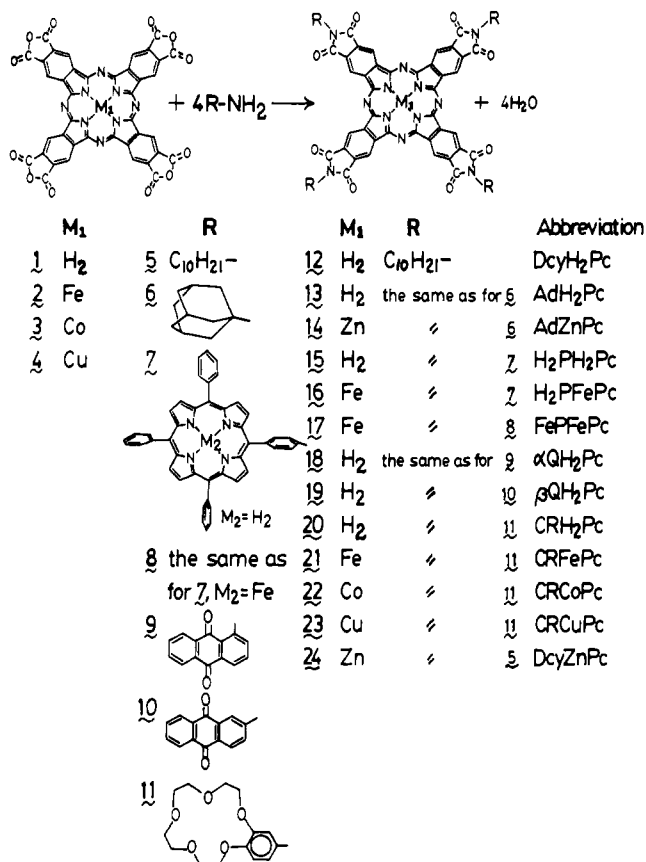
Figure 1. The structures of tetraanhydrides 1–4 and primary amines 5–11 used and the resultant symmetrically tetrasubstituted Pcs 12–24.
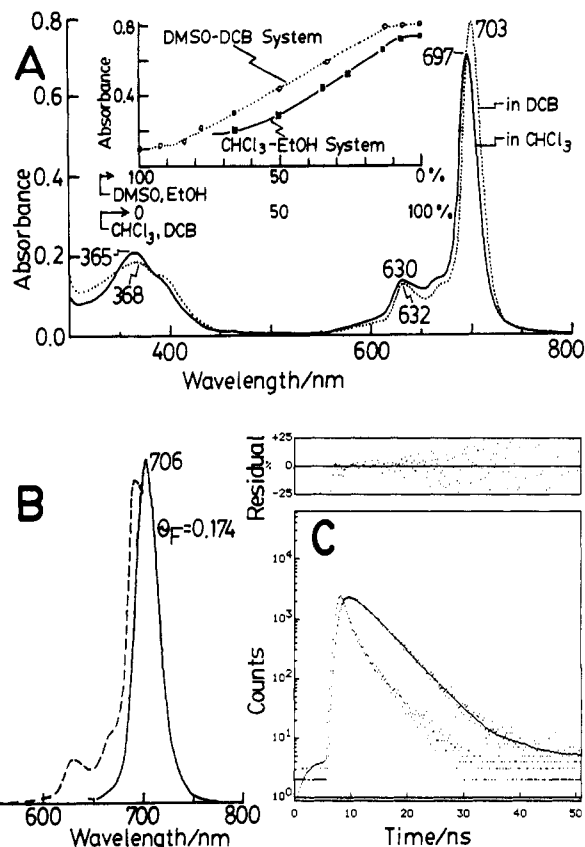
Figure 2. (A) Absorption spectra of **24** in DCB (dotted line) and chloroform (solid line). The inset shows absorbance of the Q_{0-0} band of **24** in the DMSO–DCB and chloroform–EtOH systems. [24] = 5.00 × 10^{-6} mol/L, and path length = 10 mm. (B) Emission and excitation spectra of **24** in degassed chloroform. Excitation was at 633 nm. (C) Fluorescence decay of **24** in degassed chloroform and its typical biexpotential fit. τ_1 = 3.17 ns (98.1%), and τ_2 = 3.03 ns (1.9%).

benzene, resulting in yields of between 88 and 95% of the tetra-anhydride. Compound **1** showed IR (KBr) bands at 1837 and 1772 cm⁻¹, which are ascribable to an anhydride ring.[6]

Amine Derivatives. 5-(p-Aminophenyl)-10,15,20-triphenylporphyrin (**7**)[7] and 1-amino-3,4-(1,4,7,10,13-pentaoxatridecane-1,13-diyl)benzene (**11**)[8] were prepared according to the literature.

Symmetrically Tetrasubstituted Pcs (12–23). Method A. The tetraanhydrides (**1–4**) and excess amines (**5–11**) were reacted in N-methyl-2-pyrrolidone at 70 °C for 5–14 h under nitrogen, and after cooling, the solution was diluted with either benzene (**13, 18, 19**), chloroform (**15–17**), or ethyl ether (**12, 20–23**). The precipitates were collected and heated in vacuo at 200 °C for 12 h and then redissolved in the least amount of N,N-dimethylformamide (DMF) (**13, 15, 18, 19, 21–23**) or chloroform (**12, 20**), and benzene (**13, 15–19, 21–23**) or ethyl ether (**12, 20**) was added to precipitate the products. This last procedure was often repeated three times. In the cases of **12** and **20–23**, they were further purified by basic alumina column chromatography using respectively chloroform or DMF–chloroform as eluents. Compound **15** was recrystallized from methylene chloride–MeOH, and **14** and **24** were obtained by zinc insertion reaction to **13** and **12**, respectively, in DMF in the dark. In the last stage of purifiction, compound **17** was dissolved in DMF and the solution was poured into dilute HCl solution in order to coordinate Cl⁻ ions to the Fe atoms in the porphyrin moiety. The yields in method A were between 38 and 77%.

Method B. The tetraanhydride (**1–4**) and excess amines (**5–11**) were reacted in N-methyl-2-pyrrolidone at 200 °C for 10–27 h under nitrogen, and after cooling, the solution was diluted with either benzene, chloroform, or ethyl ether, depending on the kind of amine used. The precipitates were collected and, after drying, imposed on a basic alumina column using dimethyl sulfoxide (DMSO)–DMF (**13, 18, 19**), DMF–chloroform (**15, 16, 20, 23**), or chloroform–MeOH (**12**) as eluents. In the cases of **13, 15, 16, 18, 19,** and **23**, the eluates were concentrated in vacuo and precipitated by the addition of benzene. The precipitates were filtered off and dried in vacuo at ca. 60 °C overnight. The yields were nearly the same or slightly better than method A.

Because of low solubility and due to the extremely high level of aggregation of the compounds, ¹H NMR spectra could be recorded only for a several compounds and signals were generally broad and not well-resolved. For example, NMR: **20** (CDCl₃ + 0.5% CD₃OD), δ 5.8–8.3 (br m, 20H), 2.8–4.4 (m, 64H); and **24** (CDCl₃), δ 6.6–9.5 (br s, 8H, peak at δ 7.9), 0.7–1.7 (m, 84H).

The following are representative examples of synthesis by methods A and B. The elemental analytical data for the compounds synthesized in this study are summarized in Table I.

Phthalocyanine-2,3:9,10:16,17:23,24-tetrakis(N-decyldicarboximide) (12) (Method A). A mixture of **1** (159 mg, 0.2 mmol), n-decylamine (630 mg, 4 mmol), and N-methyl-2-pyrrolidone (8 mL) was heated at 70 °C (oil bath) for 14 h under a nitrogen atmosphere. The solution was evaporated to ca. 3 mL and ethyl ether (ca. 150 mL) was added. The resultant precipitate was collected and heated in vacuo at 200 °C for 12 h and redissolved in chloroform (ca. 20–25 mL), and then ethyl ether (ca. 200 mL) was added to induce precipitation. The product was further purified using a 3 × 10 cm basic alumina column (act. III) with chloroform as eluent, to give 165 mg of **12** in 61% yield as a very dark blue shining solid. IR (cm⁻¹): 3100, 1770, and 1720 (cyclic imides[9]). ¹H NMR (DMF-d₇; δ): 7.3–6.2(8H, br s), 4.1–3.1 (8H, br t), 2.1–0.6 (76H, m), −8.5 to −12.7 (2H, very br s, a peak at −10.6 ppm).

Copper Phthalocyanine-2,3:9,10:16,17:23,24-tetrakis{N-[3,4-(1,4,7,10,13-pentaoxatridecane-1,13-diyl)phenyl]dicarboximide} (23) (Method B). Compounds **4** (86 mg, 0.1 mmol) and 2,3-(3′-aminobenzo)-1,4,7,10,13-pentaoxacyclopentadeca-2-ene (**11**) (566 mg, 2 mmol) were heated in 8 mL of N-methyl-2-pyrrolidone at 200 °C for 14 h under nitrogen. After cooling of the dark violet mixture to room temperature, it was diluted with chloroform (10 mL) and ethyl ether (80 mL), and the resultant precipitate was purified using a basic alumina column (2 × 10 cm) and

(6) Nakamoto, K. *IR Absorption Spectroscopy*, Nankodo: Tokyo, 1960.
(7) Ho, T. F.; McIntosh, A. R.; Weedon, A. C. *Can. J. Chem.* **1984**, *62*, 967.
(8) Ungaro, R.; El Haj, P.; Smid, J. *J. Am. Chem. Soc.* **1976**, *98*, 5198.

(9) Matsuo, T. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 1844. Shirai, H.; Kobayashi, K.; Takemae, Y.; Suzuki, A.; Hirabaru, O.; Hojo, N. *Makromol. Chem.* **1977**, *178*, 1889.

Table I. Elemental Analytical Data for Compounds 12–24

compd	method, yield	molecular formula	M_r	calcd C	calcd H	calcd N	found C	found H	found N
DcyH₂Pc (12)	A,61	$C_{80}H_{94}N_{12}O_8$	1351.712	71.09	7.01	12.43	70.28	7.20	12.10
AdH₂Pc (13)	B,67	$C_{80}H_{82}N_{12}O_8$	1339.616	71.73	6.17	12.55	71.04	6.33	12.05
AdZnPc (14)	69ᵃ	$C_{80}H_{80}N_{12}O_8Zn$	1402.970	68.49	5.75	11.98	67.95	5.92	12.29
H₂PH₂Pc (15)	A,73; B,74	$C_{216}H_{126}N_{28}O_8$	3241.572	80.03	3.92	12.10	78.97	4.16	11.66
H₂PFePc (16)	B,70	$C_{216}H_{124}N_{28}O_8Fe$	3295.406	78.73	3.79	11.90	77.80	4.25	11.49
FePFePc (17)	63ᵇ	$C_{216}H_{116}N_{28}O_8Cl_4Fe_5$	3652.554	71.03	3.20	10.74	70.05	3.55	10.25
αQH₂Pc (18)	A,38; B,56	$C_{96}H_{38}N_{12}O_{16}$	1615.440	71.38	2.37	10.40	70.53	2.60	10.02
βQH₂Pc (19)	A,77	$C_{96}H_{38}N_{12}O_{16}$	1615.440	71.38	2.37	10.40	70.45	2.61	9.86
CRH₂Pc (20)	A,42	$C_{96}H_{86}N_{12}O_{28}$	1855.824	62.13	4.67	9.06	61.28	4.43	8.63
CRFePc (21)	B,58	$C_{96}H_{84}N_{12}O_{28}Fe$	1909.658	60.38	4.43	8.80	59.74	4.21	8.37
CRCoPc (22)	B,64	$C_{96}H_{84}N_{12}O_{28}Co$	1912.741	60.28	4.43	8.79	59.46	4.39	8.35
CRCuPc (23)	B,71	$C_{96}H_{84}N_{12}O_{28}Cu$	1917.348	60.14	4.42	8.77	59.59	4.64	8.13
DcyZnPc (24)	73ᶜ	$C_{80}H_{92}N_{12}O_8Zn$	1415.066	67.90	6.55	11.88	67.54	6.40	11.60

ᵃ Yield from **13**. ᵇ Yield from **15**. ᶜ Yield from **12**.

Table II. Absorption Spectra of DcyZnPc (24) at 5.00×10^{-6} mol/L in Various Solvents[a]

solvent	$\lambda(max)/nm$ $(10^{-4}\epsilon)$			
o-dichlorobenzene	703 (15.6)	632 (2.5)	397 (sh)	368 (4.2)
chloroform	697 (14.0)	630 (2.7)	395 (sh)	365 (3.6)
nitrobenzene	705 (14.0)	635 (2.4)		
bromobenzene	703 (13.5)	633 (2.6)	397 (sh)	367 (3.9)
chlorobenzene	701 (11.1)	632 (2.5)	397 (sh)	366 (3.9)
toluene	697 (9.0)	665 (2.8), 632 (2.5)	397 (sh)	359 (4.1)
pyridine	702 (9.1)	650 (3.1)	400 (sh)	365 (3.7)
dioxane	691 (8.0)	643 (3.2)	397 (sh)	363 (4.4)
methylene chloride	696 (7.2)	645 (4.0)	396 (sh)	361 (4.1)
tetrahydrofuran	690 (6.0)	643 (3.9)	397 (sh)	360 (4.2)
carbon tetrachloride	695 (5.2)	643 (2.9)	400 (sh)	362 (3.7)
benzene	695 (5.4)	645 (3.3)	393 (sh)	358 (3.6)
dimethylformamide	697 (4.9)	652 (4.4)	400 (sh)	357 (3.2)
ethyl acetate	687 (3.7)	643 (4.3)	399 (sh)	357 (4.1)
acetonitrile	712 (2.8)	645 (2.9)	402 (sh)	359 (3.4)
dimethyl sulfoxide		632 (2.4)	401 (sh)	355 (3.1)

[a] In order to minimize concentration differences among each of the solutions, the following procedures were adopted in data collection. Initially, a concentrated solution of **24** was prepared in chloroform. From this solution, a fixed small amount was transferred into a 1-cm cuvette using a microsyringe, and the solvent was evaporated. To this cuvette was added 3.0 cm³ of a solvent, and the spectra were recorded.

DMF–chloroform as eluent. The eluate containing the blue fraction was concentrated to ca. 4–5 mL, and ca. 40 mL of benzene was added to induce precipitation. After filtration and drying at ca. 60 °C in vacuo overnight, 137 mg (71%) of compound **23** was obtained as a blue shining solid.

Phthalocyanine-2,3:9,10:16,17:23,24-tetrakis{N-(meso-tetraphenylporphyrinyl)dicarboximide} (15) and Its Pentairon Complex (17) (Method B). A finely ground mixure of tetraanhydride **1** (199 mg, 0.25 mmol) and the monoaminoporphyrin **7** (3.0 g, 4.77 mmol) was heated in 20 mL of N-methyl-2-pyrrolidone at 200 °C (oil bath) for 27 h under a nitrogen atmosphere. After cooling of the mixture to room temperature, ca. 80 mL of benzene was added. The resultant precipitate was collected and diluted with benzene. By repetition of the last procedure several times, unreacted **7** was transferred into the filtrate. Finally, the product was purified by chromatography using basic alumina (3 × 15 cm) and DMF–chloroform (3:7 v/v) as eluent. The greenish brown eluate was concentrated to ca. 4–5 mL, and benzene (ca. 50 mL) was added to induce precipitation. After drying, 595 mg (74%) of the desired **15** was obtained as a bluish purple solid. ¹H NMR (DMF-d_7; δ): 7.50–8.95 (116H, m) and –2.92 (8H, s).

In order to obtain **17**, excess FeCl₃ and **15** were heated in DMF for several hours and the solution was poured into dilute HCl solution. After filtration and drying, the residue was imposed on a short alumina column
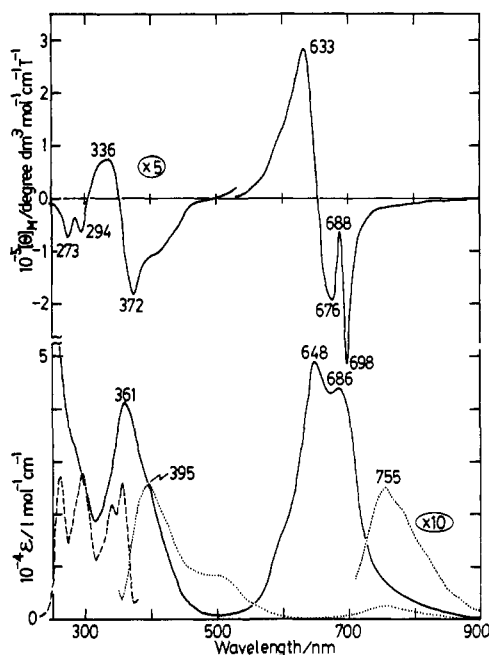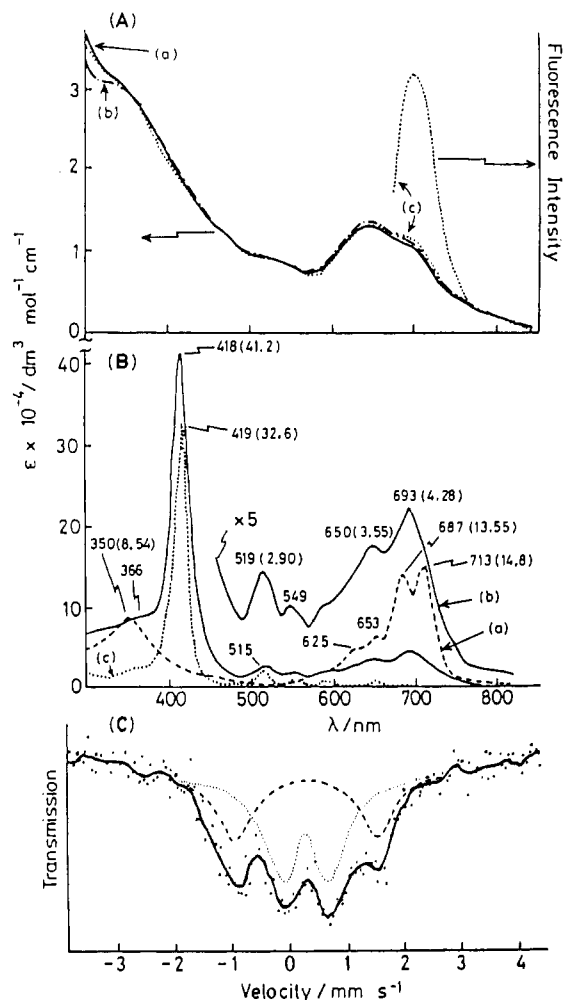
(10) (a) Stillman, M. J.; Nyokong, T. In *Phthalocyanines-Properties and Applications*; Leznoff, C. C.; Lever, A. B. P., Eds.; VCH: New York, 1989; Chapter 3. (b) Tajiri, A.; Winkler, J. *Z. Naturforsch.* **1983**, *38a*, 1263.

Figure 3. Absorption (solid line), emission (dotted line), excitation (broken line) (bottom), and MCD (top) spectra of **14** in dichloromethane–EtOH (4:1 v/v). Excitation was at 340 nm, and the excitation spectrum was recorded for an emission peak at 395 nm.

using DMF–CHCl₃ (1:1 v/v) as eluent. The yield of the brownish purple **17** was ca. 63%.

Results and Discussion

Some spectroscopic data are shown in Figures 2–7. Of **12–24**, **24** *alone* showed typical monomeric Pc spectra but only in some solvents, including chloroform and o-dichlorobenzene (DCB) at a concentration of as low as 5.00×10^{-6} M (Figure 2A). By a change of solvent from chloroform or DCB, the intensity of the Q_{0-0} band of **24** decreased markedly, while that of the aggregation band[10a] increased (Table II). The data in Table II suggest that the higher the monomer content, the larger the ϵ value of the main Q band will be and that **24** is prone to aggregation, since the intensity and shape of the Q band of general Pcs do not change as sensitively as in this case. Compounds **13–23** gave spectra which are ascribed to aggregated Pcs in almost all the solvents examined in this study even at concentrations as low as ca. 10^{-6} M. The ¹H NMR spectrum of **12** also supports the conclusion that the imino Pcs in the present study are apt to aggregate; i.e., two pyrrole proton signals appeared at –10.6 ppm as a very broad singlet ([**12**]/M = 1×10^{-4} in CDCl₃, TMS reference) as compared with –3 to –6 ppm of general Pcs.[3] This large upfield

Figure 4. (A) Absorption and emission spectra of (a) **18**, (b) **19**, and (c) **12** in DMSO–benzene (1:4 v/v). Excitation was at 633 nm at room temperature. (B) Absorption spectra of (a) **1** in DMF–DMSO (9:1 v/v), (b) **15** in DMF, and (c) 5-(p-aminophenyl)-10,15,20-triphenylporphyrin (**7**) in DMF. (C) Mössbauer spectrum of **17** at 4.5 K. The velocity scale is relative to Fe metal. The solid line represents the average of the experimental data (dots), and the dotted and dashed lines are two doublets constructed so that their sum reproduces the solid lines.

shift is rationalized by considering cofacially arranged Pcstacking[11] which produces an intense diamagnetic ring current effect.[12]

Fluorescence data of **24** in deaerated chloroform are shown in Figure 2B,C. Fluorescence emission from the S_1 state and the corresponding excitation spectra showed mirror-image relationships with small Stokes shifts, and the ϕ_F value of 0.174 is about 60% of that of ZnPc in 1-chloronaphthalene ($\phi_F = 0.30$).[5c] Concerning the emission lifetimes, two values of around 3 ns ($\tau_1 = 3.17$ ns, 98.1%; $\tau_2 = 3.03$ ns, 1.9%) were obtained by biexponential fit of the fluorescence decay curve (Figure 2C). Since ϕ_F values of the S_1 emission of Pcs in chloroform and 1-chloronaphthalene do not differ significantly, the present data suggest that attachement of polar electron withdrawing substituent groups like the imino group decreases ϕ_F.

Figure 3 shows the spectra of adamantane-substituted **14**. The shape of the absorption spectrum is unusual compared to that of mononuclear zinc complexes, but it does not significantly change, even at ca. 10^{-7} M concentration. The Q bandwidth (ca. 2300 cm^{-1} at half-height) is much wider than that of mononuclear species (ca. 350–750 cm^{-1})[11] and is composed of two intense peaks. Of the two peaks, the one to shorter wavelength is more prominent, and the one at longer wavelength posseses a broad, weak tail to
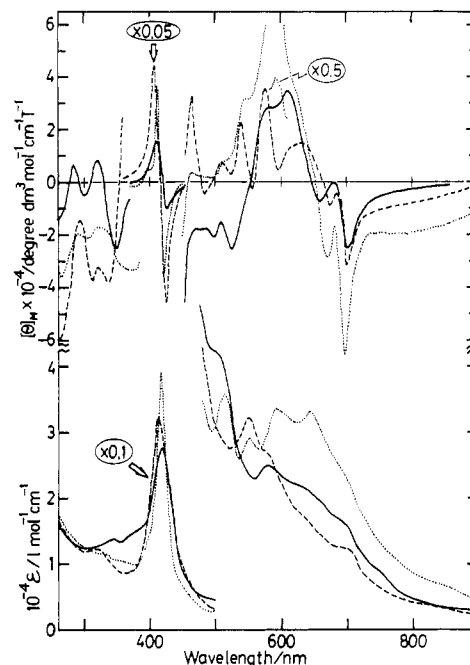
Figure 5. Absorption (bottom) and MCD (top) spectra of **17** (solid lines), bisimidazole derivative of **16** (dotted lines), and decaimidazole derivative of **17** (broken lines) in chloroform–MeOH (4:1 v/v). [16]/M = 2.396 × 10^{-5}, [17]/M = 1.404 × 10^{-5}, [imidazole]/[(16)] = 613, and [imidazole]/[17] = 1046.

the red. These features are characteristic of aggregated Pcs having a cofacial arrangement.[10a] Indeed, the shape of not only the Soret but also the Q bands of both the MCD and absorption spectra is very similar to that of the zinc complexes of 1,8-naphthalene- and 1,8-anthracene-linked cofacial dinuclear Pcs recently reported.[13] Thus, these data at high dilution manifest that **14** is prone to aggregation in cofacial arrangements. Faint S_1 fluorescence as compared with stronger S_2 emission is also indicative of a cofacial configuration.[11]

Interaction between the Pc moiety and the substituent groups was seen in **15**, and **17–19**. For example, we were unable to detect fluorescence emission from **18** and **19** but could recognize it when **12** was irradiated (Figure 4A). As described in our preliminary report,[1] by examining the fluorescence intensity of **12** in the presence of anthraquinone **9** or **10**, we concluded that the failure to detect emission from **18** or **19** can be attributed to very extensive intramolecular quenching. That is, it was found that the quenching ability of the anthraquinone unit in **18** and **19** is about 10^4 times stronger than that in solution. The absorption spectra of **15** also showed evidence of interaction between **1** and 5-(p-aminophenyl)-10,15,20-triphenylporphyrin (**7**) (Figure 4B). The Soret band was broadened (22-nm half-width, 70% increase in half-width), but its position was unchanged and its absorption coefficient (ϵ) was about 32% of [4 times the Soret ϵ value of the porphyrin + ϵ of **1** at 418 nm]. The decrease in the Q band intensity was also significant (29% of that of **1** alone). With respect to the band positions, those originating mainly from the porphyrin did not shift, while those from **1** shifted significantly; i.e., the Soret band shifted to the red and the Q band to the blue by 1250 and 450 cm^{-1}, respectively (judging from the proton signal in the NMR spectrum (−2.92 ppm in DMF-d_7), these are not caused by aggregation).

The Mössbauer spectrum of **17** gives further evidence of interaction (Figure 4C). The spectrum could be fitted by a sum of two components by a least-squares approximation assuming

(11) Kobayashi, N.; Lever, A. B. P. *J. Am. Chem. Soc.* **1987**, *109*, 7433.
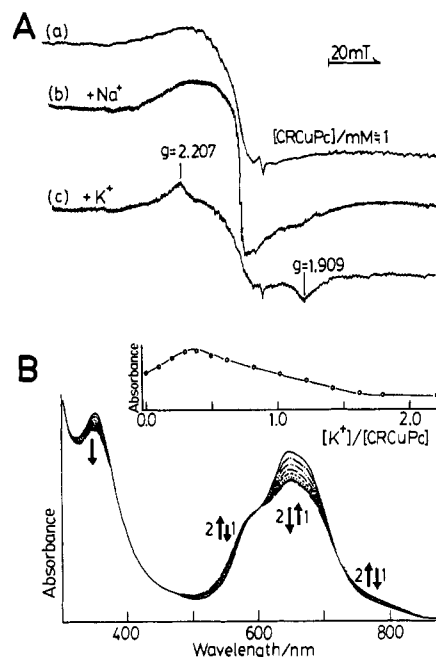(12) Satterlee, J. D.; Shelnutt, J. A. *J. Phys. Chem.* **1984**, *88*, 5487.

(13) Kobayashi, N.; Yanagisawa, Y.; Osa, T.; Lam, H.; Leznoff, C. C. *Anal. Sci.* **1990**, *6*, 813.
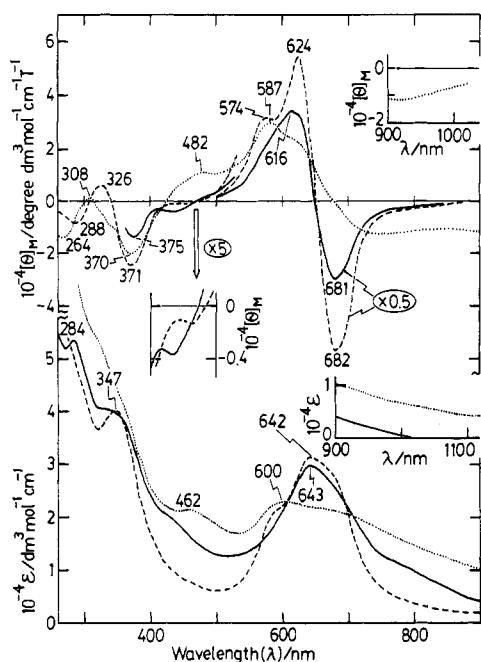
Figure 6. Absorption (bottom) and MCD (top) spectra of **20** (solid lines), **22** (dotted lines), and **23** (broken lines) in chloroform–MeOH (4:1 v/v). [20]/M = 5.001 × 10⁻⁵, [22]/M = 7.162 × 10⁻⁵, and [23]/M = 3.630 × 10⁻⁵.

Figure 7. (A) ESR spectra of **23** in chloroform–MeOH (ca. 4:1 v/v) (a) in the absence of any cation and in the presence of (b) saturated CH_3COONa or (c) CH_3COOK ([K⁺]/[23] = 20) at 77 K. (B) 2nd stage change of absorption spectra by the addition of CH_3COOK to 3 mL of a chloroform–MeOH (4:1 v/v) solution of **23** in a 10-mm cell. CH_3COOK was dissolved in chloroform–MeOH (4:1 v/v) and was added with a microsyringe; 60 μL was added in all. Arrows indicate the direction of the spectroscopic change. The inset shows the dependence of absorbance on [K⁺]/[23] for the Q band.

Lorenzian line shapes. Judged from the Mössbauer parameters,[14] the isomer shift (δ) and quadrupole splitting (ΔE_Q), the inner doublet (δ = 0.37, ΔE_Q = 0.88 mm s⁻¹) corresponds to high-spin iron(III) (iron in the porphyrin moiety) and the outer doublet (δ = 0.44, ΔE_Q = 2.57 mm s⁻¹) to intermediate-spin iron(II) (iron in the Pc moiety). In contrast, the δ and ΔE_Q values of iron-inserted **12** were 0.30 and 1.96 mm s⁻¹ at 4.3 K, respectively, and those of *meso*-(tetraphenylporphyrinato)iron(III) chloride[15] were 0.52 and 1.51 mm s⁻¹ at 4.2 K, respectively. Thus, the differences in δ and ΔE_Q values from those in typical mononuclear control molecules suggest the existence of an interaction between the porphyrin and Pc moieties. In addition, therefore, iron exists in two oxidation states in **17**.

When strong nitrogeneous bases such as imidazoles are added to solutions containing iron porphyrins[16] and Pcs,[17] they coordinate at both the 5th and 6th positions, since the complex formation constants for the formation of monoadducts (K_1) are much smaller than those of bisadducts (K_2). Therefore, a large excess of imidazole was added to **16** and **17**, and the absorption and MCD spectra were recorded (Figure 5). Coordination of imidazole to **17** caused hypsochromic (blue-shift) and hyperchromic (intensifying of ε) effects on both the Soret and Q bands. A peak at ca. 560 nm is produced by bisligation of imidazole molecules to iron in the porphyrin moiety[16] and is characteristic of iron(III) low-spin porphyrins. However, the spectroscopic changes in the Soret region cannot be simply explained by the coordination of imidazoles, since bisligation of imidazole to high-spin iron(III) generally produces the opposite effects (red-shift and decrease in ε[16,18]) and that to intermediate-spin iron(II) Pcs causes red-shifting of the Soret band.[17] Thus, these data indicate, as in the results of Figure 4B,C, that the spectroscopic properties in **17** are not expressed simply by the sum of the porphyrin moiety

(peripheral substituent groups) and the Pc moiety, suggesting again some interaction between these two moieties.

The Soret band of the porphyrin moiety of **16** is sharper and more intense than that of **17**, in accord with the general phenomenon that the Soret band of non-metalated porphyrins is sharper and more intense than that of iron-inserted porphyrins.[19] Although, both **16** and **17** show dispersion type MCD curves corresponding to the Soret band of the porphyrin moiety, their contents are, at least theoretically, different. Since the porphyrin moiety of **16** is metal-free and, accordingly, there is no degenerate excited state, the dispersion curve in **16** is considered to be caused by the superimposition of two Faraday *B*-terms (two adjacent Faraday *B*-terms give seemingly *A*-term-like MCD curves).[10b] In contrast, if iron in the porphyrin moiety of **17** is in high-spin trivalent state, as suggested by Mössbauer data in Figure 4, the Soret MCD band is mainly a contribution of Faraday *A*-terms.[20] When two imidazole molecules are coordinated to iron in the porphyrin moiety in **17**, the iron transforms to a trivalent low-spin state and concomitantly the Soret MCD increases (Figure 5). In this case, the MCD shows a contribution from the Faraday *C*-term.[20] The ground-state degeneracy is rationalized by taking the iron d-orbitals into account. In MCD spectra, the band due to the Pc moiety appeared at around 260–360 and 660–750 nm.[10a]

Phthalocyanines with four 15-crown-5 units attached directly to the benzene rings of the Pc skeleton are known to dimerize by the addition of cations such as K⁺ or Ca²⁺.[11] Accordingly, we also introduced 15-crown-5 units to compounds **1–4** and prepared new Pcs **20–23**. These were barely soluble in chloroform or DCB, in which **24** gave a typical monomer type spectrum (Figure 2A). Figure 6 shows the spectra of **20**, **22**, and **23** in chloroform–MeOH (4:1 v/v). Obviously, the absorption spectra are not those of typical monomeric Pcs,[10a] the Q band tail being stretched to

(14) Maeda, Y. *J. Phys. (Orsey) Colloq.* **1979**, 514. Sams, J.; Tsin, T. B. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, London, 1979; Vol. 4, Chapter 9.

(15) Collman, J. P.; Hoard, J. L.; Kim, N.; Lang, G.; Reed, C. A. *J. Am. Chem. Soc.* **1975**, *97*, 2676.

(16) Pasternack, R. F.; Gillies, B. S.; Stahlbush, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 2613 refs 10, 14, 19, 22–24, and 42–44 cited therein.

(17) Jones, J. G.; Twig, M. V. *Inorg. Chim. Acta* **1975**, *12*, L15 and references cited therein; **1974**, *10*, 103.

(18) Smith, D. W.; Williams, R. J. P. *Struct. Bonding* **1970**, *7*, 1.

(19) Gouterman, M. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. 3, Chapter 1.

(20) Kobayashi, N. *Inorg. Chem.* **1985**, *24*, 3324; Kobayashi, N.; Koshiyama, M.; Osa, T. *Ibid.* **1985**, *24*, 2502.

ca. 900 (Mt = H$_2$), 1000 (Mt = Fe), or 1200 (Mt = Co) nm, although their MCD spectra gave Faraday A-terms in the main Q band region which are expected for MtPc monomers[10a] and cofacial type eclipsed MtPc dimers.[21]

Of the several crowned Pcs investigated, the copper complex is expected to provide the most definitive ESR spectra (Figure 7A). The ESR spectrum obtained in the absence of any cations (curve a) is structureless and seems to be that of a somewhat aggregated species.[22] Addition of sodium ions led to an intensifying of the signal (curve b), suggesting partial de-aggregation of the species.[11] In contrast, addition of K$^+$ produced new signals at g = 2.207 and 1.909 (curve c) which are not seen in curves a and b. Although the seven-line pattern expected for two equivalent Cu(II) ions coupled together is not seen, these two strong perpendicular transitions are unmistakable evidence for the formation of a dimeric molecule.[11,22,23] The failure to detect seven lines may perhaps reflect the presence of several cofacial dimers, produced as a result of the rotation of phenyl (accordingly crown) groups. In this way, of somehow aggregated crowned Pcs in the absence of cations, two Pcs dimerize utilizing K$^+$ ions.

(21) Gasyna, Z.; Kobayashi, N.; Stillman, M. J. *J. Chem. Soc., Dalton Trans.* **1989**, 2397. Kobayashi, N.; Ojima, F.; Osa, T.; Vigh, S.; Leznoff, C. C. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 3469.
(22) Smith, T. D.; Pilbrow, J. R. *Coord. Chem. Rev.* **1974**, *13*, 173. Chikira, M.; Yokoi, H.; Isobe, T. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2208. Chikira, M.; Kon, H.; Hawley, R. A.; Smith, K. M. *J. Chem. Soc., Dalton Trans.* **1979**, 246.
(23) Kobayashi, N.; Lam, H.; Nevin, W. A.; Janda, P.; Leznoff, C. C.; Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 3415.

Figure 7B shows the spectroscopic change observed when K$^+$ ions were added to **23**. As shown by the arrows, the Q band first intensified and then decreased with the increase of [K$^+$]. This change is shown as a function of [K$^+$]/[**23**] in the inset. As with our previous crowned Pc systems,[11] the absorbance changes in a two-step three-stage process, and a cofacial dimer is formed when ([K$^+$]/[**23**]) > 1.5, i.e. when two Pcs capture more than three K$^+$ ions.

Conclusions

The use of **1** and its metal complexes have shown the following merits in the derivatization of Pcs. (i) Any compound containing amino groups can be attached to **1** or its metal derivatives in a one-step high-yield reaction. (ii) The resultant compounds are generally symmetrical, and isomers are not produced. (iii) The preparation of phthalonitrile and/or phthalic acid precursors is avoided. In addition, as manifested above, the resultant compounds have various interesting properties depending upon the introduced substituent groups. However, one disadvantage of this method is that we need excess amine so that if the required amine is precious, this method may not be good enough.