Synthesis of Rigid Porphyrin-Quinone Compounds for Studying Mutual Orientation Effects on Electron Transfer and Their Photophysical Properties

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(Received May 19, 1994)

A series of covalently linked porphyrin-quinone molecules in which a porphyrin ring is connected at two fixed distances with two different kinds of rigid spacers to benzoquinone were synthesized. The spacer is either spiro[4.4]nonane or *trans*-decalin. These compounds were designed to have a fixed orientation of different kinds with the same redox pair, the same separation distance, and the same number of intervening bonds. The forward electron-transfer rates were studied by fluorescence–lifetime measurements. Large differences in the rates were found in each pair, and the rates for those compounds having a spiro spacer were larger than those with a *trans*-decalin spacer. These differences were attributed to a difference in the molecular geometry of the spacer groups in each pair.

During the early stage of photosynthesis, electron transfer (ET) plays a crucial role in achieving a long-lived charge-separation state for the use of subsequent chemical reactions by a combination of fast-forward and slow-backward ET. If we fully understand the ET mechanism and can completely control ET, we will be able to build up artificial photosynthetic systems or molecular devices. Several factors control ET, i. e., the separation distance, free-energy change associated with the reaction, relative orientation between chromophores, and environmental factors, such as proteins and solvents. To understand these factors, various model compounds which can isolate one particular factor have been exploited.[1] Excellent model compounds for the factors concerning the separation distance[2] and free-energy change[3] have so far been prepared, and the factors were analyzed quantitatively. On the other hand, the orientation effects upon ET are not well understood, because only a limited number of suitable model compounds[4] are known. Theoretical calculations[5] and the unique orientation of the chromophores in the reaction center of bacterial photosynthesis[6] strongly suggest that a large orientation effect should exist in ET. Therefore, the synthesis of model compounds from which one can extract only orientation effects is a big challenge for organic chemists. To construct such models, the following conditions are necessary. The set of compounds should have the same redox pair separated by a rigid spacer with the same distance between chromophores, but with different orientations. Furthermore, there should be no interaction between the chromophores in the ground state, and the number of intervening bonds between the redox pair should be the same in order to clarify the discussion. Bearing these ideas in mind, we designed and synthesized a pair of **1**[7] and **3**[7] and that of **2**[8] and **4**.[8] On the basis of MM2 calculations[9] the center-to-center (edge-to-edge) distances between the porphyrin and the quinone in these four molecules are: **1**, 12.5 Å (8.2 Å); **2**, 9.0 Å (6.4 Å); **3**, 12.9 Å (8.6 Å); **4**, 9.3 Å (6.3 Å). One can see from the structures of **1**—**4** and the separation-distance data that the above requirements are satisfied in each pair (Chart 1).

Results and Discussion

Synthesis and Structure. Synthetic schemes are shown in Schemes 1 and 2. The spirononane spacer in **1** and **2** was prepared by a treatment of indanone **5** with 3- or 4-bromosubstituted bis(bromomethyl)benzene **6a,b** in the presence of sodium hydride in THF followed by a reduction of the carbonyl group using a combination of triethylsilane and trifluoroacetic acid.[10] On the other hand, the synthesis of a *trans*-decalin spacer in **3** and **4** was carried out by a Diels–Alder reaction of **10** and **11** or **17** and **6b**, followed successively by a reduction of the carbonyl group, by a ring closure, and finally by a reduction of the carbonyl group to give **15** and **22**. The formylation of **8a,b**, **15**, and **22** was carried out in the usual manner by using BuLi and DMF. An acid-catalyzed coupling reaction of tetrapyrrole **24** with aldehydes **9a,b**, **16**, and **23** in methanol gave porphyrins **25**—**28** (Chart 2). The target compounds **1**—**4** were obtained by the demethylation of **25**—**28** with BBr_3 in CH_2Cl_2, followed by oxidation with PbO_2.

The structures of the new compounds were determined by spectral data and an elemental analysis. A restricted rotation around the single bond at the *meso* position of the porphyrin ring was confirmed by the NMR spectra. Ring-current effects due to the porphyrin ring of **25**—**28** were experimentally obtained for protons H_a–H_d by subtracting the chemical shifts of the corresponding protons of reference compounds **9a,b**, **16**, and **23** lacking the porphyrin ring from the chemical shifts of **25**—**28**. This ring-current shift was

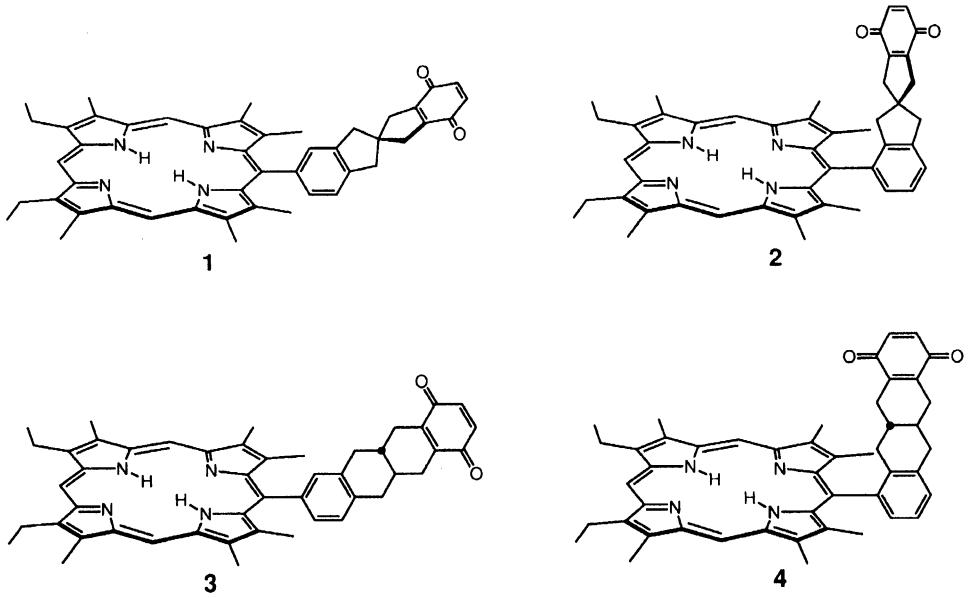
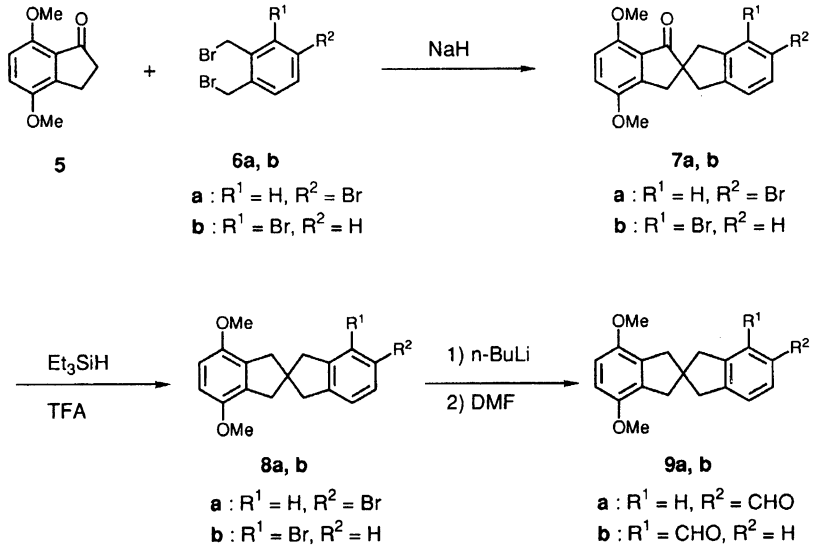


Chart 1.



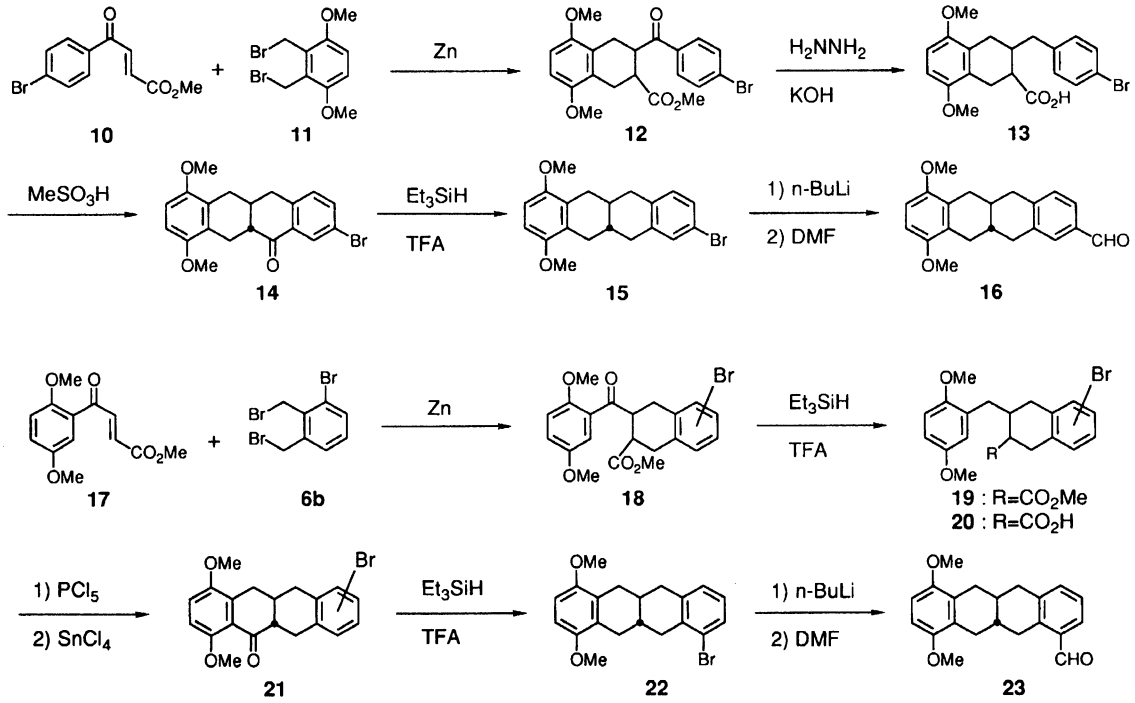
Scheme 1.

then calculated by the well-established dipole model,[11] in which eight point dipoles in a porphyrin ring are assumed. The calculation was carried out for **25**—**28** assuming that the structures have a dihedral angle of 90° between the porphyrin and phenyl rings. In the calculation we also assumed that the indan ring is planar and the tetralin ring is a half-chair. Furthermore, the chemical shifts of the methoxyl groups were averaged over their rotational profiles. The very good agreement between the calculated and observed values in Table 1 is conclusive evidence for the orthogonal conformation in solution at room temperature. This is very probably true for **1**—**4**, because the carbon framework remains unchanged. The above result agrees well with the observation[12] that the rotation of the *meso*-phenyl group is strongly restricted by the steric effect of the adjacent methyl groups, so that the diastereomers in 5,15-diarylsubstituted porphyrin can be separated at room

Table 1. Observed and Calculated Ring Current Effect[a] of Porphyrin Ring

Compd		H_a	H_b	H_c	H_d
25	Obsd	0.09	0.05	0.05	0.09
	Calcd	0.11	0.05	0.08	0.12
26	Obsd	−0.21	−0.28	−0.28	−0.21
	Calcd	−0.21	−0.25	−0.25	−0.21
27	Obsd	0.00	0.03	0.03	−0.07
	Calcd	0.02	0.05	0.08	0.12
28	Obsd	−0.54	−0.28	−0.14	−0.03
	Calcd	−0.54	−0.28	−0.13	−0.01

a) Minus value implies upfield shift.



Scheme 2.

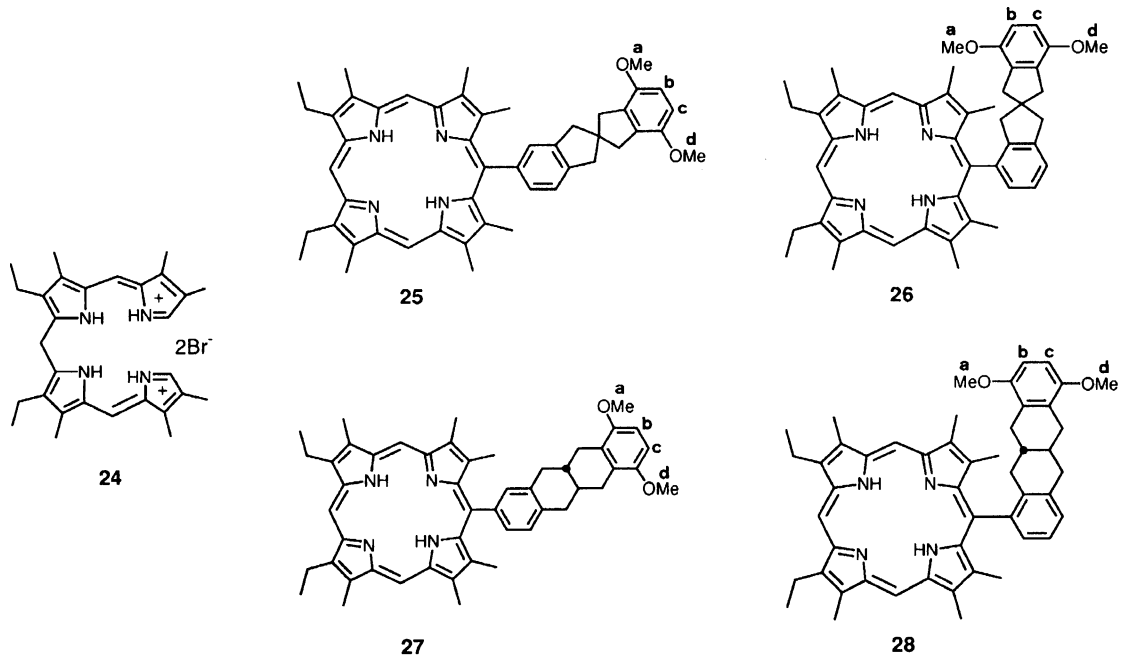


Chart 2.

temperature.

Redox and Photophysical Properties. Redox potentials of **1**—**4** have been examined by cyclic voltammetry (CV) and by differential pulse voltammetry (DPV). One reversible one-electron oxidation and reduction waves and several irreversible ones were observed in CV between +1.5 V and −1.5 V. The values of the DPV peak potentials (vs. Ag/AgCl) in CH_2Cl_2 are summarized in Table 2. The free-energy change ($-\Delta G$) for the present ET reaction was calculated using

$$-\Delta G = E_0 - (E_{ox} - E_{red}) - \frac{e^2}{4\pi\varepsilon_0}\left[\left(\frac{1}{2r_1}+\frac{1}{2r_2}-\frac{1}{r_{12}}\right)\frac{1}{\varepsilon_s}-\left(\frac{1}{2r_1}+\frac{1}{2r_2}\right)\frac{1}{\varepsilon'_s}\right], \quad (1)$$

where $r_1 = 5.5$ Å and $r_2 = 3.75$ Å are the radii of the porphyrin and quinone rings, respectively, and r_{12} is the center-to-center distance from porphyrin to quinone

Table 2. Redox Potentials of **1**—**4** Determined by DPV vs. Ag/AgCl in CH_2Cl_2 with Bu_4NClO_4 and Estimated Free Energy Change for Forward ET Reaction

Compound	Ox/V	Red/V	$-\Delta G$/eV
1	0.85	−0.50	0.47
2	0.85	−0.52	0.43
3	0.87	−0.49	0.43
4	0.87	−0.51	0.40

(given earlier). The excited energy (E_0) in THF was estimated from the electronic and fluorescence spectra to be 1.97 eV. The values of $E_{ox}-E_{red}$ in THF (ε_s=7.58) were calculated using the redox potentials in CH_2Cl_2 (ε_s'=9.1). The calculated values of $-\Delta G$ for **1**—**4** are summarized in Table 2. The table shows that the free energy change for the intramolecular ET of **1**—**4** is actually the same.

The electronic spectra of **1**—**4** are superimposable to those of the reference compounds (Fig. 1) for **4** and **28**, as a typical example. This indicates that there is no special interaction between the porphyrin and quinone rings in **1**—**4** in the ground state, and, hence, the ET rates can be obtained on the basis of the fluorescence lifetimes.

The fluorescence lifetimes of **1**—**4** were measured by a time-correlated single-photon counting apparatus excited at 360 nm and monitored at 630 nm in two solvents (THF and DMF) with different polarities. All of the decay curves can be analyzed by the sum of two components (Values of χ^2 are in the range of 1.2 and 1.6.). A typical example is shown in Fig. 2. The lifetimes of one component agree well with that of the reference compounds lacking the quinone group. Some decomposed products of the quinone chromophores may be assigned to that component. The other component with shorter lifetimes was taken for the value of **1**—**4**; the values are summarized in Table 3. Using these data, the ET rates (k_{et}) from the exited singlet state of porphyrin to quinone are evaluated by

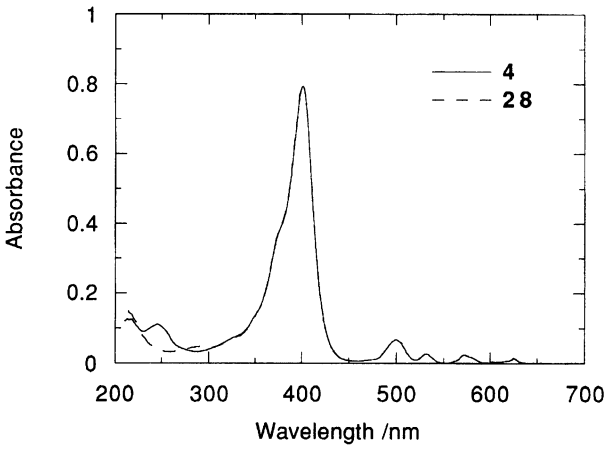


Fig. 1. Electronic spectra of **4** and **28** in THF.

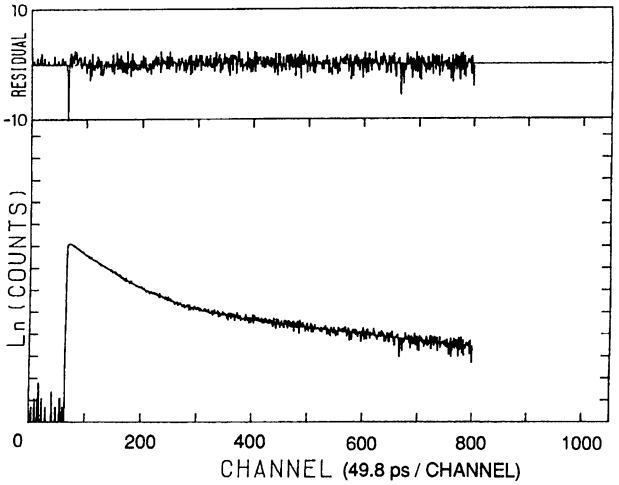


Fig. 2. Fluorescence decay profile (lower panel) of **1** in DMF by excitation at 360 nm and emission at 630 nm and weighted residuals (upper panel) between the fitted curve (solid line, lower panel) and the fluorescence data (points, lower panel).

$$k_{et} = 1/\tau - 1/\tau_0, \quad (2)$$

where τ and τ_0 are the fluorescence lifetimes of porphyrin-quinone and reference compounds lacking a quinone chromophore, respectively. The results are listed in Table 3. Attempts to determine the decay kinetics of the porphyrin cation band for estimating the back-ET rates were unsuccessful, because of its ultrafast rate, due to the quite favorable ΔG value. By changing the donor group from the free-base porphyrin to the Zn porphyrin, the formation and decay kinetics could be estimated.[13]

Discussion. In Table 3 there exist large differences in the k_{et} values between **1** and **3** and between **2** and **4**. Thus, the ET rates of the charge-separated process (k_{cs}) for compounds having a spiro spacer are larger than those with a *trans*-decalin spacer. As usually seen[14] for the k_{cs} values in intramolecular ET, no large solvent dependence of k_{cs} was observed for **1**—**4** in THF and DMF. This can be explained by saying that this

Table 3. Fluorescence Lifetimes[a] and Electron Transfer Rates of **1**—**4**

Compd	Solvent	τ/ns	τ_0/ns	k_{et}/s^{-1}
1	THF	2.6	16.8	3.3×10^8
	DMF	2.0	16.8	4.4×10^8
2	THF	0.28	17.5	3.5×10^9
	DMF	0.26	17.5	3.8×10^9
3	THF	8.2	17.4	6.5×10^7
	DMF	6.9	17.3	8.7×10^7
4	THF	2.1	15.0	4.0×10^8
	DMF	1.5	15.8	6.0×10^8

a) τ_0 is fluorescence lifetime of the corresponding reference compound replacing quinone ring with 1,4-dimethoxybenzene.

process occurs in the barrierless region[15] in the Marcus curve,[16] and that the effect of the solvent polarity on ΔG is compensated by a change in the overall reorganization energy. Generally, ET is controlled by the separation distance, exothermicity, mutual orientation, and environmental factors, as previously described. Among these factors, the separation distances and free-energy change associated with the reaction are quite similar in paired compounds, as seen before. The environmental factors can be eliminated since the spectra were measured in the same solvent. We can therefore ascribe the rate differences in Table 3 to the molecular geometry i. e., the orientation effect. The orientation effect becomes larger when the separation distance or the number of intervening bonds decreases with a value approaching nine: $k_{cs}(\mathbf{1})/k_{cs}(\mathbf{3})\approx 5$, $k_{cs}(\mathbf{2})/k_{cs}(\mathbf{4})\approx 9$. This clearly shows that the relative orientation influences the ET rates very strongly.

The orientation-dependent ET can be interpreted by two mechanisms, i. e., "through bond" and "through space". In covalently linked donor–acceptor systems it is generally accepted[17] that ET takes place through bonds, because the decay parameter of through-bond ET is constant per chemical bond, while that of through-space ET decreases exponentially. We have demonstrated[18] the through-bond ET mechanism for **2** by preparing a suitable model compound. The same mechanism is expected in **1**, **3**, and **4**. It has been reported[19] that a highly strained spacer, like cubane, accelerates ET by a factor of ten compared with that of a nonstrained hydrocarbon spacer. Since both the spiro[4.4]nonane and *trans*-decalin spacers in the present study are free from strain, the strain effect is not present in our systems. It is therefore concluded that the orientation effect observed in this study originated from a difference in the relative orientation between the p-orbitals of the chromophores and the σ-orbitals of the spacer bonds. A similar result was reported[4a] for two pairs of rigid bichromophoric molecules in which the same redox pair is connected with the same number of intervening bonds. In that system the ET rates are optimal for an all-*trans*, antiperiplanar arrangement of the intervening σ-framework. However, this all-*trans* rule is not applicable to the present system, because the compounds with the all-*trans* configuration of the *trans*-decalin spacer show smaller k_{et} values than do the corresponding compounds with the spiro[4.4]nonane spacer. Theoretical calculations[20] have revealed that the stereochemistry of the σ-bonds of the cyclohexane spacer play an important role in ET. Likewise, the stereoelectronic effect may be responsible for the ET rate differences in this study. Sophisticated calculations are required to confirm this interpretation.

The present result has clearly shown that ET rates can be greatly controlled by the nature of spacer bonds. We are working further on this problem.

Experimental

The melting and boiling points were uncorrected. NMR, mass, and IR spectra were obtained on a Bruker WM-360 (360 MHz), a JEOL DX300, a Hitachi 270-30, respectively. Elemental analysis was performed on a Perkin–Elmer 240. A Wakogel C-200 was used for column chromatography and a Merck #5745 and a Whatman PLK5 were used for preparative thin-layer chromatography. For analytical thin layer plates were used Merck #5715 and #5721.

2,3-Bis(bromomethyl)bromobenzene (6b). A solution of 3-bromo-*o*-xylene (25.7 g, 139 mmol), *N*-bromosuccinimide (50.8 g, 285 mmol) and a small amount of benzoyl peroxide in carbon tetrachloride (500 ml) was refluxed under irradiation of a 500 W lamp (Toshiba) for 30 min. The reaction mixture was extracted with chloroform. The extract was washed with aqueous sodium thiosulfate, saturated aqueous sodium chloride, and dried over anhydrous magnesium sulfate. After filtration, the solvent was removed under reduced pressure. Distillation (153—154 °C, 5.0 mmHg, 1 mmHg=133.322 Pa) afforded 43.6 g (94.1% yield) of colorless oil. ^{1}H NMR ($CDCl_3$) δ=7.92 (d, J=7.8 Hz, 1H, Ar-H), 7.31 (d, J=7.9 Hz, 1H, Ar-H), 7.14 (dd, J=7.9 and 7.8 Hz, 1H, Ar-H), 4.83 (s, 2H, benzylic H), 4.63 (s, 2H, benzylic H). Found: C, 28.25; H, 2.04; Br, 70.06%. Calcd for $C_8H_7Br_3$: C, 28.02; H, 2.06; Br, 68.92%.

5′-Bromo-4,7-dimethoxy-2,2′-spirobiindan-1-one (7a). To a stirred solution of **5**[21] (57.0 g, 296 mmol) and **6a**[22] (101 g, 296 mmol) in dry THF (300 ml) was added 60% sodium hydride (17.8 g, 444 mmol) at room temperature. The resultant suspension was heated under reflux for 2 h. After an additional 60% sodium hydride (17.8 g, 444 mmol) was added, the mixture was refluxed for 4 h. To the cooled reaction mixture ice-water was carefully added, and the mixture was extracted with benzene. The organic layer was washed with saturated aqueous sodium chloride and dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue was subjected to column chromatography on silica gel with 5% ethyl acetate–benzene to give **7a** (43.3 g, 39.2% yield) as colorless solids. MS (EI) m/z 372, 374 (M^+); IR (Nujol) 1704 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=7.28 (s, 1H, Ar-H), 7.24 (d, J=8.3 Hz, 1H, Ar-H), 7.02 (d, J=8.3 Hz, 1H, Ar-H), 6.98 (d, J=8.7 Hz, 1H, Ar-H), 6.75 (d, J=8.7 Hz, 1H, Ar-H), 3.88 (s, 3H, OMe), 3.78 (s, 3H, OMe), 3.43 (d, J=15.9 Hz, 1H, benzylic H), 3.37 (d, J=15.5 Hz, 1H, benzylic H), 2.76 (d, J=15.9 Hz, 1H, benzylic H), 2.73 (d, J=15.5 Hz, 1H, benzylic H). Found: C, 61.41; H, 4.25; Br, 21.34%. Calcd for $C_{19}H_{17}BrO_3$: C, 61.14; H, 4.59; Br, 21.41%.

5′-Bromo-4,7-dimethoxy-2,2′-spirobiindan (8a). To a stirred solution of **7a** (12.1 g, 32.3 mmol) in trifluoroacetic acid (100 ml) was added triethylsilane (13.0 ml, 80.5 mmol). After the mixture was stirred for 30 min at room temperature, most of the trifluoroacetic acid was removed under reduced pressure. The reaction mixture was extracted with chloroform. The extract was washed successively with saturated aqueous sodium hydrogencarbonate and saturated aqueous sodium chloride, and then dried over anhydrous magnesium sulfate. The solvent was evaporated and the resulting residue was purified by column chromatography on silica gel with 30% benzene–hexane to afford **8a** (4.06 g, 35.0% yield) as colorless solids, mp 102—103 °C.

MS (EI) m/z 358, 360 (M^+); ^{1}H NMR ($CDCl_3$) δ=7.30 (s, 1H, Ar-H), 7.25 (d, J=8.1 Hz, 1H, Ar-H), 7.03 (d, J=8.1 Hz, 1H, Ar-H), 6.63 (s, 2H, Ar-H), 3.76 (s, 6H, OMe), 2.95 (s, 2H, benzylic H), 2.92 (s, 4H, benzylic H), 2.91 (s, 2H, benzylic H). Found: C, 63.28; H, 5.05; Br, 22.08%. Calcd for $C_{19}H_{19}BrO_2$: C, 63.52; H, 5.33; Br, 22.24%.

4′,7′-Dimethoxy-2,2′-spirobiindan-5-carbaldehyde (9a). To a cooled solution of **8a** (5.23 g, 14.6 mmol) in dry THF (20 ml) was added butyllithium in hexane (11.8 ml, 18.9 mmol) at −78 °C under a nitrogen stream. After stirring for 5 min, dry *N*,*N*-dimethylformamide (12.5 ml, 162 mmol) was added and the reaction mixture was stirred for 1 h at −78 °C. After the temperature of the reaction flask was allowed to rise to room temperature, saturated aqueous ammonium chloride was added. The reaction mixture was extracted with chloroform. The organic layer was washed with saturated aqueous sodium chloride and dried over anhydrous magnesium sulfate. After removal of the solvent, the resulting residue was subjected to column chromatography on silica gel with 5% ether–benzene to give **9a** (4.06 g, 90.4%) as colorless solids, mp 109 °C. MS (EI) m/z 308 (M^+); IR (Nujol) 1692 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=9.96 (s, 1H, CHO), 7.70 (s, 1H, Ar-H), 7.66 (d, J=7.7 Hz, 1H, Ar-H), 7.33 (d, J=7.7 Hz, 1H, Ar-H), 6.64 (s, 2H, Ar-H), 3.77 (s, 6H, OMe), 3.04 (s, 4H, benzylic H), 2.95 (s, 4H, benzylic H). Found: C, 77.78; H, 6.26%. Calcd for $C_{20}H_{20}O_3$: C, 77.90; H, 6.54%.

4′-Bromo-4,7-dimethoxy-2,2′-spirobiindan-1-one (7b). Compound **7b** was prepared starting from **5** and **6b** by a similar procedure as that described for **7a**. **7b**: 24.6% yield, colorless solids, mp 178—179 °C. MS (EI) m/z 374, 372 (M^+); IR (Nujol) 1698 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=7.33 (d, J=7.7 Hz, 1H, Ar-H), 7.12 (d, J=7.4 Hz, 1H, Ar-H), 7.04 (dd, J=7.7, 7.4 Hz, 1H, Ar-H), 7.02 (d, J=8.7 Hz, 1H, Ar-H), 6.77 (d, J=8.7 Hz, 1H, Ar-H), 3.93 (s, 3H, OMe), 3.82 (s, 3H, OMe), 3.58 (d, J=15.8 Hz, 1H, benzylic H), 3.46 (d, J=16.1 Hz, 1H, benzylic H), 3.07 (s, 2H, benzylic H), 2.91 (d, J=16.1 Hz, 1H, benzylic H), 2.90 (d, J=15.8 Hz, 1H, benzylic H). Found: C, 61.41; H, 4.25; Br, 21.34%. Calcd for $C_{19}H_{17}BrO_3$: C, 61.14; H, 4.59; Br, 21.41%.

4′-Bromo-4,7-dimethoxy-2,2′-spirobiindan (8b). Compound **8b** was synthesized in the same manner as **8a**. **8b**: 97.3% yield, colorless solids, mp 131—132 °C. MS (EI) m/z 360, 358 (M^+); ^{1}H NMR ($CDCl_3$) δ=7.28 (d, J=7.7 Hz, 1H, Ar-H), 7.09 (d, J=7.3 Hz, 1H, Ar-H), 6.99 (dd, J=7.7, 7.3 Hz, 1H, Ar-H), 6.63 (s, 2H, Ar-H), 3.77 (s, 6H, OMe), 3.07 (s, 2H, benzylic H), 3.03 (s, 2H, benzylic H), 2.95 (s, 4H, benzylic H). Found: C, 63.46; H, 5.06; Br, 22.50%. Calcd for $C_{19}H_{19}BrO_2$: C, 63.52; H, 5.33; Br, 22.24%.

4′,7′-Dimethoxy-2,2′-spirobiindan-4-carbaldehyde (9b). This compound was synthesized starting from **8b** by a similar method as that described for **9a**. **9b**: 39.4% yield, colorless solids, mp 136—137 °C. MS (EI) m/z 308 (M^+); IR (Nujol) 1694 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=10.19 (s, 1H, CHO), 7.72 (d, J=7.5 Hz, 1H, Ar-H), 7.51 (d, J=7.5 Hz, 1H, Ar-H), 7.42 (dd, J=7.5, 7.5 Hz, 1H, Ar-H), 6.73 (s, 2H, Ar-H), 3.86 (s, 6H, OMe), 3.46 (s, 2H, benzylic H), 3.10 (s, 2H, benzylic H), 3.05 (s, 4H, benzylic H). Found: C, 77.92; H, 6.35%. Calcd for $C_{20}H_{20}O_3$: C, 77.90; H, 6.54%.

Methyl 3-(4-Bromobenzoyl)-5,8-dimethoxy-1,2,3,4-tetrahydro-2-naphthalenecarboxylate (12). To a stirred solution of **10**[23] (18.0 g, 67.0 mmol) and **11**[24] (20.0 g, 61.8 mmol) in dry dioxane (400 ml) was added activated zinc powder (ca. 40 g), which was prepared according to the procedure of Kerdesky.[25] After the exothermic reaction ceased, the reaction mixture was filtered through Celite and the filtrate was concentrated under reduced pressure. Ether and water were added and the resulting mixture was filtered to remove polymer. The filtrate was washed with saturated aqueous sodium chloride and dried over anhydrous sodium sulfate. Removal of the solvent gave crude **12**, which was purified by column chromatography on silica gel with 10% ethyl acetate–hexane. Recrystallization from ethanol afforded colorless prisms (15.3 g, 57.0%), mp 120—121.5 °C. MS (EI) m/z 434, 432 (M^+); IR (Nujol) 1730 (C=O) and 1688 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=7.89 (d, J=8 Hz, 2H, Ar-H), 7.62 (d, J=8 Hz, 2H, Ar-H), 6.66 (d, J=9 Hz, 1H, Ar-H), 6.64 (d, J=9 Hz, 1H, Ar-H), 3.79 (s, 3H, OMe), 3.71 (s, 3H, OMe), 3.66 (s, 3H, CO_2Me), 3.9—2.4 (m, 6H, CH and benzylic H). Found: C, 58.11; H, 4.91; Br, 18.32%. Calcd for $C_{21}H_{21}BrO_5$: C, 58.21; H, 4.89; Br, 18.44%.

3-[(4-Bromophenyl)methyl]-5,8-dimethoxy-1,2,3,4-tetrahydro-2-naphthalenecarboxylic acid (13). A mixture of **12** (5.00 g, 11.5 mmol), hydrazine monohydrate (40 ml), potassium hydroxide (3.5 g), and diethylene glycol (100 ml) was refluxed for 1 h. The mixture was heated at 200 °C for an additional 4 h; during this period hydrazine was removed by distillation. After cooling, the reaction mixture was poured into dilute hydrochloric acid (500 ml). The yielded precipitates were filtered, washed with water, and dried in vacuo. Recrystallization from ethyl acetate–hexane afforded **13** (4.00 g, 85.9%) as orange yellow powder. MS (EI) m/z 406, 404 (M^+); ^{1}H NMR (DMSO-d_6) δ=7.50 (d, J=8 Hz, 2H, Ar-H), 7.18 (d, J=8 Hz, 2H, Ar-H), 6.69 (d, J=7 Hz, 1H, Ar-H), 6.65 (d, J=7 Hz, 1H, Ar-H), 3.71 (s, 3H, OMe), 3.64 (s, 3H, OMe), 2.9—2.2 (m, 8H, CH and benzylic H).

***trans*-3-Bromo-7,10-dimethoxy-5a,6,11,11a,12-pentahydro-5-naphthacenone (14).** A mixture of **13** (2.50 g, 6.17 mmol) and methanesulfonic acid (500 ml) was stirred at 50 °C for 30 min, then at 90 °C for 15 min. After cooling, the reaction mixture was poured onto ice-water. The resulting mixture was extracted with chloroform. The organic layer was washed with saturated aqueous sodium hydrogencarbonate and dried over anhydrous sodium sulfate. After removal of the solvent, the residue was dissolved in ethanol (50 ml) and 5% aqueous potassium hydroxide (50 ml). The mixture was refluxed for 4 h. While the solution was still hot, 6 M hydrochloric acid (1 M=1 mol dm^{-3}) was carefully added until the pH of the solution became about 3. After cooling, the mixture was extracted with chloroform. The extract was washed with saturated aqueous sodium hydrogencarbonate and dried. The solvent was evaporated, and the resulting residue was separated by column chromatography on silica gel using 10% ethyl acetate–hexane as an eluent. Recrystallization from carbon tetrachloride–hexane afforded pale-yellow needles (0.68 g, 29.6% yield), mp 181—182 °C. MS (EI) m/z 388, 386 (M^+); IR (Nujol) 1682 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=8.21 (d, J=2 Hz, 1H, Ar-H), 7.59 (dd, J=2, 8 Hz, 1H, Ar-H), 7.17 (d, J=8 Hz, 1H, Ar-H), 6.65 (s, 2H, Ar-H), 3.80 (s, 6H, OMe), 3.6—2.2 (m, 8H, CH and benzylic H). Found: C, 61.90; H, 4.74; Br, 20.55%. Calcd for $C_{20}H_{19}BrO_3$: C, 62.03; H, 4.95; Br, 20.63%.

***trans*-8-Bromo-1,4-dimethoxy-5,5a,6,11,11a,12-hexahydronaphthacene (15).** This compound was prepared starting from **14** by a similar procedure as that described for **8a**. **15**: 80.6% yield, colorless needles from ethanol, mp 178.5—180 °C. MS (EI) *m/z* 374, 372 (M^+); ^{1}H NMR ($CDCl_3$) δ=7.24 (d, J=2 Hz, 1H, Ar-H), 7.22 (dd, J=2, 8 Hz, 1H, Ar-H), 6.96 (d, J=8 Hz, 1H, Ar-H), 6.64 (s, 2H, Ar-H), 3.80 (s, 6H, OMe), 3.2—1.8 (m, 10H, CH and benzylic H). Found: C, 64.17; H, 5.44; Br, 21.59%. Calcd for $C_{20}H_{21}BrO_2$: C, 64.35; H, 5.67; Br, 21.41%.

***trans*-7,10-Dimethoxy-5,5a,6,11,11a,12-hexahydro-2-naphthacenecarbaldehyde (16).** Compound **16** was synthesized from **15** via the same method as described for **9a**. **16**: 79.0% yield, colorless needles from ethanol, mp 204—205 °C. MS (EI) *m/z* 322 (M^+); IR (Nujol) 1688 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=9.94 (s, 1H, CHO), 7.62 (m, 2H, Ar-H), 7.26 (d, J=8 Hz, 1H, Ar-H), 6.65 (s, 2H, Ar-H), 3.81 (s, 6H, OMe), 3.2—1.9 (m, 10H, CH and benzylic H). Found: C, 78.37; H, 6.81%. Calcd for $C_{21}H_{22}O_3$: C, 78.23; H, 6.88%.

Isomeric Mixture of Methyl 5-Bromo-3-(2,5-dimethoxybenzoyl)-1,2,3,4-tetrahydro-2-naphthalenecarboxylate and Methyl 8-Bromo-3-(2,5-dimethoxybenzoyl)-1,2,3,4-tetrahydro-2-naphthalenecarboxylate (18). This compound was prepared starting from **6b** and **17**[26] by a similar procedure as that described for **12**. Compound **18** was confirmed only by MS and IR spectra, because **18** has theoretically four isomers. **18**: 58% yield, colorless oil. MS (EI) *m/z* 434, 432 (M^+); IR (neat) 1722 (C=O), 1672 cm^{-1} (C=O).

Isomeric Mixture of Methyl 5-Bromo-3-[(2,5-dimethoxyphenyl)methyl]-1,2,3,4-tetrahydro-2-naphthalenecarboxylate and Methyl 8-Bromo-3-[(2,5-dimethoxyphenyl)methyl]-1,2,3,4-tetrahydro-2-naphthalenecarboxylate (19). This compound was synthesized by the same method as that described for **8a**. This compound was also an isomeric mixture, and was confirmed by its MS and IR spectra. **19**: 77% yield, colorless oil. MS (EI) *m/z* 420, 418 (M^+); IR (neat) 1736 cm^{-1} (C=O).

Isomeric Mixture of 5-Bromo-3-[(2,5-dimethoxyphenyl)methyl]-1,2,3,4-tetrahydro-2-naphthalenecarboxylic Acid and 8-Bromo-3-[(2,5-dimethoxyphenyl)methyl]-1,2,3,4-tetrahydro-2-naphthalenecarboxylic Acid (20). A mixture of **19** (3.30 g, 7.87 mmol), ethanol (30 ml), and 5% aqueous potassium hydroxide (30 ml) was heated under reflux for 4 h. After cooling, dilute hydrochloric acid was carefully added until the pH of the solution became about 5. The mixture was extracted with ethyl acetate and the extract was washed with a saturated aqueous solution of sodium chloride successively. Removal of the solvent gave **20** quantitatively as a colorless oil. This compound was also an isomeric mixture, and was confirmed only by the MS and IR spectra. Colorless oil. MS (EI) *m/z* 406, 404 (M^+); IR (neat) 1706 cm^{-1} (C=O).

Isomeric Mixture of *trans*-7-Bromo-1,4-dimethoxy-5a,6,11,11a,12-pentahydro-5-naphthacenone and *trans*-10-Bromo-1,4-dimethoxy-5a,6,11,11a,12-pentahydro-5-naphthacenone (21). To a cooled solution of **20** (0.88 g, 2.2 mmol) in dry nitrobenzene (30 ml) was added phosphorus pentachloride (0.59 g, 2.8 mmol) at 0 °C. After stirring for 30 min at 100 °C, the reaction mixture was cooled at 0 °C. Tin(IV) chloride (0.38 ml, 3.3 mol) was added dropwise, and the solution was stirred for 4 h at 5 °C. After ice-water was added, the mixture was extracted with chloroform. The extract was washed with a saturated aqueous solution of sodium hydrogencarbonate and of sodium chloride and dried over anhydrous sodium sulfate. After removal of the solvent under reduced pressure, the residue was dissolved in ethanol (5 ml) and 5% aqueous potassium hydroxide (5 ml). The mixture was refluxed for 4 h. While the solution was still hot, 6 M hydrochloric acid was carefully added until the pH of the solution became ca. 3. After cooling, the mixture was extracted with chloroform. The extract was washed with saturated aqueous sodium hydrogencarbonate and dried over anhydrous sodium sulfate. The solvent was evaporated, and the resulting residue was purified by column chromatography on silica gel with 10% ethyl acetate–hexane to give 0.57 g (68%) of **25** as a colorless solid. This compound was also an isomeric mixture, and was confirmed by only the MS spectrum. MS (EI) *m/z* 388, 386 (M^+).

***trans*-7-Bromo-1,4-dimethoxy-5,5a,6,11,11a,12-hexahydronaphthacene (22).** This compound was prepared starting from **21** in a similar manner as that for **8a**. **22**: 89% yield, colorless fine needles from ethanol, mp 185—186 °C. MS (EI) *m/z* 374, 372 (M^+); ^{1}H NMR ($CDCl_3$) δ=7.34 (d, J=7.9 Hz, 1H, Ar-H), 7.06 (d, J=7.2 Hz, 1H, Ar-H), 6.97 (dd, J=7.9, 7.2 Hz, 1H, Ar-H), 6.64 (s, 2H, Ar-H), 3.80 (s, 6H, OMe), 3.32—1.82 (m, 10H, CH and benzylic H). Found: C, 64.62; H, 5.31; Br, 21.20%. Calcd for $C_{20}H_{21}BrO_2$: C, 64.35; H, 5.63; Br, 21.44%.

***trans*-7,10-Dimethoxy-5,5a,6,11,11a,12-hexahydro-1-naphthacenecarbaldehyde (23).** Compound **23** was synthesized from **22** via the same method as that described for **9a**. **23**: 89% yield, colorless fine needles from ethanol, mp 161—163 °C. MS (EI) *m/z* 322 (M^+); IR (Nujol) 1686 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=10.23 (s, 1H, CHO), 7.65 (d, J=7.2 Hz, 1H, Ar-H), 7.35 (d, J=6.8 Hz, 1H, Ar-H), 7.29 (dd, J=7.2, 6.8 Hz, 1H, Ar-H), 6.65 (s, 2H, Ar-H), 3.81 (s, 6H, OMe), 3.87—1.82 (m, 10H, CH and benzylic H).

5-(4,7-Dimethoxy-2,2′-spirobiindan-5′-yl)-13,17-diethyl-2,3,7,8,12,18-hexamethyl-21*H*,23*H*-porphine (25). A stirred solution of **9a** (90 mg, 0.29 mmol) and **24**[27] (176 mg, 292 μmol) in dry MeOH (50 ml) containing 1 drop of 47% hydrobromic acid was heated for 24 h under reflux. The reaction mixture was poured into water and extracted with chloroform. The organic layer was washed with a saturated aqueous solution of sodium hydrogencarbonate and of sodium chloride and dried over anhydrous sodium sulfate. After removal of the solvent, the residue was purified by preparative thin-layer chromatography with 5% ether–chloroform to give 89.7 mg (42.1%) of **25** as dark-brown solids, mp >300 °C. MS (EI) *m/z* 728 (M^+); ^{1}H NMR ($CDCl_3$) δ=10.12 (s, 2H, *meso*-H), 9.91 (s, 1H, *meso*-H), 7.80 (d, J=7.4 Hz, 1H, Ar-H), 7.77 (s, 1H, Ar-H), 7.49 (d, J=7.4 Hz, 1H, Ar-H), 6.65 (s, 2H, Ar-H), 4.04 (q, J=7.7 Hz, 4H, CH_2CH_3), 3.82 (s, 6H, OMe), 3.60 (s, 6H, Me), 3.51 (s, 6H, Me), 3.32 (s, 2H, benzylic H), 3.19 (s, 2H, benzylic H), 3.19 (d, J=15.8 Hz, 2H, benzylic H), 3.13 (d, J=15.8 Hz, 2H, benzylic H), 2.50 (s, 6H, Me), 1.86 (t, J=7.7 Hz, 6H, CH_2CH_3), −3.2 (br s, 2H, NH).

5-(4,7-Dioxo-4,7-dihydro-2,2′-spirobiindan-5′-yl)-13,17-diethyl-2,3,7,8,12,18-hexamethyl-21*H*,23*H*-porphine (1). To a cooled solution of **25** (58.4 mg, 80.1 μmol)

in dry methylene chloride (30 ml) was added a solution of boron tribromide (1 ml, 11 mmol) in dry methylene chloride (10 ml) at 0 °C. The reaction mixture was stirred at 0 °C for 2 h, then at ambient temperature for 4 h. After a small amount of water was added, the organic layer was separated off, washed with a saturated aqueous solution of sodium hydrogencarbonate and brine and dried over anhydrous sodium sulfate. After removal of the solvent, the residue was dissolved in dry methylene chloride (20 ml). Lead (II) oxide (99.99% pure, 0.80 g, 3.6 mmol) was added to the solution, and the mixture was stirred for 2 h at room temperature. The reaction mixture was filtered through Celite, and the filtrate was concentrated under reduced pressure. The resulting residue was purified by preparative thin-layer chromatography with 5% ether–chloroform to give 45.7 mg (81.6%) of **1** as dark-brown solids, mp >300 °C. MS (EI) *m/z* 698 (M^+); ^{1}H NMR ($CDCl_3$) δ=10.13 (s, 2H, *meso*-H), 9.92 (s, 1H, *meso*-H), 7.73 (d, J=6.8 Hz, 1H, Ar-H), 7.57 (s, 1H, Ar-H), 7.38 (d, J=6.8 Hz, 1H, Ar-H), 6.64 (s, 2H, quinone-H), 4.04 (q, J=7.6 Hz, 4H, CH_2CH_3), 3.61 (s, 6H, Me), 3.52 (s, 6H, Me), 3.08 (s, 2H, benzylic H), 2.79 (d, J=17.1 Hz, 2H, benzylic H), 2.64 (s, 2H, benzylic H), 2.54 (d, J=17.1 Hz, 2H, benzylic H), 2.38 (s, 6H, Me), 1.86 (t, J=7.6 Hz, 6H, CH_2CH_3), −3.2 (br s, 2H, NH).

5-(4,7-Dimethoxy-2,2′-spirobiindan-4′-yl)-13,17-diethyl-2,3,7,8,12,18-hexamethyl-21*H*,23*H*-porphine (26). This compound was prepared starting from **9b** and **24** via the same procedure as that described for **25**. **26**: 11.0% yield, dark-brown solids from chloroform–hexane, mp >300 °C. MS (EI) *m/z* 728 (M^+); ^{1}H NMR ($CDCl_3$) δ=10.14 (s, 2H, *meso*-H), 9.91 (s, 1H, *meso*-H), 7.87 (d, J=6.0 Hz, 1H, Ar-H), 7.62 (d, J=6.7 Hz, 1H, Ar-H), 7.60 (dd, J=6.0, 6.7 Hz, 1H, Ar-H), 6.45 (s, 2H, Ar-H), 4.06 (q, J=7.7 Hz, 4H, CH_2CH_3), 3.65 (s, 6H, OMe), 3.63 (s, 6H, Me), 3.55 (s, 6H, Me), 3.24 (s, 2H, benzylic H), 3.03 (d, J=15.8 Hz, 2H, benzylic H), 2.69 (d, J=15.8 Hz, 2H, benzylic H), 2.56 (s, 2H, benzylic H), 2.51 (s, 6H, Me), 1.86 (t, J=7.7 Hz, 6H, CH_2CH_3), −3.2 (br s, 2H, NH).

5-(4,7-Dioxo-4,7-dihydro-2,2′-spirobiindan-4′-yl)-13,17-diethyl-2,3,7,8,12,18-hexamethyl-21*H*,23*H*-porphine (2). This compound was synthesized from **26** by the same procedure as that described for **1**. **2**: 66.0% yield, dark-brown solids from chloroform–hexane, mp >300 °C. MS (EI) *m/z* 698 (M^+); ^{1}H NMR ($CDCl_3$) δ=10.15 (s, 2H, *meso*-H), 9.94 (s, 1H, *meso*-H), 7.88 (d, J=6.8 Hz, 1H, Ar-H), 7.63 (d, J=6.1 Hz, 1H, Ar-H), 7.59 (dd, J=6.8, 6.1 Hz, 1H, Ar-H), 6.48 (s, 2H, quinone-H), 4.06 (q, J=7.6 Hz, 4H, CH_2CH_3), 3.63 (s, 6H, Me), 3.55 (s, 6H, Me), 3.26 (s, 2H, benzylic H), 2.93 (d, J=16.3 Hz, 2H, benzylic H), 2.61 (d, J=16.3 Hz, 2H, benzylic H), 2.48 (s, 8H, Me and benzylic H), 1.87 (t, J=7.6 Hz, 6H, CH_2CH_3), −3.21 (br s, 1H, NH), −3.35 (br s, 1H, NH).

5-(*trans*-1,4-Dimethoxy-5,5a,6,11,11a,12-hexahydro-8-naphthacenyl)-13,17-diethyl-2,3,7,8,12,18-hexamethyl-21*H*,23*H*-porphine (27). This compound was prepared starting from **16** and **24** by the same manner as that for **25**. **27**: 16.9% yield, dark-brown solids, mp >300 °C. MS (EI) *m/z* 743 (M^+); ^{1}H NMR ($CDCl_3$) δ=10.15 (s, 2H, *meso*-H), 9.93 (s, 1H, *meso*-H), 7.78 (d, J=7 Hz, 1H, Ar-H), 7.74 (s, 1H, Ar-H), 7.45 (d, J=7 Hz, 1H, Ar-H), 6.70 (d, J=9 Hz, 1H, Ar-H), 6.68 (d, J=9 Hz, 1H, Ar-H), 4.06 (q, J=7 Hz, 4H, CH_2CH_3), 3.88 (s, 3H, OMe), 3.81 (s, 3H, OMe), 3.64 (s, 6H, Me), 3.53 (s, 6H, Me), 2.53 (s, 3H, Me), 2.52 (s, 3H, Me), 1.87 (t, J=7 Hz, 6H, CH_2CH_3), 3.5—2.1 (m, 10H, CH and benzylic H), −3.15 (br s, 1H, NH), −3.28 (br s, 1H, NH). Found: C, 80.66; H, 7.53; N, 7.45%. Calcd for $C_{50}H_{54}N_4O_2$: C, 80.83; H, 7.33; N, 7.54%.

5-(*trans*-1,4-Dioxo-1,4,5,5a,6,11,11a,12-octahydro-8-naphthacenyl)-13,17-diethyl-2,3,7,8,12,18-hexamethyl-21*H*,23*H*-porphine (3). This compound was synthesized from **27** by the same procedure as that described for **1**. **3**: 87.9% yield, dark-brown solids, mp >300 °C. MS (EI) *m/z* 713 (M^+); ^{1}H NMR ($CDCl_3$) δ=10.13 (s, 2H, *meso*-H), 9.93 (s, 1H, *meso*-H), 7.79 (d, J=7 Hz, 1H, Ar-H), 7.73 (s, 1H, Ar-H), 7.42 (d, J=7 Hz, 1H, Ar-H), 6.52 (d, J=10 Hz, 1H, quinone-H), 6.40 (d, J=10 Hz, 1H, quinone-H), 4.06 (q, J=8 Hz, 4H, CH_2CH_3), 3.63 (s, 6H, Me), 3.52 (s, 6H, Me), 2.50 (s, 3H, Me), 2.49 (s, 3H, Me), 1.88 (t, J=8 Hz, 6H, CH_2CH_3), 3.4—1.8 (m, 10H, CH and benzylic H), −3.1 (br s, 2H, NH).

5-(*trans*-1,4-Dimethoxy-5,5a,6,11,11a,12-hexahydro-7-naphthacenyl)-13,17-diethyl-2,3,7,8,12,18-hexamethyl-21*H*,23*H*-porphine (28). This compound was prepared starting from **23** and **24** via the same manner as that described for **25**. **28**: 24.0% yield, dark-brown solids from chloroform–methanol, mp >300 °C. ^{1}H NMR ($CDCl_3$) δ=10.15 (s, 1H, *meso*-H), 10.14 (s, 1H, *meso*-H), 9.94 (s, 1H, *meso*-H), 7.67 (d, J=6.6 Hz, 1H, Ar-H), 7.57 (d, J=6.4 Hz, 1H, Ar-H), 7.51 (dd, J=6.4, 6.6 Hz, 1H, Ar-H), 6.51 (d, J=8.7 Hz, 1H, Ar-H), 6.37 (d, J=8.7 Hz, 1H, Ar-H), 4.08 (q, J=7.0 Hz, 4H, CH_2CH_3), 3.77 (s, 3H, OMe), 3.644 (s, 3H, Me), 3.638 (s, 3H, Me), 3.54 (s, 3H, Me), 3.53 (s, 3H, Me), 3.26 (s, 3H, OMe), 2.50 (s, 3H, Me), 2.45 (s, 3H, Me), 1.88 (t, J=7.0 Hz, 6H, CH_2CH_3), 3.46—1.75 (m, 10H, CH and benzylic H), −3.12 (br s, 1H, NH), −3.27 (br s, 1H, NH). Found: *m/z* 742.4257. Calcd for $C_{50}H_{54}N_4O_2$: 742.4244.

5-(*trans*-1,4-Dioxo-1,4,5,5a,6,11,11a,12-octahydro-7-naphthacenyl)-13,17-diethyl-2,3,7,8,12,18-hexamethyl-21*H*,23*H*-porphine (4). This compound was synthesized from **28** by the same procedure as that described for **1**. **4**: 87.9% yield, dark-brown solids from chloroform–hexane, mp >300 °C. MS (FAB) *m/z* 715 (M^++2); ^{1}H NMR ($CDCl_3$) δ=10.16 (s, 1H, *meso*-H), 10.14 (s, 1H, *meso*-H), 9.95 (s, 1H, *meso*-H), 7.71 (d, J=7.1 Hz, 1H, Ar-H), 7.56 (d, J=7.4 Hz, 1H, Ar-H), 7.51 (dd, J=7.1, 7.4 Hz, 1H, Ar-H), 6.56 (d, J=9.9 Hz, 1H, quinone-H), 6.42 (d, J=9.9 Hz, 1H, quinone-H), 4.07 (q, J=7.6 Hz, 4H, CH_2CH_3), 3.643 (s, 3H, Me), 3.636 (s, 3H, Me), 3.54 (s, 3H, Me), 3.53 (s, 3H, Me), 2.48 (s, 3H, Me), 2.43 (s, 3H, Me), 1.88 (t, J=7.6 Hz, 6H, CH_2CH_3), 3.46—1.78 (m, 10H, CH and benzylic H), −3.14 (br s, 1H, NH), −3.29 (br s, 1H, NH). Found: *m/z* 712.3746. Calcd for $C_{48}H_{48}N_4O_2$: 712.3775.

The authors thank Material Analysis Center of ISIR, Osaka University for the 360 MHz NMR and mass spectroscopy service. This work was partly supported by a Grand-in-Aid (No. 0403007 to Y. S.) and by that on New Program (O4NP0301 to T. O.) from the Ministry of Education, Science and Culture.

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