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# QUINONE-LINKED AND QUINONE-CAPPED PORPHYRINS. THEIR ONE-POT PHOTOCHEMICAL SYNTHESIS AND FLUORESCENCE BEHAVIOR

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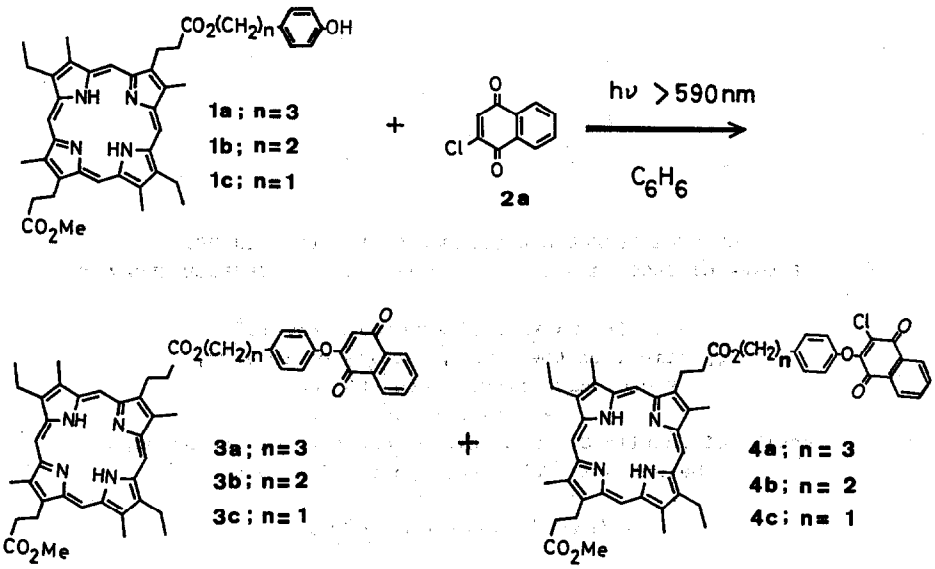
**Abstract** Irradiation of a benzene solution of phenol-linked porphyrins with red light ($\lambda_{max}$ > 590 nm) in the presence of chloronaphthoquinones under argon atmosphere resulted in the formation of quinone-linked porphyrins in good yields. This photochemical method was successfully applied to the synthesis of a series of perpendicularly, coplanarly, and orthogonally quinone-capped porphyrins bridged with different number of methylene chains. On the basis of the analysis of fluorescence lifetimes of these quinone-capped porphyrins, it could be concluded that the intramolecular electron transfer reaction from the porphyrin to the quinone proceeded mainly via "through-space" mechanism.

During the past several years the area of electron transfer photochemistry has received increasing attention owing to the intriguing mechanistic and synthetic features of excited state reactions initiated by electron transfer.[1] The reaction pathways promoted by this process are, for the most part, governed by secondary transformation of the initially formed radical ion species which competes with back electron transfer. Among these, reversible photoinduced electron transfer reactions from porphyrins to quinones have been studied extensively in recent years as a simple model of the primary events in photosynthesis.[2] On one side, considerable efforts have been devoted to increase the efficiency of charge-separation, mostly in micelle and vesicle systems,[3] but there are only a few reported irreversible reactions of synthetic interest so far.[4] On the other side, a lot of porphyrins possessing covalent linkages to quinones have been extensively synthesized in order to study the spatial and energetic requirements of fast electron-transfer reactions.[5] Thus it seems desirable to develop methods to systematically synthesize porphyrin-quinone model compounds with different separations and different orientations.

Quite recently, we have found photochemical coupling of quinones to tyrosine-linked porphyrins,[6] in which photoinduced electron transfer from a porphyrin chromophore to quinone induced the coupling of quinone to the tyrosine residue. We now report photochemical synthesis of quinone-linked and quinone-capped porphyrins from a series of phenol-linked porphyrins,[7] and the fluorescence properties of these quinone-linked porphyrins.

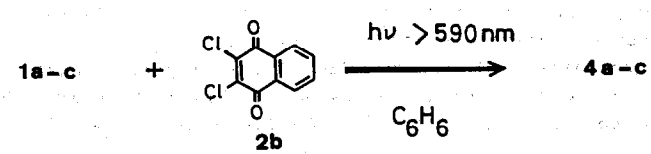



**Scheme 1**

Photochemical Synthesis of Quinone-linked Porphyrins.

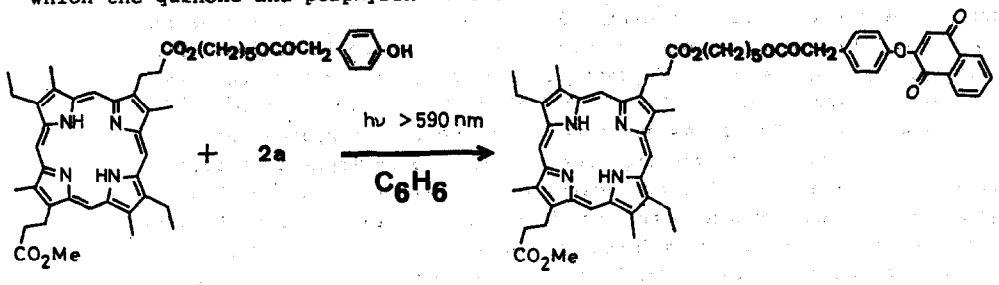
Synthesis of mono-phenol-linked porphyrins **1a-c** and bis-phenol-linked porphyrins **5a-d** was described in the experimental section. Irradiation of phenol-linked porphyrin **1a** (1 mM) in benzene in the presence of 2-chloro-1,4-naphthoquinone **2a** (5 mM) with light of wavelength longer than 590 nm under an argon atmosphere produced naphthoquinone-linked porphyrin **3a** (68 %) and 2-chloro-naphthoquinone-linked porphyrin **4a** (2%) with the liberation of HCl (scheme 1). Under identical conditions, irradiation of **1a** in the presence of 2,3-dichloro-1,4-naphthoquinone (**2b**) resulted in the exclusive formation of **4a** (70 %)(Eq. 1) The naphthoquinone end in **3a** appeared at δ 5.48(s), 7.70(m, 2H), 7.95(m, 1H), and 8.15(m, 1H), and the 2-chloro-naphthoquinone end in **4a** appeared at δ 7.50(t, 1H), 7.59(t, 1H), 7.76(d, 1H), and 8.05(d, 1H) in their 400 MHz $^1$H-NMR spectra in $CDCl_3$. Use of light of wavelength longer than 590 nm as well as strict exclusion of air from the reaction solution were crucial for high yields of quinone-linked porphyrins. As observed in the photochemical reaction of tyrosine-linked porphyrins,[6] the photo-coupling took place most efficiently at quinone concentration of ca. 5 mM and at [**2**] > 5 mM the quantum yields for the photo-coupling decreased as the concentrations of quinone increased.

Similarly with **3a** and **4a**, quinone-linked porphyrins **3b** (72 %), **4b** (75 %), **3c** (62 %), and **4c** (72 %) were synthesized by the photochemical reaction




(1)

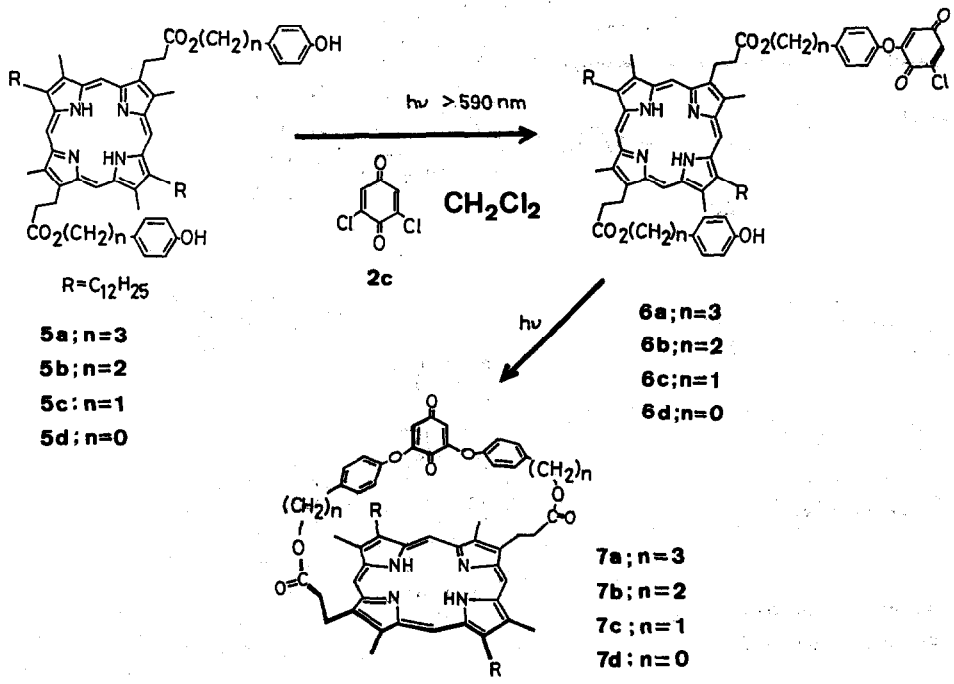
of **1b** and **1c**, respectively. Notably, this photochemical method was successfully applied to synthesis of quinone-linked porphyrin **3d** (55 %), in which the quinone and porphyrin were connected with 17 atoms.




**1d** **3d**

Photochemical Synthesis of Quinone-capped Porphyrins.

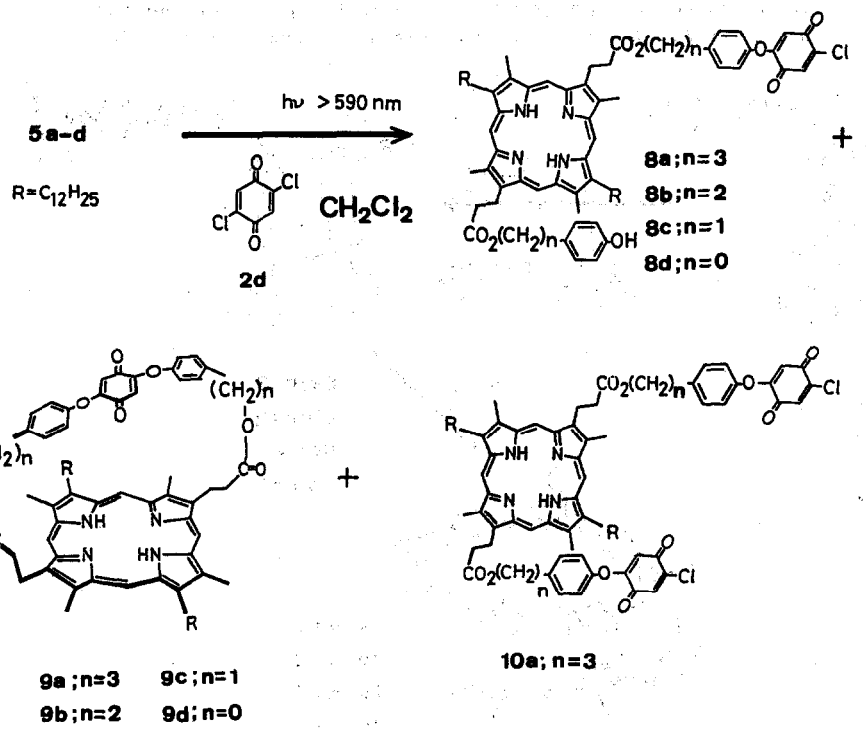
In order to improve low solubility of porphyrins carrying two phenol groups in organic solvents, we replaced two ethyl groups in a mesoporphyrin II chromophore by two dodecyl groups. As a result, the bis-phenol-linked porphyrins **5a-d** became soluble in $CH_2Cl_2$ and $CHCl_3$. Irradiation of a $CH_2Cl_2$ solution of bis-phenol-linked porphyrin **5a** (0.15 mM) and 2,6-dichloro-1,4-benzoquinone (**2c**) (0.3 mM) followed by separation by flash column chromatography gave quinone-capped porphyrin **7a** in 34% yield (Table 1, run 1). At a low conversion, mono-quinone-linked porphyrin **6a** was obtained along with **7a** (Table 1, run 2). Extended irradiation of **6a**



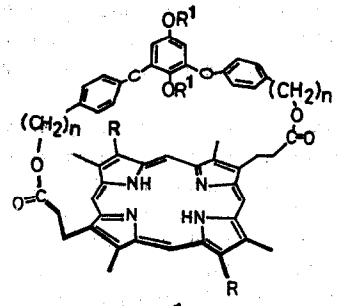

**Scheme 2**

resulted in the formation of **7a** without substantial side-reactions. The symmetric structure of **7a** was revealed by its simple $^1$H-NMR pattern, the quinone-ring proton appearing as a singlet at δ 3.90 ppm, the aromatic protons of the phenol moiety appearing as a pair of doublets at δ 5.58 and 6.20 ppm (J=8.1 Hz), and the meso protons at δ 10.07 and 10.00 ppm. The FAB mass spectrum (glycerol/m-nitrobenzyl alcohol matrix, 3 KeV acceleration) showed a parent peak at 1219.6563 (calcd; 1219.6542). Further, quinone-capped porphyrin **7a** was quantitatively reduced to hydroquinone-capped porphyrin **13a**, which was transformed into hydroquinone diacetate-capped porphyrin **14a**, in which two acetyl protons appeared at δ 1.40 and 1.43 ppm. The quinone-capped porphyrin **7a** has a very interesting structure in the sense that the quinone is forced to assume a position near the porphyrin ring and the quinone C=O bond axis has formally a perpendicular orientation to the porphyrin macrocycle.

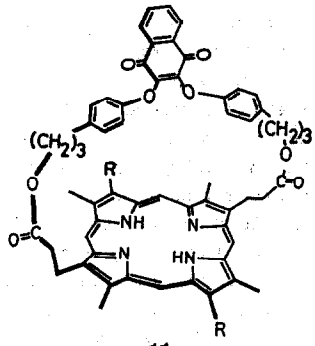
When 2,5-dichloro-1,4-benzoquinone (**2d**) was employed instead of **2c**, we obtained a coplanarly quinone-capped porphyrin **9a** in 42% yield (Table 1, run 3). Mono-quinone-linked porphyrin **8a** was again isolated at a low conversion, and was confirmed to cyclize to **9a** upon an extended irradiation. At high quinone concentration, bis-quinone-linked porphyrin **10a** was formed as a side product (Table 1, run 5 and 6). The product **10a** was apparently derived from intermolecular quenching of photo-excited **8a** with **2d**.



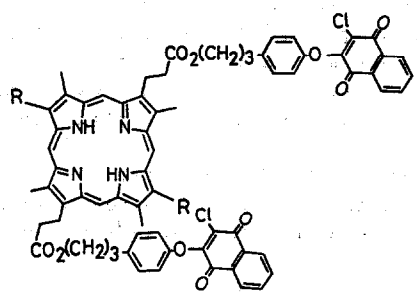

Scheme 3



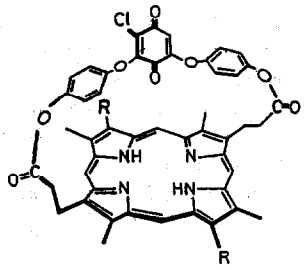
13a ; $R^1$=H
14a ; $R^1$=OAc



11a



12a



9d

Chart 1. R=$C_{12}H_{25}$

**Table 1** Photochemical Synthesis of Quinone-capped Porphyrins

| run | starting[a] porphyrin | quinone (conc., mM) | irra. time(h) | conv. (%) | product distribution (%)[b] | | |
|---|---|---|---|---|---|---|---|
| 1 | 5a | 2c (0.6) | 8 | 85 | | 7a(34%) | |
| 2 | 5a | 2c (0.6) | 2 | 55 | 6a(28%) | 7a(30%) | |
| 3 | 5a | 2d (0.6) | 8 | 87 | | 9a(42%) | |
| 4 | 5a | 2d (0.6) | 2 | 47 | 8a(21%) | 9a(29%) | |
| 5 | 5a | 2d (18) | 12 | 69 | | 9a(32%) | 10a(15%) |
| 6 | 5a | 2d (6) | 12 | 84 | | 9a(35%) | 10a(5%) |
| 7 | 5a | 2b (0.6) | 16 | 87 | 11a(8%) | 12a(14%) | |
| 8 | 5b | 2c (0.6) | 8 | 89 | 7b(32%) | | |
| 8 | 5b | 2d (0.6) | 2 | 62 | 6b(18%) | 7b(30%) | |
| 10 | 5b | 2d (0.6) | 8 | 90 | 9b(45%) | | |
| 11 | 5b | 2d (0.6) | 2 | 65 | 8b(22%) | 9b(26%) | |
| 12 | 5c | 2c (0.6) | 8 | 82 | 6c(4%) | 7c(26%) | |
| 13 | 5c | 2d (0.6) | 8 | 78 | | 9c(22%) | |
| 14 | 5d | 2c (0.6) | 8 | 90 | | 7d(53%) | |
| 15 | 5d | 2d (0.6) | 8 | 92 | | 9d(24%) | 9d'(10%) |
| 16 | 5e | 2c (0.6) | 8 | 75 | | 7e(25%) | |
| 17 | 5f | 2c (0.6) | 8 | 71 | | 7f(22%) | |

a, Solutions of 5 (0.15 mM) in $CH_2Cl_2$ were used. b, Numbers in parentheses indicate the isolated yields based on the consumed amounts of 5.

Quinone-capped porphyrin **11a**, which was formally orthogonal orientation of two chromophores was isolated in 8 % yield along with bis-quinone-linked porphyrin **12a** (14%) in the photochemical reaction of **5a** with **2b** (Table 1, run 7).

In a similar manner, all the perpendicularly quinone-capped porphyrins **7b-d** and the coplanarly quinone-capped porphyrins **9b-d** were synthesized in moderate to good yields. Among these, the photochemical reaction of **5d** with **2c** proceeded most cleanly, resulting in the formation of **7d** in 53% isolated yield, while the photochemical reaction of **5d** with **2d** led to the formation of two quinone-capped porphyrins **9d** and **9d'** (Table 1, run 15). These results may indicate that in the mono-quinone-linked porphyrin **8d** the capping pathway leading to a perpendicular geometry is conformationally favorable and the pathway leading to a coplanar geometry is conformationally suppressed. This photochemical method also realized the conversion of **5e** and **5f** to quinone-capped porphyrins **7e** and **7f** (Table 1 run 16 and 17), which contained m-phenylene bridges. The chemical shifts of the quinone-capped porphyrins **7a-f** and **9a-d** were rather insensitive to the solvent properties as well as temperature, indicating a rather restricted spatial arrangement of the quinone-cap.

As demonstrated above, this photochemical method has versatile applicability and thus provides a direct access to a set of quinone-capped porphyrins with different separations and different relative orientations.

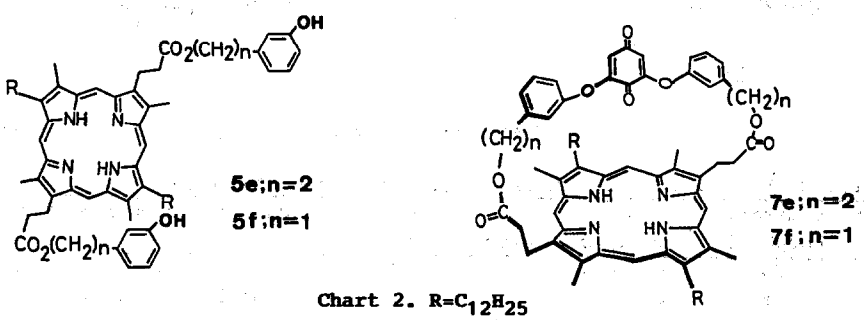



**Chart 2.** R=$C_{12}H_{25}$

Fluorescence Properties of Quinone-linked and Quinone-capped Porphyrins.

The ground-state absorption spectra and fluorescence emission spectra of the porphyrins were not perturbed by the presence of the linked- or capped-quinones and were typical of a mesoporphyrin II chromophore. However, fluorescence quantum yields of these model compounds diminished dramatically (Table 2). The fluorescence quantum yields of **4a**, **4b**, and **4c** were lower than those of **3a**, **3b**, and **3c**, respectively, in accord with the mechanism that electron transfer being the efficient nonradiative decay pathway that depleted $S_1$ in these molecules. The quinone-capped porphyrins **7** and **9** exhibited much decreased fluorescence intensities compared with the mono-quinone-linked porphyrins **3** and **4**, apparently because of close proximity of the quinone and porphyrin. The fluorescence lifetimes of a family of systematically synthesized quinone-capped porphyrins **7** and **9** were determined by pico second time-correlated single photon counting technique and were given in Table 3.[9] Single-exponential fits were found to give satisfactory deconvolutions of the fluorescence decay profiles for the phenol-linked or bis-phenol-linked porphyrins. However, at least four

**Table 2** Relative fluorescence quantum yields of quinone-linked porphyrins[a,b]

| porphyrin | $\phi_f$ | porphyrin | $\phi_f$ | porphyrin | $\phi_f$ |
|---|---|---|---|---|---|
| **1a** | 0.12 | **5a** | 0.11 | **7e** | 0.0026 |
| **1b** | 0.12 | **5b** | 0.11 | **7f** | 0.0040 |
| **1c** | 0.12 | **5c** | 0.11 | **9a** | 0.0024 |
| **1d** | 0.12 | **5d** | 0.10 | **9b** | 0.0020 |
| **3a** | 0.020 | **5e** | 0.11 | **9c** | 0.0040 |
| **3b** | 0.017 | **7a** | 0.0021 | **9d** | 0.0054 |
| **3c** | 0.016 | **7b** | 0.0014 | **11a** | 0.0022 |
| **3d** | 0.028 | **7c** | 0.0018 | | |
| **4a** | 0.014 | **7d** | 0.0025 | | |
| **4b** | 0.012 | | | | |
| **4c** | 0.0096 | | | | |

a, In $CH_2Cl_2$ at 25°C . b, The measured values are relative to the fluorescence quantum yield (0.12) of mesoporphyrin II.[11]

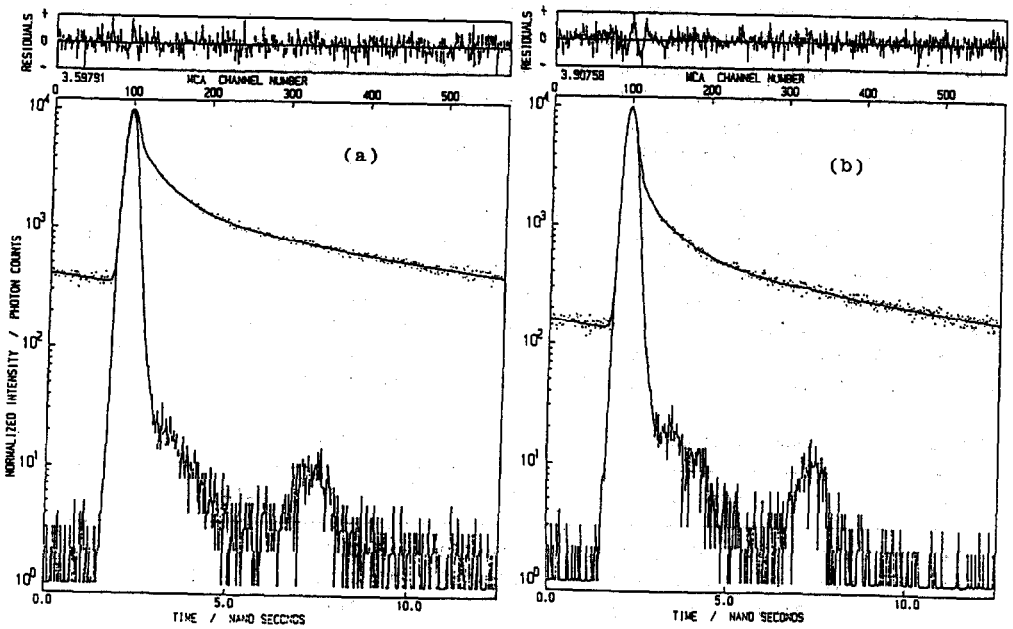



**Figure 1.** Fluorescence decay profiles obtained from $10^{-6}$ M solutions at room temperature in air-saturated $CH_2Cl_2$ (excitation wavelength 514 nm). (a) **7c**, (b) **9c**. Analyses of these curves by computer deconvolution are presented in Table 3.

components were needed to obtain satisfactory fits of the decay curves for the quinone-capped porphyrins (Figure 1 and Table 3). These low fluorescence quantum yields and multiphasic fluorescence decay profiles may be attributed to an excited state electron transfer reaction forming a $P^+Q^-$

charge-separated state. The results summarized in Table 3 may indicate that the intramolecular electron transfer quenching takes place in several conformers which do not undergo appreciable interconversion. Longer-lived components of lifetimes of 8-10 ns probably arise from fluorescence of residual amounts of porphyrins not linked with quinones. The length of the intervening methylene chains has a strong influence on the fluorescence lifetimes of the quinone-capped porphyrins. In the all cases, most of the fluorescence of the porphyrin decayed within 50 ps. Among these, the most efficient fluorescence quenching was observed in **7b** with a lifetime of 11 ps in 7-series and in **9c** with a lifetime of 7 ps in 9-series. These short lifetimes ( $\tau$ ) of the quinone-capped porphyrins can be correlated with the rates of the intramolecular electron transfer by assuming that the sole additional deactivation pathway relative to **5a-d** is electron transfer. Taking the lifetime of 5 (12 ns, $\tau_0$) to define the radiative lifetime of the porphyrin, we can calculate the rate of electron transfer, $k_e$, from the equation, $k_e = 1/\tau - 1/\tau_0$.

Mechanistic questions concerning intramolecular electron transfer in covalently linked donor-acceptor complexes have focused on the issue of "through-space" versus "through-bond" electron transmission pathway.[10] The former mechanism should be strongly dependent on the distance between the porphyrin and quinone moieties. However, the latter mechanism would be less sensitive to geometrical factors between the donor and acceptor moieties but be strongly dependent on the number of atoms connecting the donor and acceptor. A set of the quinone-capped porphyrins **7** and **9** provide a test of the relative importance of through-space versus though-bond conduction in this system, since the number of methylene bridge decreases in the order of **7a=9a** > **7b=9b** > **7c=9c** > **7d=9d** and the relative orientations of the quinone to porphyrin are different in each set of **7** and **9**. If through-bond mechanism would be predominantly operative in this system, the rates of the intramolecular electron transfer reaction should be in the order of **7d=9d** > **7c=9c** > **7b=9b** > **7a=9a**. This is not the case. As noted above, the fluorescence data for **7** and **9** as a function of the length of the

**Table 3.** Fluorescence lifetimes of quinone-capped porphyrins

| porphyrin | fluorescence lifetime, ns(%)[a] | | | | $k_e$($\times 10^{-10}$, $s^{-1}$)[b] |
|---|---|---|---|---|---|
| **7a** | 0.037(71) | 0.35(8.3) | 1.16(18) | 10.3(2) | 2.7 |
| **7b** | 0.011(96) | 0.54(2) | 1.29(18) | 10.0(1) | 9.1 |
| **7c** | 0.032(90) | 0.63(7) | 2.14(2) | 11.3(1) | 3.1 |
| **7d** | 0.018(97) | 0.56(0.5) | 1.83(1.3) | 8.7(1.1) | 5.6 |
| **9a** | 0.029(70) | 0.35(23) | 1.35(6) | 9.0(1) | 3.4 |
| **9b** | 0.048(83) | 0.22(13) | 1.36(2) | 10.1(1) | 2.1 |
| **9c** | 0.007(97.8) | 0.52(1.4) | 1.70(0.5) | 8.4(0.3) | 14 |
| **9d** | 0.033(85) | 0.59(8.3) | 1.7(4.3) | 8.4(2.4) | 3.0 |
| **11a** | 0.063(60) | 0.54(23) | 1.2(16) | 8.4(1) | 1.6 |

a, Numbers in parentheses indicate normalized pre-exponential factors.
b, Rates of the intramolecular electron transfer reaction calculated by eq.3, using the shortest fluorescence lifetime in each compounds.

methylene bridge indicated an apparent optimum at n=2 for **7** series and at n=1 for **9** series. Seemingly, these results are best compatible with through-space mechanism. Probably, sterical constrains imposed by the capped structure and limited number of bridging atoms may allow **7b** and **9c** to take a optimum conformation suitable for the intramolecular electron transfer.

However unfortunately, at the present stage, it is difficult to discuss these data in relation to the relative spatial arrangements of the porphyrin and quinone, since we cannot define precisely each of exact conformers in the quinone-capped porphyrins.

Experimental Section.

The instruments and procedures were as previously reported.[6] Mass spectra were taken by FAB ionization method in m-nitrobenzyl alcohol matrix at 3 KeV accelerating voltage (JEOL JMX-DX 303 HF combined with JMA-DA 5000 data system). Fluorescence quantum yields were determined using $10^{-7}$ M $CH_2Cl_2$ solutions in 1 cm cuvettes. The samples were excited at 532 nm. The fluorescence lifetimes were measured by the time-correlated single-photon counting technique.[9] The lifetime calculation was carried out on a micro-computer TRS-80 using a program based on an iterative non-linear least-squares method and modified to cope with pump pulse shift. The most appropriate number of exponentials required to deconvolute the decays were determined in the same manner as in ref. 9.

Synthesis of Phenol-Linked Porphyrins; Typically, the synthesis of **1a** was described. Mesoporphyrin II Monomethyl ester[6] (464 mg, 0.8 mmol) was suspended in dry $CH_2Cl_2$ (20 mL) and treated with oxalyl chloride (0.2 mL). The mixture was stirred in the dark for 15 min by which time it had become a clear red solution. The solvent and excess of reagent were removed on a rotary evaporator to yield the mono acid chloride as a red gum which was used immediately in the condensation reaction. The mono acid chloride dissolved in dry $CH_2Cl_2$ (20 mL) was slowly added with stirring to a solution of 3-(4-hydroxy)phenyl-1-propanol (243 mg, 1.6 mmol) in $CH_2Cl_2$ (20 mL) or THF (70 mL). The resulting mixture was stirred for 24 h in the dark and then poured into water and extracted with $CH_2Cl_2$. The organic layer was separated and washed successively with aqueous $NaHCO_3$ solution and brine, and dried over $Na_2SO_4$. After removal of the solvent, the product was separated by flash column chromatography (silica gel, ether/$CH_2Cl_2$=1/15) and purified by recrystallization from methanol/$CH_2Cl_2$, 571 mg (84 %): mp 180-181°C; mass spectrum (FAB), m/e 715 ($M^+$ +1); IR(KBr) 3300 and 1740 $cm^{-1}$. $^1$H-NMR data of phenol-linked porphyrins were summarized in Table 4. The phenol-linked porphyrins **1b** and **1c** were prepared in the same method used for **1a**. **1b** (73 %), mp 195-197°C, mass spectrum (FAB), m/e 701 ($M^+$ +1); IR(KBr) 3300 and 1740 $cm^{-1}$. **1c** (55 %); mp 173-175 C, mass spectrum (FAB), m/e 687 ($M^+$ +1); IR(KBr) 3300 and 1740 $cm^{-1}$. **1d** (65%); mp 133-135 ° C; mass spectrum (FAB), m/e 801($M^+$ +1); IR(KBr) 3200 and 1750 $cm^{-1}$.

The bis-phenol-linked porphyrins **5a** and **5b** were prepared in the same fashion as for **1a** from the didodecyldeuteroporphyrin II bis acid chloride[6,12] in 84 % and 62 %, respectively. **5a**; mp 131-133 °C, mass spectrum (FAB), m/e 1116 ($M^+$ +1); $^1$H-NMR($CDCl_3$) 10.07(s, 2H, meso), 10.04(s, 2H, meso), 5.97(d, J=8 Hz, 4H), 5.69(d, J=8 Hz, 4H), 4.42(t, 4H),

4.06(t, 4H), 3.64(s, 6H), 3.62(s, 6H), 3.91(t, 4H), 3.28(t, 4H), 2.26(m, 4H), 1.96(t, 4H), 1.71(m, 4H), 1.55(m, 4H), 1.40(m, 4H), 1.2-1.3(m, 28H), 0.88(t, 6H), -2.96(NH, 2H). **5b**; mp 155-156°C, mass spectrum (FAB), m/e 1088 ($M^+$ +1); $^1$H-NMR($CDCl_3$) 10.07(s, meso, 2H), 10.04(s, meso, 2H), 6.40(d, J=8.5 Hz, 4H), 5.62(d, J=8.5 Hz, 4H), 4.37(t, 4H), 4.17(t, 4H), 4.08(t, 4H), 3.64(s, 6H), 3.62(s, 6H), 3.25(t, 4H), 2.54(t, 4H), 2.28(m, 4H), 1.73(m, 4H), 1.55(m, 4H), 1.2-1.3(m, 28H), 0.85(t, 6H). The similar condensation reaction of the bis-acid chloride with (4-hydroxy)phenylmethanol in $CH_2Cl_2$/THF (1:1) gave **5c** (24 %) together with mono-phenol-linked porphyrin (52 %). **5c**; mp 130-132°C. mass spectrum (FAB), 1060 ($M^+$ +1); $^1$H-NMR($CDCl_3$) 10.07(s, meso, 2H), 10.06(s, meso, 2H), 6.63(d, J=8.6 Hz, 4H), 5.86(d, J=8.6 Hz, 4H), 4.90(s, 4H), 4.39(t, 4H), 4.09(t, 4H), 3.63(s, 6H), 3.59(s, 6H), 3.29(t, 4H), 2.29(m, 4H), 1.73(m, 4H), 1.55(m, 4H), 1.2-1.3(m, 28H), 0.84(t, 6H). The bis-phenol-linked porphyrin **5d** was prepared stepwise by the esterification of the bis-acid chloride with hydroquinone monobenzyl ether to give bis-benzyloxyphenol-linked porphyrin **15** (92%), which was debenzylated by catalytic hydrogenation over Pd-charcoal to give **5d** (60%). **15**; mp 140-141°C; mass spectrum (FAB), m/e 1213($M^+$ +1); IR, 2990 and 1740 $cm^{-1}$; $^1$H-NMR($CDCl_3$) 10.13(s, 2H, meso), 10.12(s, 2H, meso), 7.2-7.5(m, 10H), 6.80(s, 8H), 4.96(s, 4H), 4.50(t, 4H), 4.10(t, 4H), 3.66(s, 6H), 3.63(s, 6H), 3.50(t, 4H), 2.30(m, 4H), 1.74(m, 4H), 1.55(m, 4H), 0.84(t, 6H), 1.2-1.3(m, 28H), -3.72(2H, NH). **5d**; mp 202-204°C; mass spectrum (FAB), m/e 1032($M^+$ +1); $^1$H-NMR($CDCl_3$) 10.13(s, 2H, meso), 10.12(s, 2H, meso), 6.69(d, J=8.5 Hz, 4H), 6.59(d, J=8.5Hz, 4H), 4.50(t, 4H), 4.10(t, 4H), 3.66(s, 6H), 3.62(s, 6H), 3.47(t, 6H), 2.29(m, 4H), 1.73(m, 4H), 1.55(m, 4H), 1.2-1.3(m, 28H), 0.83(t, 6H), -2.9(br, 2H, NH). **5e** (85%); mp 231-232°C; mass spectrum (FAB), m/e 1088($M^+$ + 1); IR, 2990 and 1730 $cm^{-1}$; $^1$H-NMR($CDCl_3$) 10.13(s, meso, 2H), 10.11(s, meso, 2H), 6.46(t, 2H), 6.24(d, J=7 Hz, 2H), 5.27(d, J=7 Hz, 2H), 4.71(s, 2H), 4.38(t, 4H), 4.15(t, 4H), 4.10(t, 4H), 3.62(s, 6H), 3.56(s, 6H), 3.33(t, 4H), 2.35(t, 4H), 2.29(m, 4H), 1.75(m, 4H), 1.56(m, 4H), 1.2-1.3(m, 28H), 0.85(t, 6H), -2.9(NH, 2H). **5f** (82%); mp 165-167°C; mass spectrum (FAB), m/e 1060($M^+$ +1); IR(KBr) 3000 and 1730 $cm^{-1}$; $^1$H-NMR($CDCl_3$) 10.16(s, meso, 2H), 10.11(s, meso, 2H), 6.51(t, 2H), 6.32(d, J=7.3 Hz. 2H), 5.48(br, 2H), 4.60(s, 4H), 4.46(t, 4H), 4.06(t, 4H), 3.96(s, 2H), 3.60(s, 6H), 3.57(s, 6H), 3.39(t, 4H), 2.29(m, 4H), 1.74(m, 4H), 1.55(m, 4H), 1.2-1.3(m, 28H), 0.85(t, 6H).

Synthesis of Quinone-linked Porphyrins. Typically the procedure for the synthesis of **3a** was described. A solution of **1a** (38 mg, 0.05 mmol) and **2a** (44 mg, 0.25 mmol) in 50 mL of benzene through which argon had been bubbled for 30 min was irradiated with a tungsten-halogen lamp through a cut-off filter (Toshiba VO-59) ($\lambda$ >590 nm) with water-cooling. The progress of the reaction was followed by TLC. The reaction mixture was washed with $NaHCO_3$ solution and dried over $Na_2SO_4$. The solvent was removed on a rotary evaporator. The residue was chromatographed on flash column over silica gel (Merck, Kieselgel 60F) with $CH_2Cl_2$/ether (93/7) as an eluant. The first fraction was the unreacted quinone and the second fraction was the quinone-linked porphyrin **4a**, 1 mg (2%), and the third fraction was **3a**, 30 mg (68 %); mp 159-160°C; mass spectrum (FAB), m/e 872($M^+$ +1); IR(KBr) 3200, 1740, 1660 $cm^{-1}$. **4a**; mp 112-114 C; mass spectrum (FAB), m/e 908($M^+$($^{37}$Cl) +1); IR(KBr) 3100, 1755, 1640 $cm^{-1}$. **3b**; mp 137-139°C; mass spectrum (FAB),

**Table 4** Selected $^1$H-NMR data of **1**, **3**, and **4**

| porphyrins | $H_o$,[a] | $H_m$,[b] | other selected protons[c] |
|---|---|---|---|
| **1a** | 5.58 | 5.78 | 1.29(m, 2H), 1.78(m, 2H), 3.91(t, 2H) |
| **3a** | 6.25 | 6.37 | 1.58(m, 2H), 2.10(t, 2H), 4.02(t, 2H), 5.48(s, quinone-ring, 1H), 7.70(m, 2H), 7.95(m, 1H), 8.15(m, 1H) |
| **4a** | 6.60 | 6.70 | 1.42(m, 2H), 2.10(t, 2H), 4.20(t, 2H), 7.50(t, 1H), 7.59(t, 1H), 7.76(d, 1H) 8.05(d, 1H) |
| **1b** | 5.65 | 6.38 | 2.50(t, 2H), 4.14(t, 2H) |
| **3b** | 6.17 | 6.59 | 2.58(t, 2H), 4.29(t, 2H), 5.35(s, quinone-ring, 1H), 7.73(m, 2H), 8.04(m, 1H), 8.18(m, 1H) |
| **4b** | 6.72 | 6.94 | 2.73(t, 2H), 4.29(t, 2H), 7.41(t, 1H), 7.55(t, 1H), 7.73(d, 1H), 8.05(d, 1H) |
| **1c** | 5.81 | 6.57 | 4.88(s, 2H) |
| **3c** | 6.37 | 6.84 | 5.01(s, 2H), 5.47(s, quinone-ring, 1H) 7.72(m, 2H), 8.05(m, 1H), 8.18(m, 1H) |
| **4c** | 6.70 | 7.06 | 5.05(s, 2H), 7.68(t, 1H), 7.74(t, 1H), 7.92(d, 1H), 8.17(d, 1H) |
| **1d** | 6.31 | 6.85 | 1.08(m, 2H), 1.33(m, 2H), 1.40(m, 2H) 3.29(s, 2H), 3.79(t, 2H), 4.01(t, 2H) |
| **3d** | 6.95 | 7.18 | 1.16(m, 2H), 1.36(m, 2H), 1.48(m, 2H) 3.40(s, 2H), 3.82(t, 2H), 4.07(t, 2H), 7.57(m, 2H), 7.90(m, 1H), 8.03(m, 1H) |

a, Ortho-protons in the phenol moieties. b, Meta-protons in the phenol moieties. c, Protons in the phenol-linked or quinone-linked chains.

m/e 858($M^+$ +1); IR(KBr) 3200, 1750, 1735 $cm^{-1}$. **4b**; mp 129-130 °C; mass spectrum (FAB), m/e 894($M^+$($^{37}$Cl) + 1); IR(KBr) 1755 and 1630 $cm^{-1}$. **3c**; mp 178-182°C; mass spectrum (FAB), m/e 844($M^+$ +1); IR(KBr) 3200, 1750, 1640 $cm^{-1}$. **4c**; mp 178-180° C; mass spectrum (FAB), m/e 880($M^+$($^{37}$Cl) +1); IR(KBr) 3200, 1730, 1650 $cm^{-1}$. **3d**; mp 128-131°C; mass spectrum (FAB), m/e, 957($M^+$ + 1); IR(KBr) 1750, 1720, 1630 $cm^{-1}$.

Synthesis of Quinone-capped Porphyrins. Typically, the procedure for the synthesis of **7d** was described. A solution of **5d** (77 mg, 0.075 mmol) and **2c** (53 mg) in 500 mL of $CH_2Cl_2$ was irradiated in the same method as used for the photoreaction of **1a**. After evaporation of the solvent, the residue was separated by flash column chromatography, to give **7d** (40 mg) along with recovery of the starting porphyrin **5d** (8 mg).

**6a**; mp 96-98° C; mass spectrum (FAB), m/e 1258($M^+$($^{37}$Cl) +1); UV( $\lambda_{max}$ in $CH_2Cl_2$) 623, 570, 532, 499, 399, 275 nm; IR(KBr) 3100, 1740, 1630 $cm^{-1}$; $^1$H-NMR($CDCl_3$) 10.10(s, meso, 1H), 10.07(s, meso, 1H), 10.06(s, meso, 1H), 10.04(s, meso, 1H), 6.80(d, J=2.1 Hz, quinone-ring, 1H), 6.25(d, J=8.5 Hz, 2H), 6.05(d, J=8.5 Hz, 2H), 6.03(d, J=8.2 Hz, 2H), 5.74(d, J=8.2 Hz, 2H), 5.15(d, J=2.1 Hz, quinone-ring, 1H), 4.41(m, 4H), 4.05(m, 4H), 3.96(t, 4H),

3.65(s, 6H), 3.63(s, 3H), 3.61(s, 3H), 3.31(t, 2H), 3.24(t, 2H), 2.24(m, 4H), 2.07(t, 2H), 1.97(t, 2H), 1.71(m, 4H), 1.2-1.2(m, 32H), 0.85(t, 6H).

**7a**; mp 82-86 °C; mass spectrum (FAB), m/e 1220($M^+$ +1); UV($\lambda_{max}$ in $CH_2Cl_2$) 622, 570, 532, 500, 399, 275 nm; IR(KBr) 3100, 1740, 1640 $cm^{-1}$; $^1$H-NMR($CDCl_3$) 10.03(s, meso, 2H), 9.96(s, meso, 2H), 6.20(d, J=8.1 Hz, 4H), 5.58(d, J=8.1 Hz, 4H), 4.32(m, 2H), 4.22(m, 2H), 4.04(m, 4H), 3.90(s, quinone-ring, 2H), 3.66(s, 6H), 3.58(s, 6H), 3.23(m, 2H), 3.14(m, 2H), 2/34(4H), 2.30(m, 4H), 1.76(m, 4H), 1.55(m, 8H), 1.2-1.3(m, 28H), 0.86(t, 6H), -3.9(NH, 2H).

**8a**; mp 150-153°C; mass spectrum (FAB), m/e 1258 ($M^+(^{37}Cl)$ +1); UV($\lambda_{max}$ in $CH_2Cl_2$) 623, 569, 522, 499, 400, 270 nm; IR(KBr) 3200, 1750, 1640 $cm^{-1}$; $^1$H-NMR($CDCl_3$ 10.10(s, meso, 1H), 10.07(s, meso, 1H), 10.06(s, meso, 1H), 10.05(s, meso, 1H), 6.80(d, J=2.1 Hz, quinone-ring, 1H), 6.27(d, J=8.4 Hz, 2H), 6.05(d, J=8.4 Hz, 2H), 6.03(d, J=8.5 Hz, 2H), 5.74(d, J=8.5 Hz, 2H), 4.4(m, 4H), 4.04(m, 4H), 3.96(t, 4H), 3.65(s, 6H), 3.63(s, 3H), 3.61(s, 3H), 3.31(t, 2H), 3.24(t, 2H), 2.26(m, 4H), 2.10(m, 2H), 1.95(m, 2H), 1.70(m, 4H), 1.55(m, 8H), 1.2-1.3(m, 28H), 0.85(t, 6H), -3.9(NH, 2H).

**9a**; mp 180-182°C; mass spectrum (FAB), m/e 1258 ($M^+$ +1); UV($\lambda_{max}$ in $CH_2Cl_2$) 623, 570, 534, 500, 400, 270 nm; IR(KBr) 3100, 1740, 1630 $cm^{-1}$; $^1$H-NMR($CDCl_3$) 10.07(s, meso, 2H), 10.00(s, meso, 2H), 6.14(d, J=8.5 Hz, 4H), 5.04(d, J=8.5 Hz, 4H), 4.17(s, quinone-ring, 2H), 4.40(m, 2H), 4.0(m, 6H), 3.64(s, 6H), 3.58(s, 6H), 3.1(m, 4H), 2.52(m, 4H), 2.22(m, 4H), 1.75(m, 4H), 1.55(m, 8H), 1.2-1.3(m, 28H), 0.85(t, 6H), -3.78(NH, 2H).

**10a**; mp 163-166°C; mass spectrum (FAB), m/e 1400 ($M^+(^{37}Cl)$ +1); UV($\lambda_{max}$ in $CH_2Cl_2$) 623, 570, 532, 500, 400, 270 nm; IR(KBr) 3100, 1730, 1640 $cm^{-1}$; $^1$H-NMR($CDCl_3$) 10.07(s, meso, 1H), 10.05(s, meso, 2H), 6.90(s, quinone-ring, 2H), 6.22(d, J=8.5 Hz, 4H), 5.97(d, J=8.5 Hz, 4H), 5.17(s, quinone-ring, 2H), 4.39(t, 4H), 4.05(t, 4H), 3.97(t, 4H), 3.62(s, 6H), 3.58(s, 6H), 3.27(t, 4H), 2.27(m, 4H), 2.08(t, 4H), 1.77(m, 4H), 1.56(m, 8H), 1.2-1.3(m, 28H), 0.85(t, 6H), -3.8(NH, 2H).

**6b**; mp 153-155 °C; mass spectrum (FAB), m/e 1230 ($M^+(^{37}Cl)$ +1); UV($\lambda_{max}$ in $CH_2Cl_2$) 632, 570, 532, 500, 400, 280 $nm^{-1}$; IR(KBr) 3100, 1730, 1650 $cm^{-1}$; $^1$H-NMR($CDCl_3$)
10.08(s, meso, 1H), 10.07(s, meso, 1H), 10.05(s, meso), 10.00(s, meso, 1H), 6.77(d, J=2.6 Hz, quinone-ring, 1H), 6.45(d, J=8.5 Hz, 2H), 6.34(d, J=8.2 Hz, 2H), 5.72(d, J=8.5 Hz, 2H), 5.68(d, J=8.2Hz, 2H), 4.73(d, J=2.7Hz, quinone-ring. 1H), 4.41(t, 2H), 4.35(t, 2H), 4.18(t, 2H), 4.17(t, 2H), 4.07(m, 4H), 3.66(s, 3H), 3.63(s, 6H), 3.59(s, 3H), 3.28(t, 2H), 3.24(t, 2H), 2.56(t, 2H), 2.53(t, 2H), 2.27(m, 4H), 1.55(m, 4H), 1.2-1.3(m, 28H), 0.85(t, 6H).

**7b**; mp 75-77° C; mass spectrum (FAB), m/e 1192 ($M^+$ +1); UV($\lambda_{max}$ in $CH_2Cl_2$) 621, 570, 532, 499, 400, 270 nm; IR(KBr) 3100, 1740, 1640 $cm^{-1}$; $^1$H-NMR($CDCl_3$) 10.02(s, meso, 2H), 9.88(s, meso, 2H), 6.34(d, J=8.6 Hz, 4H), 5.70(d, J=8.6 Hz, 4H), 4.32(m, 6H), 4.02(m, 6H), 3.95(s, quinone-ring, 2H), 3.22(m, 2H), 3.15(m, 2H), 2.75(t, 4H), 2.27(m, 4H), 1.74(m, 4H), 1.55(m, 4H), 1.2-1.3(m, 28H), 0.86(t, 6H), -3.9(NH, 2H).

**8b**; mp 163-166 °C; mass spectrum (FAB), m/e 1230($M^+(^{37}Cl)$ +1); UV($\lambda_{max}$ in $CH_2Cl_2$) 620, 566, 533, 499, 399, 271 $nm^{-1}$; IR(KBr) 3200, 1740, 1635 $cm^{-1}$; $^1$H-NMR($CDCl_3$) 10.08(s, meso, 1H), 10.07(s, meso, 1H), 10.04(s, meso, 1H), 10.00(s, meso, 1H), 6.87(s, quinone-ring, 1H), 6.46(d, J=8.1 Hz, 2H),

6.28(d, J=8.5 Hz, 2H), 5.73(d, J=8.5 Hz, 2H), 5.58(d, J=8.1 Hz, 2H), 4.78(s, quinone-ring, 1H), 4.41(t, 2H), 4.34(t, 2H), 4.19(t, 2H), 4.16(t, 2H), 4.07(m, 4H), 3.65(s, 3H), 3.633(s, 3H), 3.629(s, 3H), 3.59(s, 3H), 3.28(t, 2H), 3.25(t, 2H), 2.57(t, 2H), 2.52(t, 2H), 2.28(m, 4H), 1.73(m, 4H), 1.55(m, 4H), 1.2-1.3(m, 28H), 0.85(t, 6H),

**9b**; mp 157-159°C; mass spectrum (FAB), m/e 1192 ($M^+$ +1); UV($\lambda_{max}$ in $CH_2Cl_2$) 623, 570, 523, 499, 400, 260 nm; IR(KBr) 3200, 1750, 1640 $cm^{-1}$; $^1$H-NMR($CDCl_3$) 10.07(s, meso, 2H), 9.86(s, meso, 2H), 6.18(d, J=8.7 Hz, 4H), 5.34(d, J=8.7 Hz, 4H), 4.65(s, quinone-ring, 2H), 4.20(m, 4H), 4.04(m, 4H), 3.62(s, 6H), 3.61(s, 6H), 3.20(m, 2H), 3.12(m, 2H), 2.48(m, 2H), 2.25(m, 2H), 1.70(m, 4H), 1.54(m, 4H), 1.2-1.5(m, 28H), 0.85(t, 6H), -3.75(NH, 2H).

**6c**; mp 105-107°C; mass spectrum (FAB), m/e 1201($M^+(^{37}Cl)$ +1); UV($\lambda_{max}$ in $CH_2Cl_2$) 623, 569, 533, 401, 285 nm; IR(KBr) 3200, 1750, 1640 $cm^{-1}$; $^1$H-NMR($CDCl_3$) 10.09(s, meso, 1H), 10.07(s, meso, 1H), 10.04(s, meso, 1H), 10.02(s, meso, 1H), 6.80(d, J=2.6 Hz, quinone-ring, 1H), 6.67(d, J=8.5 Hz, 2H), 6.63(d, J=8.5 Hz, 2H), 6.06(d, J=8.5 Hz, 2H), 5.85(d, J=8.5 Hz, 2H), 4.98(d, J=2.6 Hz, quinone-ring, 1H), 4.95(s, 2H), 4.91(s, 2H), 4.44(t, 2H), 4.37(t, 2H), 4.07(m, 4H), 3.65(s, 3H), 3.62(s, 3H), 3.61(s, 3H), 3.58(s, 3H), 3.50(s, phenol-OH, 1H), 3.34(t, 2H), 3.28(t, 2H), 2.28(m, 4H), 1.73(m, 4H), 1.54(m, 4H), 1.2-1.3(m, 28H), 0.84(t, 6H).

**7c**; mp 82-84°C; mass spectrum (FAB), m/e 1164 ($M^+$ +1); UV($\lambda_{max}$ in $CH_2Cl_2$) 623, 570, 534, 400, 270 nm; IR(KBr) 3100, 1750, 1630 $cm^{-1}$; $^1$H-NMR($CDCl_3$) 10.17(s, meso, 2H), 10.00(s, meso, 2H), 6.56(d, J=8.5 Hz, 4H), 5.78(d, J=8.5 Hz, 4H), 5.35(s, quinone-ring, 2H), 4.61(m, 2H), 4.17(m, 2H), 4.10(m, 2H), 3.98(m, 2H), 3.62(m, 2H), 3.50(s, 12H), 3.42(m, 2H), 2.23(m, 4H), 1.70(m, 4H), 1.55(m, 4H), 1.2-1.3(m, 28H), 0.85(t, 6H), -3.8(NH, 2H).

**9c**; mp 102-104°C; mass spectrum (FAB), m/e 1164 ($M^+$ +1); UV($\lambda_{max}$ in $CH_2Cl_2$) 623, 569, 532, 499, 400, 280 nm; IR(KBr) 3200, 1750, 1620 nm; $^1$H-NMR($CDCl_3$) 10.06(s, meso, 2H), 10.04(s, meso, 2H), 6.60(d, J=8.5 Hz, 4H), 6.28(d, J=8.5 Hz, 4H), 5.42(s, quinone-ring, 2H), 5.05(d, J=13 Hz, 2H), 4.80(d, J=13 hz, 2H), 4.62(m, 2H), 4.25(m, 2H), 4.05(m, 4H), 3.62(s, 12H), 3.3-3.5(m, 4H), 2.28(m, 4H), 1.74(m, 4H), 1.52(m, 4H), 1.2-1.3(m, 28H), 0.86(t, 6H), -3.82(NH, 2H).

**7d**; mp 180-182°C; mass spectrum (FAB), m/e 1136 ($M^+(^{37}Cl)$ +1); UV($\lambda_{max}$ in $CH_2Cl_2$) 623, 570, 533, 499, 399, 270 nm; IR(KBr) 3100, 1740, 1650 $cm^{-1}$; $^1$H-NMR($CDCl_3$) 10.10(s, meso, 2H), 10.06(s, meso, 2H), 6.27(s, quinone-ring, 2H), 5.81(d, J=8 Hz, 4H), 5.31(d, J= 8Hz, 4H), 4.78(m, 2H), 4.30(m, 2H), 4.07(m, 4H), 3.61(s, 6H), 3.59(s, 6H), 3.50(m, 2H), 3.26(m, 2H), 2.25(m, 4H), 1.75(m, 4H), 1.55(m, 4H), 1.2-1.3(m, 28H), 0.87(t, 6H), -3.80(broad, NH, 2H).

**9d**; mp 139-140°C; mass spectrum (FAB), m/e 1136 ($M^+$ +1); UV($\lambda_{max}$ in $CH_2Cl_2$) 623, 570, 532, 499, 399, 270 nm; IR(KBr) 3100, 1740, 1650 $cm^{-1}$; $^1$H-NMR($CDCl_3$) 10.18(s, meso, 2H), 10.11(s, meso, 2H), 6.10(d, J=9 Hz, 4H), 5.95(d, J=9 Hz, 4H), 5.24(s, quinone-ring, 2H), 4.81(m, 2H), 4.33(m, 2H), 4.11(m, 4H), 3.65(s, 12H), 3.46(m, 4H), 2.25(m, 4H), 1.70(m, 4H), 1.54(m, 4H), 1.2-1.3(m, 28H), 0.86(t, 6H), -3.85(NH, 2H).

**9d'**; mp 126-/128°C; mass spectrum (FAB), m/e 1172 ($M^+(^{37}Cl)$ +1); UV($\lambda_{max}$ in $CH_2Cl_2$) 623, 570, 533, 500, 400, 290 nm; IR(KBr) 3200, 1740, 1620 $cm^{-1}$; $^1$H-NMR($CDCl_3$) 10.12(s, meso, 1H), 10.11(s, meso, 1H), 10.08(s, meso, 1H), 10.07(s, 1H, meso), 6,38(s, quinone-ring, 1H), 5.92(d, J=9 Hz, 2H), 5.76(d,

J=8.8 Hz, 2H), 5.47(d, J=8.8 Hz, 2H), 5.24(d, J=9 Hz, 2H), 4.78(m, 2H), 4.31(m, 2H), 4.06(m, 4H), 3.61(s, 3H), 3.60(s, 3H), 3.58(s, 3H), 3.57(s, 3H), 3.50(m, 2H), 3.26(m, 2H), 2.25(m, 4H), 1.73(m, 4H), 1.56(m, 4H), 1.2-1.3(m, 28H), 0.87(t, 6H), -3.77(NH, 2H).

**7e**; mp 110-112° C; mass spectrum (FAB), m/e 1192($M^+$ +1); UV($\lambda_{max}$ in $CH_2Cl_2$) 623, 570, 532, 500, 399, 270 nm; IR(KBr) 3200, 1740, 1630 $cm^{-1}$; $^1H$-NMR($CDCl_3$) 10.08(s, meso, 2H), 10.00(s, meso, 2H), 6.58(t, 2H), 6.54(d, J=7.4 Hz, 2H), 5.93(d, J=7.3 Hz, 2H), 5.31(s, 2H), 4.48(m, 2H), 4.38(s, quinone-ring, 2H), 4.22(m, 2H), 4.08(m, 4H), 3.97(m, 2H), 3.86(m, 2H), 3.67(s, 6H), 3.59(s, 6H), 3.24(m, 2H), 3.12(m, 2H), 2.29(m, 4H), 1.72(m, 4H), 1.55(m, 4H), 1.2-1.3(m, 28H), 0.85(t, 6H), -3.74(NH, 2H).

**7f**; mp 83-85 °C; mass spectrum (FAB), m/e 1164($M^+$ +1); UV($\lambda_{max}$ in $CH_2Cl_2$) 623, 571, 533, 501, 400, 277 nm; IR(KBr) 3200, 1740, 1640 $cm^{-1}$; $^1H$-NMR($CDCl_3$) 10.11(s, meso, 2H), 10.08(s, meso, 2H), 7.11(t, 2H), 6.97(d, J=7 Hz, 2H), 6.63(d, J=7.2 Hz, 2H), 5.88(s, 2H), 4.84 and 4.54(ABq, J=12.4 Hz, 2H), 4.68(m, 2H), 4.63(s, quinone-ring, 2H), 4.28(m, 2H), 4.11(m, 2H), 4.02(m, 2H), 3.66(s, 6H), 3.64(s, 6H), 3.33(m, 2H), 3.24(m, 2H), 2.29(m, 4H), 1.74(m, 4H), 1.55(m, 4H), 1.2-1.3(m, 28H), -3.9(NH, 2H).

Transformation of Quinone-capped Porphyrins to Hydroquinone Diacetate-capped Porphyrins. A $CH_2Cl_2$ solution of **7a** (10 mg) was vigorously shaken with three portions of 2N aqueous $Na_2S_2O_4$ solution, and then washed with water, and dried over $Na_2SO_4$. After removal of the solvent, the residue was chromatographed over silica gel to give **13**, 10 mg (100%); mp 127-129° C; mass spectrum (FAB), m/e 1222 ($M^+$ +1); $^1H$-NMR($CDCl_3$) 10.08(s, meso, 2H), 10.00(s, meso, 2H), 6.46(d, J=8 Hz, 4H), 6.20(d, J=8 Hz, 4H), 4.5(m, 2H), 4.20(s, hydroquinone-ring, 2H), 4.1(m, 10H), 3.66(s, 6H), 3.56(s, 6H), 3.05(m, 4H), 2.40(m, 4H), 2.22(t, 4H), 1.75(m, 4H), 1.55(m, 8H), 1.2-1.3(m, 28H), 0.85(t, 6H).

To a pyridine solution of **13** was added acetic anhydride (0.5 mL) at room temperature. The resulting solution was stirred for 3 h in the dark, and then poured into water. The mixture was extracted with $CH_2Cl_2$ three times. Separation by flash column chromatography gave **14**; mp 83-86°C; mass spectrum (FAB), m/e 1306 ($M^+$ +1); IR(KBr) 3310, 1740 $cm^{-1}$; $^1H$-NMR($CDCl_3$) 10.06(s, meso, 2H), 10.03(s, meso, 2H), 6.16(d, J=8 Hz, 4H), 6.10(d, J=8 Hz, 4H), 5.70(s, aromatic-H, 2H), 4.50(m, 2H), 4.10(m, 8H), 4.00(m, 2H), 3.62(s, 6H), 3.58(s, 6H), 3.20(m, 4H), 2.30(t, 4H), 2.20(m, 4H), 1.75(m, 4H), 1.55(m, 8H), 1.43(s, 3H), 1.40(s, 3H), 1.2-1.3(m, 28H), 0.86(t, 6H), -3.8(NH, 2H).

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