Synthesis and Intramolecular Electron-Transfer Reaction of Distance-Fixed Quinone-Linked Porphyrins

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Synthesis is described of a series of distance-fixed quinone-linked porphyrins in which electron affinity of the attached quinone is systematically changed. The fluorescence lifetimes of the porphyrin chromophore in these model compounds were shortened due to the intramolecular electron transfer to the attached quinone. The rates of the charge separation between the singlet excited state of the porphyrin and the quinone were determined on the basis of these shortened fluorescence lifetimes and were plotted against the free energy changes associated with the charge separation. Up to ca. 1.54 eV exothermic reaction, the rates of the charge separation were found to still increase.

The appearance of the X-ray structure of bacterial photosynthetic reaction center[1] has stimulated mechanistic as well as synthetic approaches toward this natural charge separation (CS) apparatus.[2–4] Among these, quinone-linked porphyrins held at restricted geometries have been demonstrated to be particularly useful for examination of distance-dependence[5–8] and orientation-dependence[9–11] of photoinduced electron-transfer (ET) reaction from singlet excited state of porphyrin to quinone. Free energy gap dependence of the rates of charge separation (CS)[12–15] and charge recombination (CR)[12,13] have been also studied with geometry-restricted quinone-linked porphyrins. These studies have revealed the so-called Marcus normal region in the CS reaction and the inverted region in the CR reaction, respectively. However, several important questions remain to be answered, such as 1) whether inverted region in the CS reaction and normal region in the CR reaction exist or not,[16] 2) how solvent polarity and temperature influence the CS and CR reactions, 3) whether the reorganization energies in the CS and CR reactions in the same solvent are really same or not?

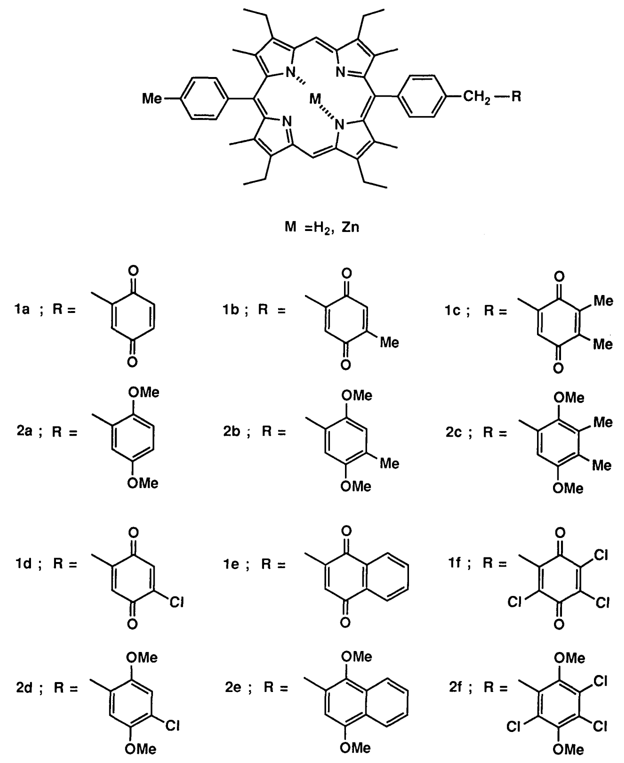
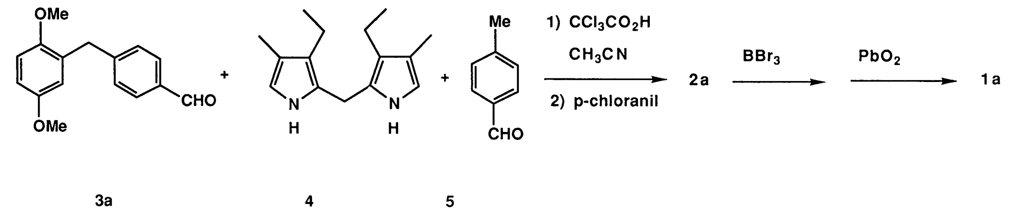


Fig. 1. Structures of quinone-linked porphyrins.

In the course of our program aiming at construction of efficient artificial photocatalyst based on the porphyrin aggregates,[3] we designed a series of distance-fixed quinone-linked porphyrins **1a**—**f** and their zinc complexes **1a(Zn)**—**f(Zn)** (Fig. 1), as models for study of intramolecular ET reaction. In our models, the center-to-center distance between the porphyrin and the quinone can be regarded as being restricted to be ca. 9.8 Å, although the linkage is somewhat flexible. The models have electron-accepting quinone moiety with different electron affinity and should be useful for study of energy gap dependence of both CS and CR reactions. In fact, with these models, energy gap dependence of CS and CR reactions have been studied in detail by picosecond time-resolved transient absorption spectroscopy,[17] which have revealed a lot of new mechanistic aspects of ET reactions of quinone-linked porphyrins. In this paper, we will describe the synthesis of the models **1a**—**f** and their zinc complexes **1a(Zn)**—**f(Zn)** and their fluorescence properties.

Results and Discussion

Synthesis of Quinone-Linked Porphyrins. The synthetic route to acceptor-free porphyrin **2a** and quinone-linked porphyrin **1a** is outlined in Scheme 1. Acid-catalyzed condensation of bis(3-ethyl-4-methyl-2-pyrrolyl)methane **4**[18] with 4-(2′,5′-dimethoxybenzyl)benzaldehyde **3a** and 4-methylbenzaldehyde **5** in a ratio

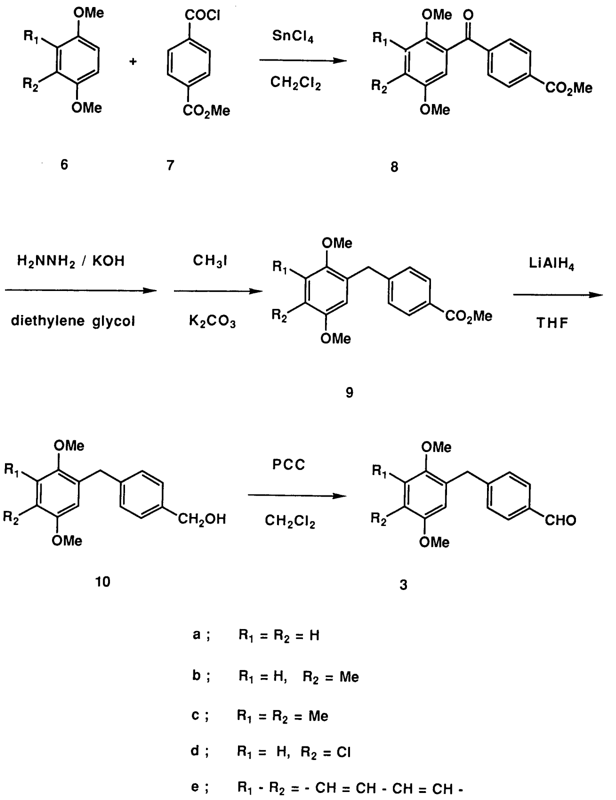


Scheme 1.

Table 1. Isolated Yields of **1a**—**f** and **2a**—**f**

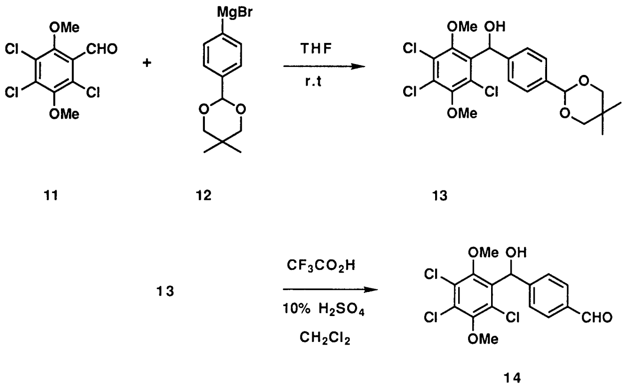
Porphyrin	Yield[a)]/%	Porphyrin	Yield[b)]/%
2a	12	**1a**	91
2b	10	**1b**	95
2c	11	**1c**	93
2d	13	**1d**	94
2e	10	**1e**	92
2f	9,[c)] 40[d)]	**1f**	91

a) Isolated yield based on the used amount of **4**. b) Isolated yield from **2**. c) Isolated yield of **15** based on the used amount of **4**. d) Isolated yield of **2f** from **15**.



Scheme 2.

of 2 : 1 : 1 under our improved conditions[19)] gave a mixture of three porphyrins. The cross-coupling product **2a** was separated by flash column chromatography in 12% yield based on the used amount of **4**. Demethylation of **2a** with an excess amount of BBr_3 followed by oxidation with PbO_2 in CH_2Cl_2 gave **1a** in 91% yield.

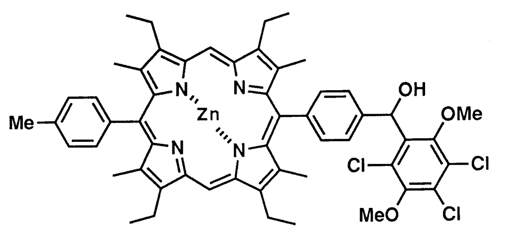


Scheme 3.

In a similar manner, the acceptor-free porphyrins **2b**—**e** and the quinone-linked porphyrins **1b**—**e** were synthesized. Isolated yields are summarized in Table 1.

In Scheme 2, the synthetic route to the functionallized aldehyde **3a**—**e** is shown. Friedel–Crafts acylation ($SnCl_4$, CH_2Cl_2, reflux) of substituted 1,4-dimethoxybenzenes **6a**—**d** and 2,4-dimethoxynaphthalene **6e** with 4-(methoxycarbonyl)benzoyl chloride **7** gave ketones **8a**—**e**, which were converted to the corresponding diarylmethane derivatives **9a**—**e** via Wolff–Kishner reduction and re-esterification. The esters **9a**—**e** were reduced with $LiAlH_4$ to alcohols **10a**—**e**, which were oxidized with pyridinium chlorochromate (PCC) to give the aldehydes **3a**—**e**.

On the other hand, the porphyrins **2f** and **1f** were prepared via the porphyrin **15**, which in turn was synthesized by the cross condensation of **4**, **5**, and **14**. The aldehyde **14** was prepared by the addition of Grignard reagent **12** to the aldehyde **11**[20)] and subsequent deprotection under acidic conditions (Scheme 3). Upon treatment with $NaBH_4$ in trifluoroacetic acid,[21)] the cross-coupling product **15** provided **2f**, which was



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demethylated and oxidized to the quinone-linked porphyrin **1f**.

Optical and Fluorescence Properties of Quinone-Linked Porphyrins. The absorption spectra of free base porphyrins **1a**—**f** show Soret band (S_2) at 406.5 nm and Q bands (S_1) at 505, 536, 575, and 624 nm in THF, while the absorption spectra of the zinc complexes **1a(Zn)**—**f(Zn)** exhibited Soret band at 415 nm and Q bands at 545 and 579 nm in THF, respectively.

The absorption spectra of **1a**—**f** and **1a(Zn)**—**f(Zn)** are almost identical with the corresponding reference compounds **2a**—**f** and **2a(Zn)**—**f(Zn)**, respectively, indicating that the attachment of the quinone to the porphyrin does not strongly perturb their electronic structure.

Although the fluorescence spectra of quinone-linked porphyrin **1a** and **1a(Zn)** are identical with those of the quinone-free porphyrins **2a** and **2a(Zn)**, respectively, the fluorescence intensities and fluorescence lifetimes of **1a**—**f** and **1a(Zn)**—**f(Zn)** are reduced in comparison with those of **2a**—**f** and **2a(Zn)**—**f(Zn)**. The fluorescence lifetimes (τ) of **1** and **1(Zn)** were determined in THF at 298 K by picosecond time-correlated single photon counting technique. In most cases, fluorescence decays can be fitted to biexponentials with one major component (97—99%) of shorter lifetime and one minor component (1—3%) of longer lifetime. The minor component may be most probably due to impurities in which the quinone moiety is altered to other non-electron-accepting group or due to porphyrin-hydroquinone formed in situ by porphyrin-sensitized photoreaction. The major fast decaying component in the observed fluorescence lifetimes can be directly related to the charge separation (CS) process by assuming that the sole additional deactivation pathway relative to the reference compounds **2** and **2(Zn)** is the CS reaction between the excited singlet porphyrin and the quinone. In fact, this was clearly confirmed by picosecond time-resolved transient absorption spectroscopy.[17] Taking the lifetime of **2** (12.4 ns) and **2(Zn)** (1.5 ns) into consideration to define the natural fluorescence lifetime of the porphyrin (τ_0), we can calculate the CS rate constants from the following equation,

$$k_{\mathrm{cs}} = 1/\tau - 1/\tau_0. \qquad (1)$$

The fluorescence lifetimes of the major component and the calculated k_{cs} values are summarized in Table 2. For the compounds **1f** and **1f(Zn)**, the accurate fluorescence lifetimes could not be determined, because the fluorescence lifetimes of these compounds were beyond the time-resolution of our measurement system. Femtosecond transient absorption spectroscopy showed the k_{cs} for **1f(Zn)** to be 5.5×10^{11} s^{-1}.[17]

The approximate free energy gap ($-\Delta G^0$) of the CS reaction was obtained from Eq. 2,

$$-\Delta G^0 = E(S_1) - E_D^{\mathrm{ox}} + E_A^{\mathrm{red}} + e_0^2/\varepsilon r, \qquad (2)$$

where $E(S_1)$ is the energy of the lowest excited singlet state of the porphyrin (1.98 eV for free base porphyrin and 2.13 eV for zinc porphyrin), E_D^{ox} and E_A^{red} are the measured $E_{1/2}$ values for the one-electron oxidation and one-electron reduction of the porphyrin donor and quinone acceptor, respectively, and the last term $e_0^2/\varepsilon r$ is the electrostatic work term where ε is the dielectric constant of the solvent (7.58 for THF), and r is the center-to-center distance between the ions. The redox potentials measured in CH_2Cl_2 were used for the above estimation, since meaningful cyclic voltammgram was not obtained in THF. E_D^{ox} are 0.13 and 0.33 V vs. ferrocene/ferrocenium reference electrode for zinc and free base porphyrins, respectively, and E_A^{red} values of the appropriately substituted methyl quinone derivatives were listed in Table 2. The electrostatic work term was estimated to be ca. 0.19 eV in THF. The estimated free energy gaps were listed in Table 2.

Figure 2 is the plot of CS rate constant ($\log k_{\mathrm{cs}}$) against the $-\Delta G^0$, showing a trend of sharp increasing rates with increasing driving force from 0.6 eV to ca. 0.9 eV and of ever slowly increasing rates from ca. 0.9 eV to 1.54 eV. Interestingly, up to 1.54 eV driving force, we could not observe the inverted region. It is even unclear whether the rate of the CS reaction in quinone-linked porphyrin will drop in a more exothermic region. A clearer understanding is expected to evolve only

Table 2. Fluorescence Lifetime and Rate of Intramolecular Charge Separation for **1** and **1(Zn)** in THF

Model	$\tau^{a)}$/ps	$k_{\mathrm{cs}}/10^9$ s^{-1}	$E_A^{\mathrm{red}\,b)}$/V	$-\Delta G^{0c)}$/eV	Model	$\tau^{a)}$/ps	$k_{\mathrm{cs}}/10^{11}$ s^{-1}	$-\Delta G^{0c)}$/eV
1a	130	7.6	−1.06	0.78	**1a(Zn)**	9.8	1.0	1.13
1b	220	4.5	−1.14	0.70	**1b(Zn)**	14	0.71	1.05
1c	520	1.8	−1.22	0.62	**1c(Zn)**	18	0.55	0.97
1d	44	23	−0.88	0.96	**1d(Zn)**	8.3	1.2	1.31
1e	410	2.4	−1.24	0.60	**1e(Zn)**	15	0.66	0.95
1f	<ca. 5$^{d)}$	>ca. 200	−0.65	1.19	**1f(Zn)**	<ca. 5$^{d)}$	>ca. 2 (5.5)$^{e)}$	1.54

a) Major fast exponential component in the deconvoluted fluorescence decay, see the text. b) One-electron reduction potential of the appropriately methyl-substituted reference quinone measured vs ferrocene/ferrocenium reference electrode in CH_2Cl_2. c) Calculated by Eq. 2. E_D^{ox} are 0.13 and 0.33 V vs. ferrocene/ferrocenium reference electrode for the zinc and free base porphyrins, respectively. d) Because the fluorescence lifetime is beyond the time-resolution of our system, the lifetime could not be measured accurately. e) The value in the parenthesis is the CS rate determined by femtosecond transient absorption spectroscopy.[17]

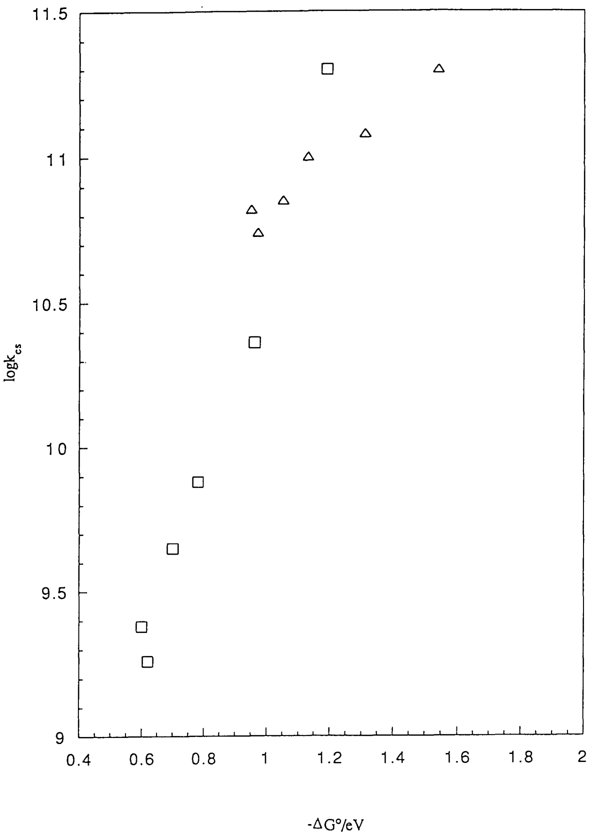

Fig. 2. A plot of log k_{cs} against $-\Delta G^\circ$ (eV) in THF. □; **1a**—**f**. △; **1a(Zn)**—**f(Zn)**.

after more systematic investigation, that is being in progress with a view to studing the CS process with more exothermicities, is completed.

Experimental

General. Unless otherwise stated, all commercially available solvents and reagents were used without further purification. Acetonitrile was stored over molecular sieves for several days before use. UV-visible spectra were obtained with a Shimadzu UV-160 spectrometer. Steady-state fluorescence spectra were taken on a Shimadzu RF-502A spectrofluorimeter. ^{1}H NMR spectra were recorded on a JEOL GX-400 spectrometer. Chemical shifts were reported in the δ scale relative to Me_4Si. Mass spectra of porphyrins were recorded on JEOL DX-300 spectrometer using the positive FAB (fast atom bombardment) method (accelerating voltages 1.5 and 10 kV, Xe atom as the primary ion source). The FAB matrix was 3-nitrobenzyl alcohol/chloroform unless otherwise stated. Fluorescence lifetimes were measured in 10^{-7} M air-saturated solution (1 M=1 mol dm^{-3}) by means of a picosecond time-correlated single photon counting system.[22]

Synthesis of 2,5-Dimethoxy-4′-(methoxycarbonyl)benzophenone (8a). Commercially available methyl 4-formylbenzoate (Tokyo Kasei) was oxidized by the literature method[23] (sulfamic acid/sodium chlorite) to 4-(methoxycarbonyl)benzoic acid, which was converted to 4-(methoxycarbonyl)benzoyl chloride with thionyl chloride (two steps, 82%. bp 75—93 °C/1 mmHg, 1 mmHg=133.322 Pa.) 1,4-Dimethoxybenzene (4.56 g, 30 mmol), 4-(methoxycarbonyl)benzoyl chloride (5.96 g, 30 mmol), and $SnCl_4$ (9.15 ml) were dissolved in CH_2Cl_2 (190 ml). This mixture was refluxed overnight. After usual work up, 2,5-dimethoxy-4′-(methoxycarbonyl)benzophenone **8a** (7.2 g, 24 mmol, 80%) was obtained as colorless solids. Mp 88—89 °C. ^{1}H NMR ($CDCl_3$) δ=8.09 (2H, d, J=7.0 Hz), 7.84 (2H, d, J=7.0 Hz), 7.05 (1H, dd, J=3.0 and 9.0 Hz), 6.98 (1H, d, J=3.0 Hz), 6.93 (1H, d, J=9.0 Hz), 3.95 (3H, s, OMe), 3.80 (3H, s, OMe), 3.63 (3H, s, CO_2Me). MS (EI) m/z 300 (M$^+$). Found: C, 67.72; H, 5.41%. Calcd for $C_{17}H_{16}O_5$: C, 67.99; H, 5.37%.

The benzophenones **8b**, **8c**, and **8d** as well as the ketone **8e** were prepared in the similar manner as **8a**. The compound data are listed below.

2,5-Dimethoxy-4-methyl-4′-(methoxycarbonyl)benzophenone (8b): Yield: 75%. Mp 136—137 °C. ^{1}H NMR ($CDCl_3$) δ=8.10 (2H, d, J=8.4 Hz), 7.83 (2H, d, J=8.4 Hz), 6.95 (1H, s), 6.81 (1H, s), 3.95 (3H, s, OMe), 3.82 (3H, s, OMe), 3.60 (3H, s, CO_2Me), 2.31 (3H, s, Me). MS (FAB) m/z 315 (M$^+$+1).

2,5-Dimethoxy-3,4-dimethyl-4′-(methoxycarbonyl)benzophenone (8c): Yield: 77%. Mp 110—111 °C. ^{1}H NMR ($CDCl_3$) δ=8.10 (2H, d, J=8.6 Hz), 7.88 (2H, d, J=8.6 Hz), 6.76 (1H, s), 3.94 (3H, s, OMe), 3.80 (3H, s, OMe), 3.46 (3H, s, CO_2Me), 2.22 (3H, s, Me), 2.20 (3H, s, Me). MS (FAB) m/z 329 (M$^+$+1). Found: C, 69.46, H, 6.20%. Calcd for $C_{19}H_{20}O_5$: C, 69.50; H, 6.14%.

4-Chloro-2,5-dimethoxy-4′-(methoxycarbonyl)benzophenone (8d): Yield: 72%. Mp 170—171 °C. ^{1}H NMR ($CDCl_3$) δ=8.10 (2H, d, J=8.3 Hz), 7.81 (2H, d, J=8.3 Hz), 7.05 (1H, s), 7.04 (1H, s), 3.95 (3H, s, OMe), 3.88 (3H, s, OMe), 3.62 (3H, s, CO_2Me). MS (FAB) m/z 335 (M$^+$+1). Found: C, 60.96; H, 4.37; Cl, 10.37%. Calcd for $C_{17}H_{15}O_5Cl$: C, 61.00; H, 4.52; Cl, 10.59%.

1,4-Dimethoxy-2-[4′-(methoxycarbonyl)benzoyl]naphthalene (8e): Yield: 82%. Mp 132—133 °C. ^{1}H NMR ($CDCl_3$) δ=8.31 (1H, m), 8.13 (3H, m), 7.94 (2H, m), 7.61 (2H, m), 6.81 (1H, s), 3.99 (3H, s, OMe), 3.95 (3H, s, OMe), 3.68 (3H, s, CO_2Me). MS (FAB) m/z 350 (M$^+$). Found: C, 72.12; H, 5.34%. Calcd for $C_{21}H_{18}O_5$: C, 71.99; H, 5.18%.

Synthesis of Methyl 4-(2′,5′-Dimethoxybenzyl)benzoate (9a): The compound **9a** was synthesized from **8a** by the following sequence: (1) reduction to 4-(2′,5′-dimethoxybenzyl)benzoic acid by Wolff-Kishner reduction, (2) esterification to methyl 4-(2′,5′-dimethoxybenzyl)benzoate **9a** with methyl iodide. A mixture of ketone **8a** (0.90 g, 3.0 mmol), KOH (0.85 g, 15 mmol), hydrazine monohydrate (2.25 g, 45 mmol), and diethylene glycol (30 ml) was heated to 200 °C. The color of the solution changed from yellow via red-orange to colorless. After 5.5 h, the reaction mixture was poured into water, and acidified by hydrochloric acid. The white precipitates were collected, washed with water, dissolved again in aqueous NaOH solution, and precipitated again by adding dilute hydrochloric acid. The precipitates were filtered and washed with water, and dissolved in chloroform. The solution was dried over Na_2SO_4 and evaporated to give 4-(2′,5′-dimethoxybenzyl)benzoic acid (0.92 g, 2.9 mmol, 96%). This was converted to the methyl ester by treatment with methyl iodide (1.6 equiv) and potassium carbonate (2.5 equiv) in acetone (reflux, overnight). The inorganic substance was removed by filtration, and acetone and excess methyl iodide were removed by rotary evaporator. The residue was dissolved in CH_2Cl_2, washed with water, dried, and evaporated. The residual yellow oil crystallized on standing. Yield: 80%.

Mp 41—42 °C. ^{1}H NMR (CDCl$_3$) δ=7.94 (2H, d, *J*=7.9 Hz), 7.27 (2H, d, *J*=7.9 Hz), 6.72 (3H, m), 3.98 (2H, s, -CH$_2$-), 3.89 (3H, s, CO$_2$Me), 3.75 (3H, s, OMe), 3.73 (3H, s, OMe). MS (EI) *m*/*z* 288 (M$^+$+2). Found: C, 71.37; H, 6.40%. Calcd for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34%.

The compounds **9b**, **9c**, **9d**, and **9e** were prepared in the similar manner. Only the physical data of the compounds are listed below. The physical data of **9b** were given elsewhere.[24]

Methyl 4-(2′,5′-Dimethoxy-3′,4′-dimethylbenzyl)benzoate (9c): Yield: 86%. Mp 47—48 °C. ^{1}H NMR (CDCl$_3$) δ=7.94 (2H, d, *J*=8.3 Hz), 7.27 (2H, d, *J*=8.3 Hz), 6.44 (1H, s), 4.04 (2H, s, -CH$_2$-), 3.89 (3H, s, CO$_2$Me), 3.71 (3H, s, OMe), 3.57 (3H, s, OMe), 2.21 (3H, s, Me), 2.13 (3H, s, Me). MS (EI) *m*/*z* 314 (M$^+$). Found: C, 72.65; H, 7.13%. Calcd for $C_{19}H_{22}O_4$: C, 72.59; H, 7.05%.

Methyl 4-(2′,5′-Dimethoxy-4′-chlorobenzyl)benzoate (9d): Yield: 75%. Mp 94—95 °C. ^{1}H NMR (CDCl$_3$) δ=7.94 (2H, d, *J*=8.3 Hz), 7.23 (2H, d, *J*=8.3 Hz), 6.90 (1H, s), 6.67 (1H, s), 3.97 (2H, s, -CH$_2$-), 3.89 (3H, s, CO$_2$Me), 3.78 (3H, s, OMe), 3.74 (3H, s, OMe). MS (EI) *m*/*z* 320 (M$^+$). Found: C, 63.20; H, 5.15; Cl, 10.85%. Calcd for $C_{17}H_{17}O_4Cl$: C, 63.65; H, 5. 34; Cl, 11.05%.

1,4-Dimethoxy-2-[4′-(methoxycarbonyl)benzyl]naphthalene (9e): Yield: 70%. Oil. ^{1}H NMR (CDCl$_3$) δ=8.12 (1H, d, *J*=7.9 Hz), 7.96 (1H, d, *J*=7.9 Hz), 7.86 (2H, d, *J*=8.2 Hz), 7.45 (1H, m), 7.37 (1H, m), 7.20 (2H, d, *J*=8.2 Hz), 6.39 (1H, s), 4.14 (2H, s, -CH$_2$-), 3.79 (3H, s, CO$_2$Me), 3.78 (3H, s, OMe), 3.74 (3H, s, OMe). MS (EI) *m*/*z* 336 (M$^+$). Found: C, 74.67; H, 5.86%. Calcd for $C_{21}H_{20}O_4$: C, 74.98; H, 5.99%.

Synthesis of 4-(2′,5′-Dimethoxybenzyl)benzaldehyde (3a). The compound **3a** was synthesized from **9a** by the following sequence: (1) reduction to the corresponding alcohol with LiAlH$_4$, (2) oxidation to the aldehyde **3a** with PCC. The compound **9a** (1.0 g, 3.5 mmol) dissolved in THF (15 ml) was added to a suspension of LiAlH$_4$ (0.13 g, 3.5 mmol) in THF (10 ml) at −78 °C under nitrogen. After addition, the temperature was raised up to room temperature slowly and overnight. The excess LiAlH$_4$ was hydrolyzed with ethyl acetate, and the reaction mixture was washed with 1 M HCl, and extracted with CH$_2$Cl$_2$. The extract was dried over Na$_2$SO$_4$ and evaporated to give the corresponding alcohol (0.86 g, 3.3 mmol, 95%). The obtained alcohol dissolved in CH$_2$Cl$_2$ (30 ml) was added to a suspension of PCC (1.07 g, 4.95 mmol) dissolved in CH$_2$Cl$_2$ (30 ml). The solution was stirred for 3 h, then ether (60 ml) was added and the supernatant liquid was decanted. The black residue was washed 3 times with ether. The combined extracts were filtered through florisil and concentrated to give the crude product **3a** which was purified by silica gel chromatography. Yield: 76%. Oil. ^{1}H NMR (CDCl$_3$) δ=9.95 (1H, s, CHO), 7.78 (2H, d, *J*=8.3 Hz), 7.37 (2H, d, *J*=8.3 Hz), 6.75 (3H, m), 4.01 (2H, s, -CH$_2$-), 3.75 (3H, s, OMe), 3.73 (3H, s, OMe). MS (EI) *m*/*z* 256 (M$^+$). Found: C, 75.11; H, 6.33%. Calod for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29%.

The compounds **3b**, **3c**, **3d**, and **3e** were prepared in the similar manner. Only the physical data of the compounds are listed below.

4-(2′,5′-Dimethoxy-4′-methylbenzyl)benzaldehyde (3b): Yield: 72%. Mp 68—69 °C. ^{1}H NMR (CDCl$_3$) δ=9.96 (1H, s, CHO), 7.78 (2H, d, *J*=8.2 Hz), 7.37 (2H, d, *J*=8.2 Hz), 6.70 (1H, s), 6.55 (1H, s), 4.06 (2H, s, -CH$_2$-), 3.71 (3H, s, OMe), 3.68 (3H, s, OMe), 2.20 (3H, s, Me). MS (EI) *m*/*z* 270 (M$^+$).

4-(2′,5′-Dimethoxy-3′,4′-dimethylbenzyl)benzaldehyde (3c): Yield: 70%. Mp 55—56 °C. ^{1}H NMR (CDCl$_3$) δ=9.96 (1H, s, CHO), 7.78 (2H, d, *J*=8.2 Hz), 7.37 (2H, d, *J*=8.2 Hz), 6.44 (1H, s), 4.06 (2H, s, -CH$_2$-), 3.71 (3H, s, OMe), 3.58 (3H, s, OMe), 2.20 (3H, s, Me), 2.12 (3H, s, Me). MS (EI) *m*/*z* 284 (M$^+$). Found: C, 75.73; H, 7.05%. Calcd for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09%.

4-(2′,5′-Dimethoxy-4′-chlorobenzyl)benzadehyde (3d): Yield: 68%. Mp 83-84 °C. ^{1}H NMR (CDCl$_3$) δ=9.95 (1H, s, CHO), 7.78 (2H, d, *J*=8.3 Hz), 7.22 (2H, d, *J*=8.3 Hz), 6.88 (1H, s), 4.01 (2H, s, -CH$_2$-), 3.77 (3H, s, OMe), 3.75 (3H, s, OMe), 2.20 (3H, s, Me), 2.12 (3H, s, Me). MS (EI) *m*/*z* 290 (M$^+$). Found: C, 66.19; H, 5.21; Cl, 12.04%. Calcd for $C_{16}H_{15}O_3Cl$: C, 66.10; H, 5.20; Cl, 12.19%.

1,4-Dimethoxy-2-(4′-formylbenzyl)naphthalene (3e): Yield: 65%. Oil. ^{1}H NMR (CDCl$_3$) δ=9.86 (1H, s, CHO), 8.12 (1H, d, *J*=8.3 Hz), 7.95 (1H, d, *J*=8.3 Hz), 7.70 (2H, d, *J*=8.3 Hz), 7.47—7.35 (2H, m), 7.31 (2H, d, *J*=8.3 Hz), 6.49 (1H, s), 4.16 (2H, s, -CH$_2$-), 3.75 (3H, s, OMe), 3.74 (3H, s, OMe); MS (EI) *m*/*z* 306 (M$^+$). Found: C, 77.75; H, 5.56%. Calcd for $C_{20}H_{18}O_3$: C, 78.41; H, 5.92%.

Synthesis of 5-[4′-(2″,5″-dimethoxyphenyl)methylphenyl]-15-(4‴-methylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphine (2a). 4-(2′,5′-Dimethoxybenzyl)benzaldehyde **3a** (128 mg, 0.5 mmol) and 4-methylbenzaldehyde **5** (60 mg, 0.50 mmol) were dissolved in acetonitrile (10 ml) containing trichloroacetic acid (20 mg, 0.12 mmol). A solution of dipyrromethane **4** (230 mg, 1.0 mmol) in acetonitrile (5 ml) was added, and the mixture was stirred overnight at room temperature in the dark under nitrogen. *p*-Chloranil (230 mg) dissolved in THF (10 ml) was added, and the stirring was continued for 5 h, then the solution was poured into water containing concentrated hydrochloric acid, extracted with CHCl$_3$, and neutralized with aq NaHCO$_3$. To the organic extracts, Zn(OAc)$_2$/MeOH (30 ml) was added and the solution was refluxed for 1 h. The solution was poured into water, and the organic layer was separated, dried over Na$_2$SO$_4$ and evaporated. The zinc complexes were separated by silica gel column chromatography using benzene as eluent. The desired compound **2a(Zn)** was isolated in 12% yield. The free base **2a** was obtained by acidic demetallation of zinc ion. Mp >300 °C. ^{1}H NMR (CDCl$_3$) δ=10.20 (2H, s, meso), 8.00 (2H, d, *J*=7.8 Hz), 7.98 (2H, d, *J*=7.0 Hz), 7.56 (2H, d, *J*=7.8 Hz), 7.54 (2H, d, *J*=7.0 Hz), 6.96 (1H, d, *J*=2.9 Hz), 6.93 (1H, d, *J*=8.0 Hz), 6.83 (1H, dd, *J*=2.9 and 8.0 Hz), 4.32 (2H, s, -CH$_2$-), 4.00 (8H, q, $\underline{CH_2}CH_3$, *J*=7.3 Hz), 3.94 (3H, s, -OMe), 3.86 (3H, s, -OMe), 2.74 (3H, s, Ar-$\underline{Me}$), 2.47 (6H, s, Me), 2.43 (6H, s, Me), 1.77 (12H, t, CH$_2\underline{CH_3}$, *J*=7.3 Hz), −2.38 (2H, broad, NH). MS (FAB) H$_2$P *m*/*z* 795 (M$^+$+1); ZnP *m*/*z* 860 (M$^+$+2). UV-vis (THF) H$_2$P λ_{max}: 406.5, 505, 536, 575.5, 623 nm; ZnP λ_{max}: 415, 544, 580 nm.

Other porphyrins **2b**, **2c**, **2d**, and **2e** were prepared in the similar manner. Only the physical data of these compounds are listed below.

2b: Mp >300 °C. ^{1}H NMR (CDCl$_3$) δ=10.19 (2H, s, meso), 7.98 (2H, d, *J*=7.8 Hz), 7.96 (2H, d, *J*=8.3 Hz), 7.58 (2H, d, *J*=7.8 Hz), 7.55 (2H, d *J*=8.3 Hz), 6.89 (1H, s, Ar), 6.86 (1H, s, Ar), 4.33 (2H, s, -CH$_2$-), 4.02 (8H, q, $\underline{CH_2}CH_3$, *J*=7.3 Hz), 3.94 (3H, s, -OMe), 3.91 (3H, s, -OMe), 2.75 (3H, s, Ar-$\underline{Me}$), 2.52 (6H, s, Me), 2.50 (6H, s, Me), 2.33 (3H, s, Ar-$\underline{Me}$), 1.78 (12H, t, CH$_2\underline{CH_3}$, *J*=7.3 Hz), −2.43 (2H, broad, NH). MS (FAB) H$_2$P *m*/*z* 809 (M$^+$+1); ZnP *m*/*z* 871 (M$^+$). UV-vis, (THF) H$_2$P λ_{max}: 407, 505.5, 536, 577.5, 623 nm; ZnP λ_{max}: 415, 543, 578 nm.

2c: Mp >300 °C. ^1H NMR ($CDCl_3$) δ=10.14 (2H, s, meso), 7.90 (2H, d, J=7.8 Hz), 7.88 (2H, d, J=7.8 Hz), 7.49 (2H d J=7.8 Hz), 7.45 (2H, d, J=7.8 Hz), 6.63 (1H, s, Ar), 4.24 (2H, s, $-CH_2-$), 3.91 (8H, q, $\underline{CH_2}CH_3$, J=7.3 Hz), 3.78 (3H, s, OMe), 3.68 (3H, s, OMe), 2.63 (3H, s, Ar-$\underline{Me}$), 2.39 (6H, s, Me), 2.38 (6H, s, Me), 2.20 (3H, s, Ar$\underline{Me}$), 2.12 (3H, s, Ar-$\underline{Me}$), 1.70 (12H, t, $CH_2\underline{CH_3}$, J=7.3 Hz), −2.45 (2H, broad, NH). MS (FAB) H_2P m/z 823 (M^++1); ZnP m/z 886 (M^++1). UV-vis (THF) H_2P λ_{max}: 407, 505, 538, 574, 623 nm; ZnP λ_{max}: 415, 545, 579.5 nm.

2d: Mp >300 °C. ^1H NMR ($CDCl_3$) δ=10.23 (2H, s, meso), 7.98 (2H, d, J=7.3 Hz), 7.95 (2H, d J=7.8 Hz), 7.56 (2H, d, J=7.3 Hz), 7.54 (2H, d, J=7.8 Hz), 7.20 (1H, s, Ar), 6.82 (1H, s, Ar), 4.30 (2H, s, $-CH_2-$), 4.05 (6H, s, OMe), 4.04 (6H, s, OMe), 4.03 (8H, q, $\underline{CH_2}CH_3$, J=7.3 Hz), 2.71 (3H, s, Ar-$\underline{Me}$), 2.52 (6H, s, Me), 2.47 (6H, s, Me), 1.79 (12H, t, $CH_2\underline{CH_3}$, J=7.3 Hz), −2.33 (2H, broad, NH). MS (FAB) H_2P m/z 829 (M^++1); ZnP m/z 892 (M^++1). UV-vis (THF) H_2P λ_{max}: 407, 505.5, 536, 574.5, 624 nm; ZnP λ_{max}: 415, 545.5, 579.5 nm.

2e: Mp >300 °C. ^1H NMR ($CDCl_3$) δ=10.19 (2H, s, meso), 8.33 (1H, d, J=7.8 Hz), 8.20 (1H, d, J=7.8 Hz), 8.01 (2H, d, J=6.0 Hz), 7.94 (2H, d, J=7.0 Hz), 7.64 (2H, d, J=6.0 Hz), 7.63 (1H, t, J=7.8 Hz), 7.54 (2H, d, J=7.0 Hz), 7.53 (1H, t, J=7.8 Hz), 6.82 (1H, s, Ar), 4.60 (2H, s, $-CH_2-$), 4.10 (3H, s, OMe), 4.08 (3H, s, OMe), 4.00 (8H, q, $\underline{CH_2}CH_3$, J=7.3 Hz), 2.75 (3H, s, Ar-$\underline{Me}$), 2.52 (6H, s, Me), 2.50 (6H, s, Me), 1.78 (12H, t, $CH_2\underline{CH_3}$, J=7.3 Hz), −2.47 (2H, broad, NH). MS (FAB) H_2P m/z 846 (M^++2); ZnP m/z 907 (M^+). UV-vis (THF) H_2P λ_{max}: 407.5, 506, 536.5, 577, 630 nm; ZnP λ_{max}: 415.5, 546.5, 579.5 nm.

Synthesis of Quinone-Linked Porphyrin 1a. Compound **2a(Zn)** (20 mg) was dissolved in CH_2Cl_2 (50 ml). To this solution BBr_3 (0.3 ml) was added at −78 °C. The solution was stirred overnight under nitrogen at room temperature. Then the solution was poured into water and neutralized with aq $NaHCO_3$. The organic layer was separated, dried over Na_2SO_4 and evaporated, and the residue was dissolved in CH_2Cl_2 (50 ml). PbO_2 (600 mg) was added to the solution and the resulting solution was stirred for 3—5 h at room temperature. Then the solids were filtered off, and the filtrate was evaporated and the residue was recrystallized from MeOH to obtain **1a** (free base) as red-violet crystals in 93% yield. The **1a(Zn)** was obtained by inserting zinc ion with $Zn(OAc)_2$/MeOH. Mp >300 °C. ^1H NMR ($CDCl_3$) δ=10.23 (2H, s, meso), 8.05 (2H, d, J=7.8 Hz), 7.94 (2H, d, J=7.8 Hz), 7.57 (2H, d, J=7.8 Hz), 7.55 (2H, d, J=7.8 Hz), 6.95 (1H, d, J=10.3 Hz), 6.88 (1H, dd, J=2.4 and 10.3 Hz), 6.66 (1H, d, J=2.4 Hz), 4.13 (2H, s, $-CH_2-$), 4.00 (8H, q, $\underline{CH_2}CH_3$, J=7.3 Hz), 2.73 (3H, s, Ar-$\underline{Me}$), 2.52 (6H, s, Me), 2.51 (6H, s, Me), 1.77 (12H, t, $CH_2\underline{CH_3}$, J=7.3 Hz), −2.43 (2H, broad, NH). MS (FAB) H_2P m/z 766 (M^++2); ZnP m/z 830 (M^++3). UV-vis (THF) H_2P λ_{max}: 406.5, 505.5, 536, 575, 624 nm; ZnP λ_{max}: 415, 546, 579 nm.

Other porphyrins **1b**, **1c**, **1d**, and **1e** were prepared in the similar manner. Only physical data of these compounds are listed below.

1b: Mp >300 °C. ^1H NMR ($CDCl_3$) δ=10.21 (2H, s, meso), 8.04 (2H, d, J=7.8 Hz), 7.93 (2H, d, J=7.3 Hz), 7.56 (2H, d, J=7.8 Hz), 7.54 (2H, d, J=7.3 Hz), 6.78 (1H, s, Ar), 6.64 (1H, s, Ar), 4.11 (2H, s, $-CH_2-$), 4.04 (8H, q, $\underline{CH_2}CH_3$, J=7.3 Hz), 2.74 (3H, s, Ar-$\underline{Me}$), 2.48 (6H, s, Me), 2.47 (6H, s, Me), 2.16 (3H, s, Ar-$\underline{Me}$), 1.78 (12H, t, $CH_2\underline{CH_3}$, J=7.3 Hz), −2.45 (2H, broad, NH). MS (FAB) H_2P m/z 781 (M^++3); ZnP m/z 842 (M^++1). UV-vis (THF) H_2P λ_{max}: 406.5, 504.5, 536, 575.5, 623 nm; ZnP λ_{max}: 415, 544.5, 578.5 nm.

1c: Mp >300 °C. ^1H NMR ($CDCl_3$) δ=10.22 (2H, s, meso), 8.04 (2H, d, J=8.1 Hz), 7.92 (2H, d, J=7.8 Hz), 7.55 (2H, d, J=8.1 Hz), 7.52 (2H, d, J=7.8 Hz), 6.58 (1H, s, Ar), 4.12 (2H, s, $-CH_2-$), 4.01 (8H, q, $\underline{CH_2}CH_3$, J=7.3 Hz), 2.72 (3H, s, Ar-$\underline{Me}$), 2.51 (6H, s, Me), 2.50 (6H, s, Me), 2.17 (3H, s, Ar-$\underline{Me}$), 2.12 (3H, s, Ar-$\underline{Me}$), 1.79 (12H, t, $CH_2\underline{CH_3}$, J=7.3 Hz), −2.43 (2H, broad, NH). MS (FAB) H_2P m/z 795 (M^++3); ZnP m/z 856 (M^++1). UV-vis (THF) H_2P λ_{max}: 407, 505, 536, 574.5, 624 nm; ZnP λ_{max}: 415, 543.5, 579.5 nm.

1d: Mp >300 °C. ^1H NMR ($CDCl_3$) δ=10.23 (2H, s, meso), 8.04 (2H, d, J=8.1 Hz), 7.94 (2H, d, J=7.8 Hz), 7.56 (2H, d, J=8.1 Hz), 7.50 (2H, d, J=7.8 Hz), 7.16 (1H, s, Ar), 6.72 (1H, s, Ar), 4.06 (2H, s, $-CH_2-$), 4.01 (8H, q, $\underline{CH_2}CH_3$, J=7.3 Hz), 2.72 (3H, s, Ar-$\underline{Me}$), 2.51 (6H, s, Me), 2.47 (6H, s, Me), 1.79 (12H, t, $CH_2\underline{CH_3}$, J=7.3 Hz), −2.43 (2H, broad, NH). MS (FAB) H_2P m/z 801 (M^++2); ZnP m/z 862 (M^++1). UV-vis (THF) H_2P λ_{max}: 406.5, 505.5, 536, 574, 623 nm; ZnP λ_{max}: 415, 545.5, 579.5 nm.

1e: Mp >300 °C. ^1H NMR ($CDCl_3$) δ=10.23 (2H, s, meso), 8.25 (1H, dd, J=2.5 Hz and 7.0 Hz), 8.17 (1H, dd, J=2.5 Hz and 7.0 Hz), 8.05 (2H, d, J=6.2 Hz), 7.93 (2H, d, J=7.3 Hz), 7.83 (1H, t, J=7.0 Hz), 7.81 (1H, t, J=7.0 Hz), 7.61 (2H, d, J=7.3 Hz), 7.54 (2H, d, J=6.2 Hz), 6.88 (1H, s, Ar), 4.30 (2H, s, $-CH_2-$), 4.00 (8H, q, $\underline{CH_2}CH_3$, J=7.3 Hz), 2.73 (3H, s, Ar-$\underline{Me}$), 2.52 (6H, s, Me), 2.50 (6H, s, Me), 1.78 (12H, t, $CH_2\underline{CH_3}$, J=7.3 Hz), −2.49 (2H, broad, NH). MS (FAB) H_2P m/z 815 (M^++1); ZnP m/z 877 (M^+). UV-vis (THF) H_2P λ_{max}: 406.5, 505.5, 536.5, 578, 625 nm; ZnP λ_{max}: 415.5, 545.5, 580 nm.

Synthesis of the Compound 14. To a three-necked flask magnesium turnings (364 mg, 15.2 mmol) were added and heated with stirring overnight to activate the magnesium. After anhydrous THF (2 ml) was added to the activated magnesium, 1-bromo-4-(5′,5′-dimethyl-1′,3′-dioxan-2-yl)benzene (2.71 g, 10.0 mmol) in anhydrous THF (8 ml) was added dropwise, and the reaction mixture was refluxed for 3 h, so that the Grignard reagent **12** was prepared.

To the aldehyde **11** (1.35 g, 5.00 mmol) dissolved in THF (10 ml), the Grignard reagent **12** was added dropwise over 30 min. After the addition had been completed, the mixture was stirred for additional 2 h. The contents were hydrolyzed after pouring into water containing ammonium chloride. The solution was extracted with CH_2Cl_2, and the organic layer was separated, dried, evaporated, and the residue was separated by chromatography on silica gel to yield the alcohol **13**. Colorless oil. Yield: 98%. ^1H NMR ($CDCl_3$) δ=7.50 (2H, d, J=8.2 Hz), 7.33 (2H, d, J=8.2 Hz), 6.34 (Ar_2-$\underline{CH}$-OH, d, J=7.6 Hz), 5.37 (1H, s, -CH-), 3.91 (3H, s, OMe), 3.88 (Ar_2-CH-$\underline{OH}$, d, J=7.6 Hz), 3.74 and 3.64 (4H, ABq, J=11.3 Hz), 3.34 (3H, s, OMe), 1.28 (3H, s, Me), 0.79 (3H, s, Me).

The alcohol **13** (1.85 g, 4.00 mmol) dissolved in CH_2Cl_2 (100 ml) was added to the mixture of trifluoroacetic acid (20 ml) and 10% H_2SO_4 (20 ml), and the resulting mixture was refluxed for 1 h. Then the mixture was poured into water, and the solution was treated with aq. $NaHCO_3$, washed with water. The organic layer was dried over Na_2SO_4, and evaporated. The residue was recrystallized from methanol to give white crystals **14**. Yield: 80%. Mp 180—181 °C. ^1H NMR ($CDCl_3$) δ=10.00 (1H, s, CHO), 7.88 (2H, d, J=7.9 Hz), 7.53 (2H, d, J=7.9 Hz), 6.43 (Ar_2-$\underline{CH}$-OH, d, J=11.3 Hz), 3.94

(3H, s, OMe), 3.84 ($\mathrm{Ar_2{-}CH{-}\underline{OH}}$, d, J=11.3 Hz), 3.37 (3H, s, OMe). MS m/z 374 (M^+). Found: C, 51.22; H, 3.44; Cl, 28.57%. Calcd for $C_{16}H_{13}O_4Cl_3$: C, 51.16; H, 3.49; Cl, 28.31%.

Synthesis of the Porphyrin 15(Zn). The compound **15(Zn)** was synthesized in the similar manner as **2a**. Yield: 9%. Mp >300 °C. ^{1}H NMR ($CDCl_3$) δ=10.18 (2H, s, meso), 8.11 (2H, d, J=7.8 Hz), 7.95 (2H, d, J=7.6 Hz), 7.73 (2H, d, J=7.8 Hz), 7.55 (2H, d, J=7.6 Hz), 6.79 (1H, d, J=11.6 Hz), 4.32 (1H, d, J=11.6 Hz), 4.02 (3H, s, -OMe), 4.00 (8H, m, $\mathrm{\underline{CH_2}CH_3}$, J=7.6 Hz), 3.97 (3H, s, -OMe), 2.74 (3H, s, $\mathrm{Ar{-}\underline{Me}}$), 2.49 (6H, s, Me), 2.45 (6H, s, Me), 1.78 (12H, t, $\mathrm{CH_2\underline{CH_3}}$, J=7.6 Hz). MS (FAB) m/z 976 (M^+).

Synthesis of the Porphyrin 2f. The porphyrin **15(Zn)** (44 mg, 0.045 mmol) dissolved in trifluoroacetic acid (55 ml) was added to the solution containing sodium borohydride pellets (3.2 g, 0.86 mol) carefully over 30 min at room temperature, and the mixture was stirred for 3 d. The mixture was diluted with water, neutralized with sodium hydroxide (pellets), extracted with $CHCl_3$, and dried over Na_2SO_4. To the organic extracts, $Zn(OAc)_2$/MeOH (30 ml) was added and the solution was refluxed for 1 h. The solution was poured into water, and the organic layer was separated, dried over Na_2SO_4 and evaporated. The produced zinc complexes were separated by silica gel column chromatography using benzene as eluent to give the porphyrin **2f(Zn)** in 40% yield. The free base **2f** was prepared from **2f(Zn)** by acidic demetallation. **2f**: Mp >300 °C. ^{1}H NMR ($CDCl_3$) δ=10.17 (2H, s, meso), 7.98 (2H, d, J=7.9 Hz), 7.95 (2H, d, J=7.6 Hz), 7.54 (2H, d, J=7.9 Hz), 7.52 (2H, d, J=7.6 Hz), 4.57 (2H, s, $-CH_2$), 4.00 (3H, s, OMe), 3.99 (8H, q, $\mathrm{\underline{CH_2}CH_3}$, J=7.3 Hz), 3.97 (3H, s, OMe), 2.74 (3H, s, $\mathrm{Ar{-}\underline{Me}}$), 2.49 (6H, s, Me), 2.44 (6H, s, Me), 1.78 (12H, t, $\mathrm{CH_2\underline{CH_3}}$, J=7.3 Hz), −2.46 (2H, broad, NH). MS (FAB) m/z 899 (M^++2); ZnP m/z 961 (M^++1). UV-vis (THF) H_2P λ_{max}: 407.5, 504.5, 538, 575.5, 626 nm; ZnP λ_{max}: 415, 544, 578 nm.

Synthesis of Quinone-Linked Porphyrin 1f. The compound **1f** was synthesized in the similar manner as **1a**. Mp >300 °C. ^{1}H NMR ($CDCl_3$) δ=10.16 (2H, s, meso), 8.01 (2H, d, J=7.9 Hz), 7.94 (2H, d, J=7.6 Hz), 7.59 (2H, d, J=7.9 Hz), 7.54 (2H, d, J=7.6 Hz), 4.41 (2H, s, $-CH_2-$), 4.01 (8H, q, $\mathrm{\underline{CH_2}CH_3}$, J=7.3 Hz), 2.72 (3H, s, $\mathrm{Ar{-}\underline{Me}}$), 2.52 (6H, s, Me), 2.41 (6H, s, Me), 1.77 (12H, t, $\mathrm{CH_2\underline{CH_3}}$, J=7.3 Hz), −2.42 (2H, broad, NH). MS (FAB) m/z 869 (M^++2); ZnP 932 (M^++1). UV-vis (THF) H_2P λ_{max}: 407, 505, 538.5, 575, 625 nm; ZnP λ_{max}: 415.5, 544.5, 579.5 nm.

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