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Synthesis and Fluorescence Properties of Selectively Metallated Diporphyrins with Electron-Accepting Moieties

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Synthesis of selectively metallated diporphyrins with electron-accepting moieties is described. Steady-state fluorescence spectra of these compounds showed substantial quenching of the fluorescence of the free-base porphyrin. A possible "superexchange" mechanism of long-range electron transfer is discussed.

At the initial stage of photosynthesis, an electron travels from the photoexcited (bacterio-)chlorophylls to the acceptor quinone producing a high-energy charge-separation state[1] which is utilized in the following dark processes. In the case of purple bacteria, the primary charge separation process consists of two (or three, as argued in recent reports[2]) consecutive electron transfer processes, with a bacteriopheophytin as an intermediate acceptor. The X-ray structures of bacterial photosynthetic reaction centers have been reported for several species,[3] and spatial arrangement of the chromophores is now known. However, it is still unclear what structural features are critically important for the complexes to function properly.

Many artificial chlorophyll- (or porphyrin-) quinone model compounds are being studied in order to relate

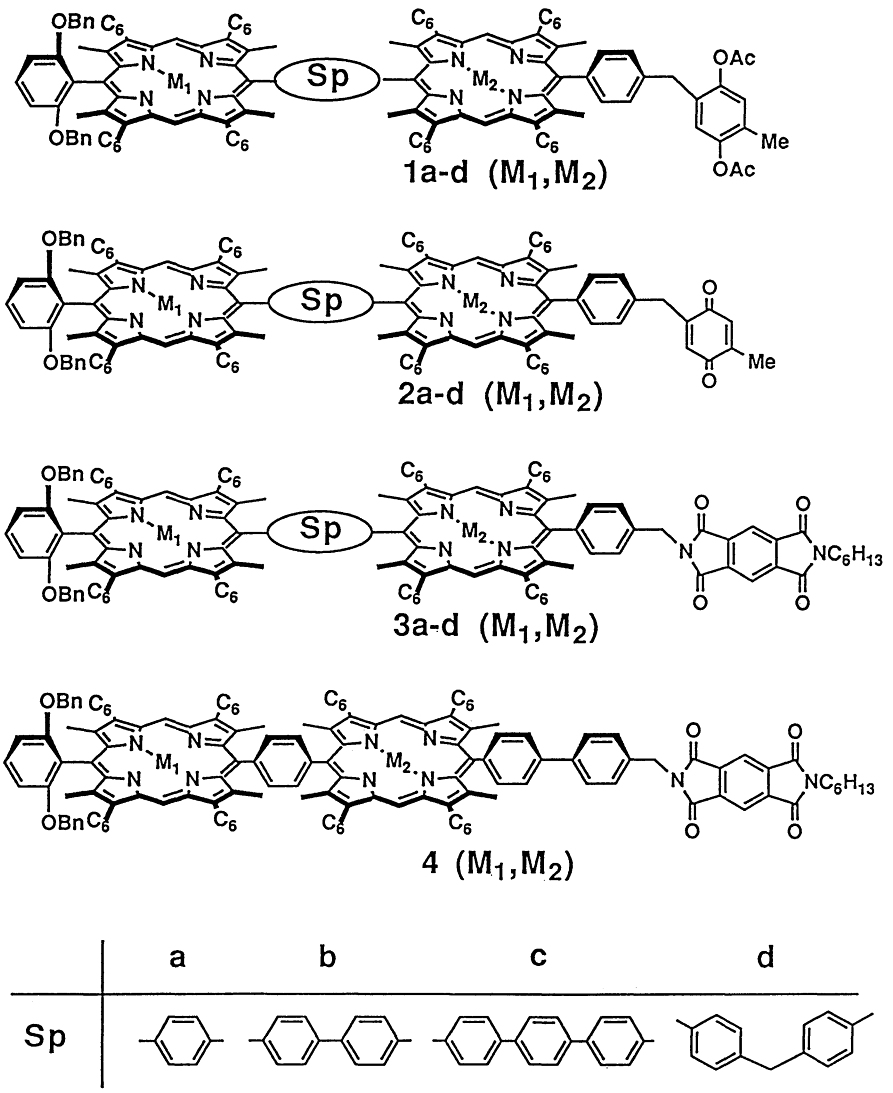


Chart 1.

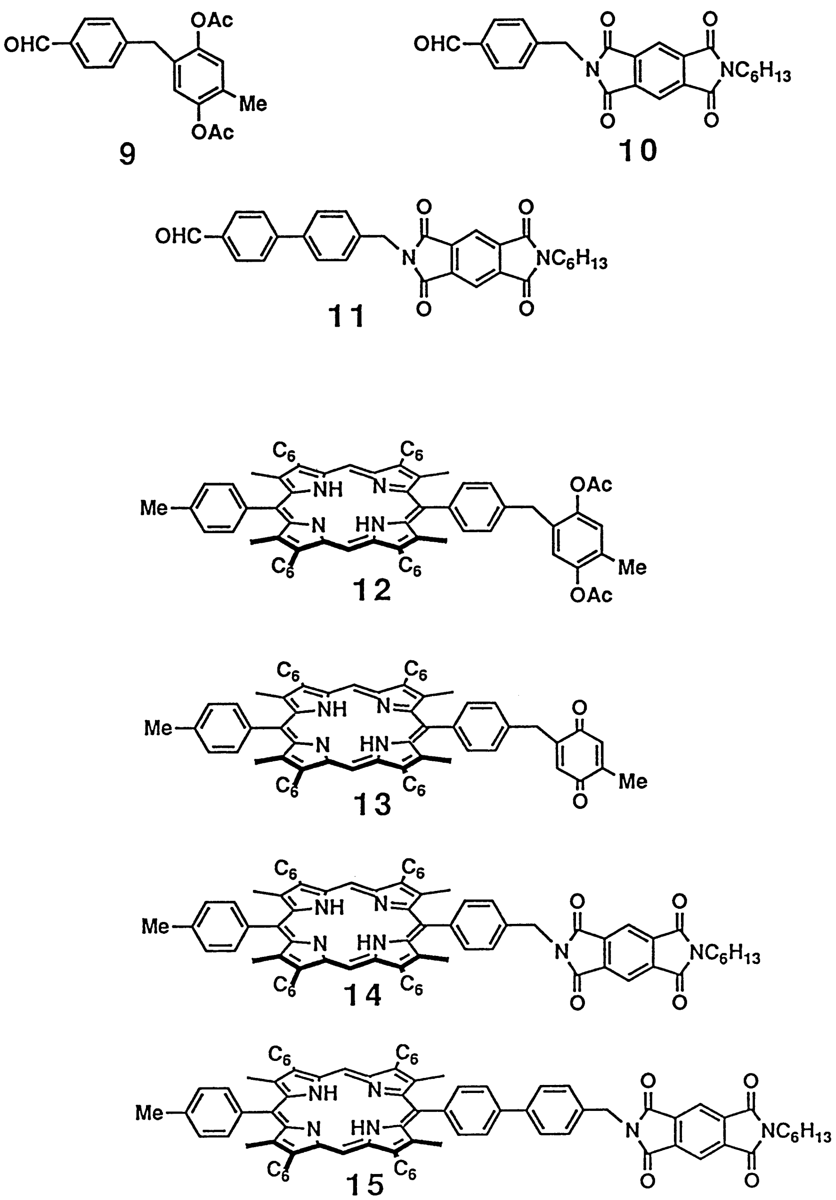


Chart 2.

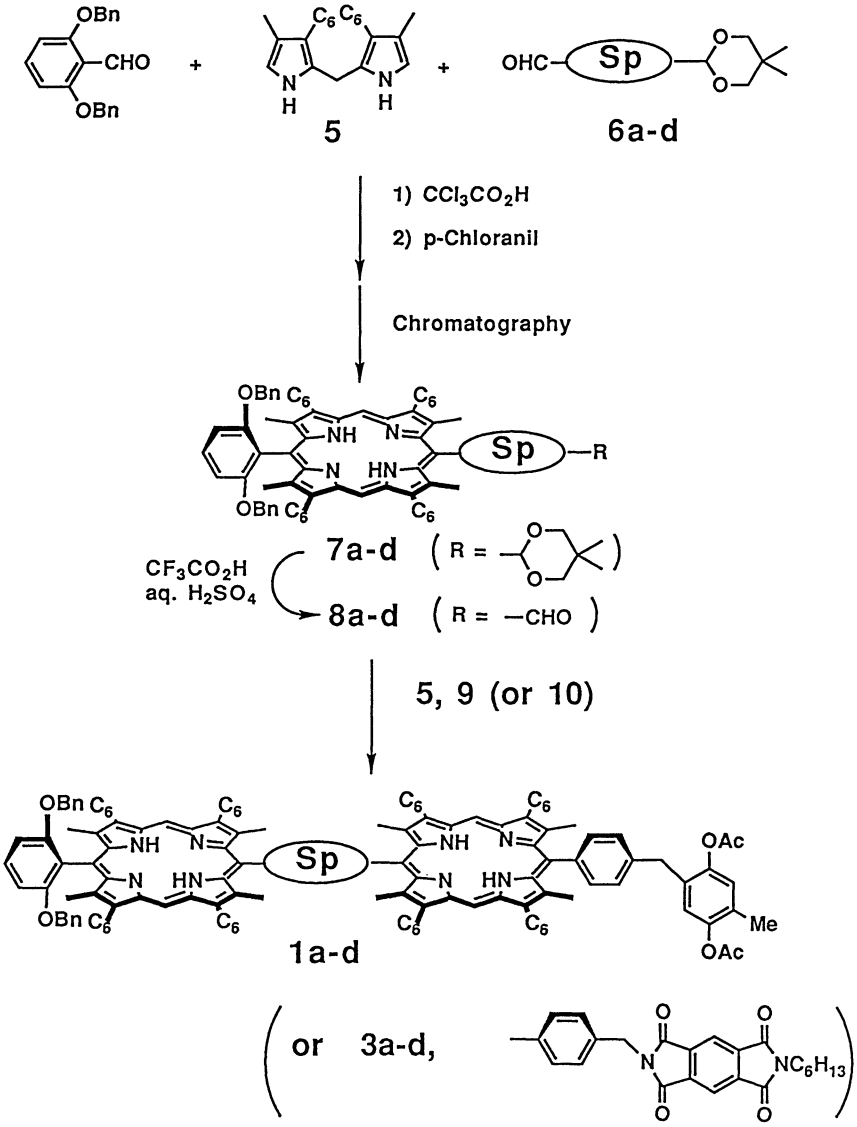
the photophysical properties to the structural parameters.[4] In the course of our study on new photosynthetic model systems,[5] we designed partially metallated functionalized diporphyrins **1a**—**d** (H_2, Zn), **2a**—**d** (H_2, Zn), and **3a**—**d** (H_2, Zn) (Chart 1), as models for studying long-range electron-transfer reactions. The compounds **2a**—**d** and **3a**—**d** have the electron-accepting benzoquinone and 1,2:4,5-benzenebis (dicarboximide) (pyromellitic diimide) moieties, while the compounds **1a**—**d** are the reference compounds with the non-electron-accepting 1,4-diacetoxybenzene (hydroquinone diacetate) moiety. For each of these series, four compounds were prepared (**a**—**d**) with different types of bridging groups between the two porphyrins; 1,4-phenylene, 4,4′-biphenylylene, 4,4″-terphenylylene, and methylenebis(1,4-phenylene). The compound **4** was also prepared, in which the distance between the diimide moiety and the "distant" porphyrin (i.e. the one which is not directly bound to the diimide moiety) is the same as that in **3b** but the distances between the neighboring chromophores are different from those in **3b**. In these systems, it was expected that the photoinduced electron transfer would occur from the free-base porphyrin to the terminal acceptor, and that the intervening zinc porphyrin might play an important role during this electron transfer, as the "accessory" bacteriochlorophyll in the natural photosynthetic system might do.[6]

In this paper, the synthesis and steady-state fluorescence spectra of these compounds are reported and discussed. The keypoint in the synthetic strategy is to introduce a bulky 2,6-bis(benzyloxy)phenyl group on one end of the diporphyrin core. This group offered some regioselectivity of metal insertion which prefers the less hindered porphyrin ring. The steady-state fluorescence spectra showed that the singlet excited state of the free-base porphyrin was quenched by the electron-accepting group. A possible "superexchange" mechanism of long-range electron transfer is also discussed.

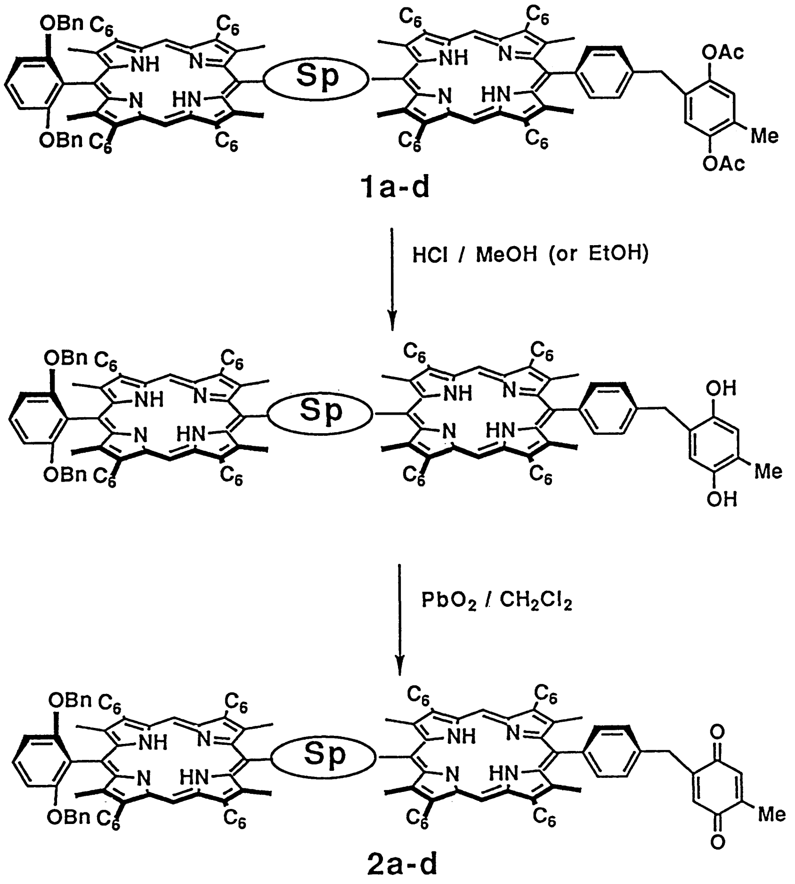
Results and Discussion

Synthesis of Selectively Metallated Diporphyrins. The synthesis of functionalized free-base diporphyrins **1**, **2**, and **3** is shown in Scheme 1. Acid-catalyzed condensation[5e] of dipyrrolylmethane **5** with 2,6-bis(benzyloxy)benzaldehyde and monoprotected aromatic dialdehyde **6** gave a mixture of three porphyrins. The cross-coupling product **7** was separated by column chromatography. The acetal **7** was hydrolyzed to give the corresponding aldehyde **8**, which was allowed to condense with dipyrrolylmethane **5** and functionalized aldehyde **9** (or **10**, **11**). The 1,4-diacetoxybenzene-linked diporphyrin **1** (or the diimide-linked diporphyrins **3**, **4**) was separated by column chromatography. The quinone-linked diporphyrin **2** was derived from **1**, by acidic hydrolysis of phenolic esters followed by oxidation with lead dioxide (Scheme 2). The functionalized monomeric porphyrins **12**, **14**, and **15** were synthesized by condensation of **5** with *p*-tolualdehyde and appropriate functionalized aldehyde, and separated and purified by column chromatography. The quinone-linked porphyrin **13** was derived from **12** in a similar manner as **1**.

Selectively metallated diporphyrins were synthesized by partial metallation followed by chromatographic separation. Treatment of free base of **1**, **2**, or **3** with a limited amount of zinc acetate (molar ratio $Zn(OAc)_2$/diporphyrin=0.5—1.0) in dichloromethane gave a mixture of four species, (Zn, Zn), (H_2, Zn), (Zn, H_2), and (H_2, H_2), which could be separated by flash column chromatography. The dizinc complex and the starting



Scheme 1.



Scheme 2.

metal-free material were easily characterized using UV-visible spectroscopy. The remaining two species were characterized as monozinc complexes. Typical UV-spectra of dizinc complex, monozinc complex and metal-free diporphyrin are shown in Fig. 1. The Q-band (460 to 650 nm) absorption spectra of the free-base and dizinc diporphyrins showed the characteristic features of the monomeric free-base and zinc porphyrins, respectively (Fig. 1, A). On the other hand, the Q-band spectra of the monozinc complex was identical to the sum of those of monomeric free-base and zinc porphyrins (Fig. 1, B). The FAB (fast atom bombardment) mass spectra of these diporphyrins also showed the correct molecular weights of dizinc, monozinc, and free-base species.

Identification of the two monozinc species was a more subtle problem. In every experiment, one species (which moves slower on TLC than the other) was obtained in larger amount than the other (about 2.5 : 1). This major species was identified as the (H_2, Zn) complex based on the ^{1}H NMR spectral patterns of the porphyrin-NH protons. Figure 2 shows the high-field regions of ^{1}H NMR Spectra of metal-free **3d**, two monometallated **3d**'s (major and minor species), and monomeric porphyrins **8d** and **14**. The NH signals of **8d** appeared in lower field than those of **14**, probably due to the substituent effect of the 2,6-bis(benzyloxy)phenyl group. The metal-free **3d** showed four signals in the NH region. The two signals in the lower field were assigned to the NH-protons of the bis(benzyloxy)phenyl substituted ring, and the two signals in the higher field to those of the other ring. Comparison of the spectra of the two monozinc species with that of the free-base led to the conclusion that the "major" one is the (H_2, Zn) complex.

Sessler et al. reported synthesis of quinone-substituted monometallated diporphyrins.[4h)] They observed complete regioselectivity in metallation of their systems, but this was not the case in the systems described here. Partial zinc insertion of **1**, **2**, and **3** always gave mixtures of all the four possible products, which were separated by column chromatography. Among the two monometallated species, one species was always obtained in higher yield, and this was identified as the (H_2, Zn) complex. Apparently, the porphyrin ring on the right side (in the drawings in Chart 1) was preferentially metallated over the ring on the left side. When the 2,6-bis(benzyloxy)phenyl group is replaced by a 2,6-dimethoxyphenyl group, the selectivity of metallation was much lower, and when the group is replaced by a hydrogen atom, essentially no selectivity was observed (data not shown). It is likely that the regioselectivity in metallation of **1**, **2**, and **3** (although not very high) is due to the bulkiness of the 2,6-bis(benzyloxy)phenyl group.

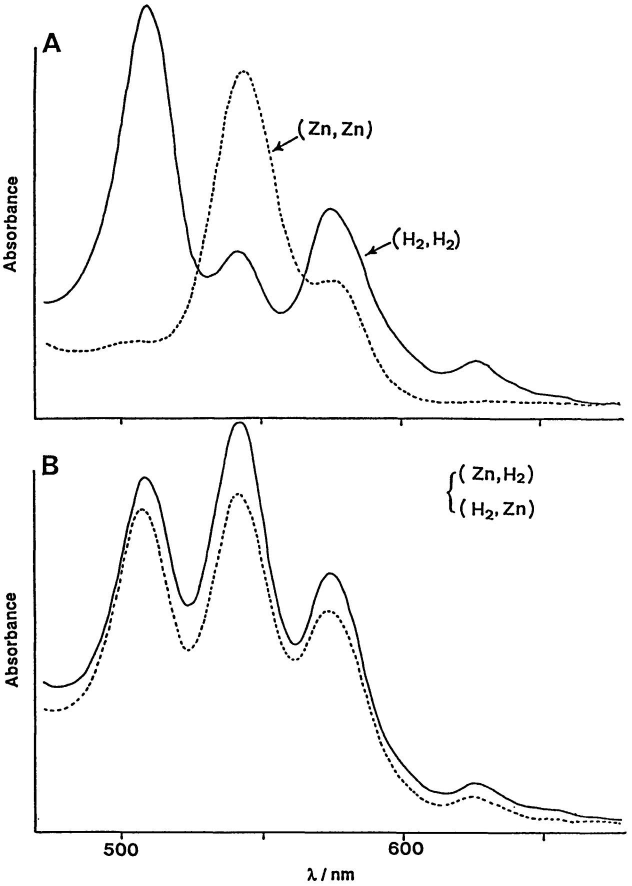


Fig. 1. Visible absorption spectra of metallated diporphyrins in THF. (A) **3d** (H_2, H_2) and **3d** (Zn, Zn). (B) Two isomeric monozinc complexes of **3d**. Solid line is the "major" complex, i.e. **3d** (H_2, Zn).

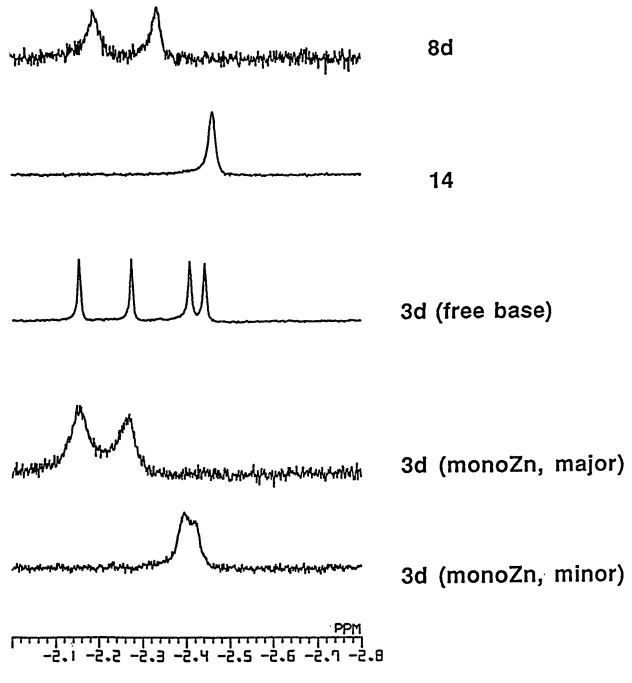


Fig. 2. ^{1}H NMR spectra of monomeric porphyrins and partially metallated diporphyrins in the high-field region.

Steady-State Fluorescence Spectra. In order to investigate the photophysical properties of monometallated diporphyrins, the fluorescence emission spectra were measured under steady-state conditions. The (H_2, Zn) compounds with attached acceptor moieties are of particular interest because of the possible long-range electron transfer from the free-base porphyrin to the acceptor.

When a THF solution of an (H_2, Zn) complex was irradiated by the 507 nm light (or 510 nm light in the case of **1a**, **2a**, and **3a**),[7] which was mainly absorbed by the free-base porphyrin moiety, characteristic emission spectrum of the free-base porphyrins was observed. Figure 3 shows the typical fluorescence spectra of the (H_2, Zn) diporphyrins with the diacetoxybenzene, quinone, and diimide moieties. The spectral shapes were essentially invariant with the various bridging groups and acceptor moieties, while the relative fluorescence intensities varied significantly. Table 1 shows the relative fluorescence intensities of these compounds (the

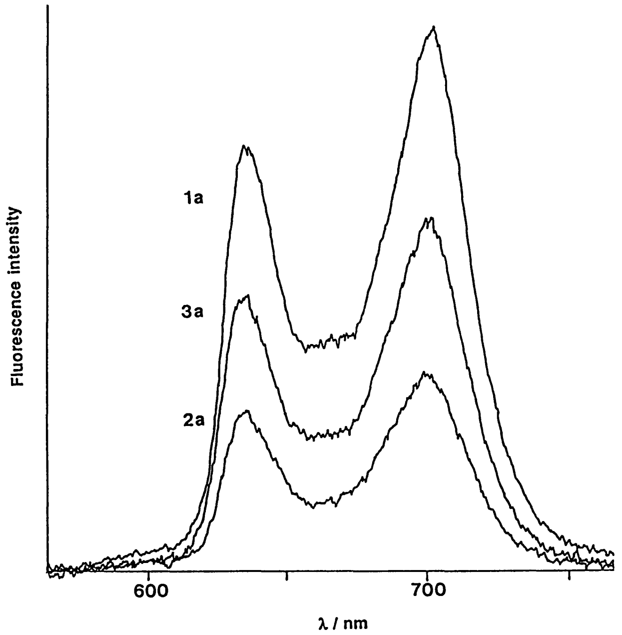


Fig. 3. Steady-state fluorescence spectra of **1a** (H_2, Zn), **2a** (H_2, Zn) and **3a** (H_2, Zn) in THF at 25 °C. Excitation at 510 nm.

Table 1. Relative Fluorescence Intensities of (H_2, Zn) Diporphyrins. Excitation at 507 nm (or 510 nm, Where Indicated). Emission at 700 nm. In THF, at 25 °C

	a	b	c	d
1	1[a)]	1	1	1
2	0.40[a)]	0.86	0.99	0.79
3	0.66[a)]	0.88	1.01	0.83
4	1.02[a)]			

a) Excitation at 510 nm.

corresponding 1,4-diacetoxybenzene-linked diporphyrins **1a**—**d** (H_2, Zn) were chosen as the references).[8] Two points should be noticed: (1) the fluorescence intensity is decreased when an acceptor moiety is present; the quinone moiety has a greater effect than the diimide moiety, and (2) the effect of the acceptor moiety is increased as the bridging group between the two porphyrin rings varies in the order 4,4″-terphenylylene< 4,4′-biphenylylene<methylenebis(1,4-phenylene)<1,4-phenylene.

It is reasonable to assume that the fluorescence of the free-base porphyrin is quenched through the electron transfer (ET) from the excited porphyrin to the acceptor quinone or diimide. A number of studies about porphyrin-quinone systems have confirmed that quinones readily accept an electron from excited molecules of porphyrins.[9] Recent transient-absorption studies have shown that quenching of porphyrin excited states by a diimide moiety also proceeds through an ET process.[10] Considering an ET quenching in the systems described here, one can explain why the quinone moiety worked as a more efficient quencher than the diimide moiety, as the ET reaction is more exothermic for the quinone than the diimide.[11] However, it is curious that the rate of "electron transfer" is unusually large for the very long donor-to-acceptor distance; k_{ET} was estimated to be 1.4×10^8 s^{-1} for **2a** (center-to-center distance 21 Å), while a rate constant less than 10^7 s^{-1} was reported for the bis(bicyclooctane) linked porphyrin-quinone system (center-to-center distance 18.8 Å).[12] It is very likely that a "superexchange" mechanism is working, in which the intervening zinc porphyrin acts as a mediator.[13]

The quenching efficiency clearly depends on the bridging group between the two porphyrins. As a general, the quenching becomes less efficient as the donor-to-acceptor distance becomes larger. However, the compound **4** offers a problem; although **4** has the same donor-to-acceptor distance as **3b**, **4** showed practically no quenching while **3b** showed quenching of 12% efficiency. The theory of superexchange can explain such a difference. It has been shown[12] that the rate of superexchange electron transfer in a D–I–A system (D, I, and A denote donor, intermediate, and acceptor) depends on the product of two transfer integrals V_{DI} and V_{IA}. In the present case, D is the free-base porphyrin, I is the zinc porphyrin, and A is the acceptor. The compound **3b** has a shorter distance between D and I and a longer distance between I and A than the compound **4**. Although there is no estimation for the values of V_{DI} and V_{IA} from the experimental data at present, the reported rates of electron transfer between two chromophores with similar geometries may be suggestive. Osuka et al. reported the rates of electron transfer in zinc–iron(III) hybrid diporphyrins;[14] 7.4×10^{10} s^{-1} for the 1,4-phenylene bridged diporphyrin and 1.6×10^{10} s^{-1} for the 4,4′-biphenylylene bridged one. The same authors also reported the rates of energy transfer in zinc–(free base) hybrid diporphyrins;[15] 6.6×10^{10} s^{-1} for the 1,4-phenylene bridged one and 7.8×10^9 s^{-1} for the 4,4′-biphenylylene bridged one. Insertion of one additional 1,4-phenylene group resulted in the decrease of the rate by a factor of 4.6 (electron transfer) or 8.5 (energy transfer). On the other hand, the fluorescence quantum yields of the two imide-linked (mono)porphyrins **14**-Zn and **15**-Zn were measured (relative values to **12**-Zn), and it was found that the fluorescence quenching in the latter was 100 times slower than in the former. These results show that, when one additional phenyl group is inserted between the two chromophores, the effect of this insertion upon the rates of electron (or energy) transfer is greater for the porphyrin–imide systems than for the porphyrin–porphyrin systems. Thus it may be possible that V_{IA} drops more severely in **4** than V_{DI} rises and hence the rate of electron transfer is smaller in **4** than in **3b**, only if it can be generally stated that the porphyrin–imide interaction is more sensitive to the distance than the porphyrin–porphyrin interaction.

Conclusion

A new series of selectively metallated diporphyrin-acceptor systems **1**, **2**, and **3** were synthesized. Introduction of a bulky substituent at one end of the diporphyrin led to preferential formation of the (H_2, Zn) isomer over the (Zn, H_2) isomer, when metallated with a limited amount of zinc acetate. Although the selectivity was not complete, the (H_2, Zn) isomers of **1**—**3** were readily purified by column chromatography, with sufficient purity for spectroscopic studies.

The (H_2, Zn) complexes of **2** and **3** showed substantial quenching of the fluorescence of the free-base porphyrin moiety. It is likely that a long-distance, superexchange electron transfer is responsible for this quenching. Synthesis and spectroscopic studies of other "partially metallated" functionalized oligoporphyrins are currently under way.

Experimental

General. For synthetic use, tetrahydrofuran (THF), dichloromethane, acetonitrile, and acetone were refluxed over and distilled from sodium benzophenone ketyl, P_2O_5, CaH_2, and $CaSO_4$, respectively. *N*,*N*-Dimethylformamide (DMF) was distilled under reduced pressure and stored over molecular sieves. Other solvents and reagents were reagent grade. Melting points were measured on a Yanagimoto micro melting point apparatus and are uncorrected. Preparative separations were usually performed by flash column chromatography on silica gel (Merck, Kieselgel 60H, Art. 7736).

UV-visible spectra were obtained with a Shimadzu UV-3000 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 (operating at 400 MHz), chemical shifts being reported in the delta scale (ppm) relative to Me_4Si. Mass spectra were recorded on JEOL DX-300 and HX-110 spectrometers. For porphyrin compounds, the positive-FAB (fast atom bombardment) ionization method was used (accelerating voltage 1.5 kV and 10 kV, Xe atom as the primary ion source). The FAB matrix was 3-nitrobenzyl alcohol/chloroform.

2,6-Bis(benzyloxy)benzaldehyde. Synthesized from 2,6-dihydroxybenzoic acid by the following sequence: (1) conversion to the methyl ester (diazomethane in THF, r.t., 98%), (2) conversion to the bis(benzyloxy) derivative by treatment with benzyl bromide (2.2 equiv) in the presence of K_2CO_3 (2.5 equiv) in acetone (reflux overnight, 71%), (3) reduction to the primary alcohol ($LiAlH_4$ in THF, r.t., 96%), and finally (4) oxidation to the aldehyde (1.2 equiv of PCC (pyridinium chlorochromate) in CH_2Cl_2, r.t., 5.5 h, 98%). Pale yellow needles, mp 76—77 °C (EtOH). ^{1}H NMR δ=10.66 (1H, s), 7.47 (4H, d, J=7.0 Hz), 7.40 (5H, m), 7.32 (2H, m), 6.63 (2H, d, J=8.5 Hz), 5.19 (4H, s). Found: H, 5.63; C, 79.16%. Calcd. for $C_{21}H_{18}O_3$: H, 5.70; C, 79.23%.

Bis(3-hexyl-4-methyl-2-pyrrolyl)methane (5). The compound **5** was synthesized from ethyl 3,5-dimethyl-4-hexyl-2-pyrrolecarboxylate[16] by the following sequence: (1) conversion to bis(5-ethoxycarbonyl-3-hexyl-4-methyl-2-pyrrolyl)methane, via 5-acetoxymethyl derivative of the starting pyrrole,[17] (2) alkaline hydrolysis of the ester groups and decarboxylation.[18] The compound **5** was purified by passing its solution in CH_2Cl_2 through a short column of silica gel. Dark brown oil, which can be stored for about a month in the freezer. Purity was checked by ^{1}H NMR before use. ^{1}H NMR δ=7.39 (2H, br), 6.37 (2H, s), 3.81 (2H, s), 2.40 (4H, t, J=7.8 Hz), 2.04 (6H, s), 1.46 (4H, m), 1.30 (12H, m), 0.89 (6H, t, J=6.9 Hz).

4-(5,5-Dimethyl-1,3-dioxan-2-yl)benzaldehyde (6a). This aldehyde was synthesized from methyl 4-formylbenzoate by the following sequence: (1) protection of the formyl group by 2,2-dimethyl-1,3-propanediol (1.1 equiv, 0.1 equiv of *p*-toluenesulfonic acid, benzene, reflux, 2 h, 100%), (2) reduction to the primary alcohol (2 equiv of $LiAlH_4$, THF, 0 °C to r.t., 4 h, 75%), (3) oxidation to the aldehyde (1.5 equiv of PCC, 0.4 equiv of anhydrous sodium acetate, CH_2Cl_2, r.t., 3 h, 92%). Mp 60—63 °C (lit,[19] 59—62 °C).

4′-(5,5-Dimethyl-1,3-dioxan-2-yl)-[1,1′-biphenyl]-4-carbaldehyde (6b). [1,1′-Biphenyl]-4,4′-dicarbaldehyde (2.0 g, 9.5 mmol) was treated with 2,2-dimethyl-1,3-propanediol (1.0 g, 9.5 mmol) in the presence of *p*-toluenesulfonic acid (0.19 g, 1.0 mmol) in 150 ml of benzene (reflux, 2 h). The reaction mixture was cooled and shaken with saturated aqueous solution of $NaHCO_3$ (30 ml). The orange solution turned colorless and white precipitates appeared. The precipitates (bisacetal compound) were removed by filtration and the filtrate was washed with water, dried and evaporated. The mixture was then treated with $LiAlH_4$ (360 mg, 9.5 mmol) in THF. After usual workup, the mixture was separated by column chromatography (eluted with CH_2Cl_2/Et_2O). The second fraction was collected (380 mg) and treated with PCC (388 mg, 1.8 mmol) in the presence of sodium acetate (40 mg). The monoprotected aldehyde **6b** was obtained (329 mg, 12%). ^{1}H NMR δ=10.06 (1H, s), 7.95 (2H, d, J=8.5 Hz), 7.74 (2H, d, J=8.2 Hz), 7.63 (4H, ABq), 5.46 (1H, s), 3.80 (2H, d, J=9.9 Hz), 3.68 (2H, d, J=10.7 Hz), 1.32 (3H, s), 0.82 (3H, s).

The compound **6c** and **6d** was synthesized in a similar manner as **6b**. The compound data are listed below:

6c: ^{1}H NMR δ=10.04 (1H, s), 7.94 (2H, d, J=8.6 Hz), 7.77 (2H, d, J=8.2 Hz), 7.68 (4H, s), 7.60 (4H, ABq), 5.43 (1H, s), 3.78 (2H, d, J=11.3 Hz), 3.66 (2H, d, J=10.6 Hz), 1.30 (3H, s), 0.80 (3H, s).

6d: ^{1}H NMR δ=9.96 (1H, s), 7.77 (2H, d, J=7.8 Hz), 7.45 (2H, d, J=7.8 Hz), 7.31 (2H, d, J=7.8 Hz), 7.19 (2H, d, J=8.0 Hz), 5.37 (1H, s), 4.05 (2H, s), 3.76 (2H, d, J=10.8 Hz), 3.64 (2H, d, J=11.0 Hz), 1.29 (3H, s), 0.79 (3H, s).

Methyl 4-[(2,5-Dimethoxy-4-methylphenyl)methyl]benzoate. The precursor ketone, methyl 4-(2,5-dimethoxy-4-methylbenzoyl)benzoate, was prepared from 4-methoxycarbonylbenzoyl chloride and 2,5-dimethoxytoluene ($SnCl_4$, CH_2Cl_2, reflux). A mixture of this ketone (2.04 g, 6.49 mmol), KOH (1.82 g, 32 mmol), hydrazine monohydrate (4.87 g, 97 mmol), and diethylene glycol (50 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 ice 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-dimethoxy-4-methylphenyl)methyl]benzoic acid (1.77 g, 6.18 mmol, 95%). 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 MeI were removed by rotary evaporation. The residue was dissolved in CH_2Cl_2, washed with water, dried, and evaporated. The residual yellow oil crystallized on standing. Yield: 96%. Mp 79—80 °C (EtOH). ^{1}H NMR δ=7.92 (2H, d, J=8.2 Hz), 7.25 (2H, d, J=7.9 Hz), 6.70 (1H, s), 6.57 (1H, s), 3.98 (2H, s), 3.89 (3H, s), 3.73 (3H, s), 3.72 (3H, s). Found: H, 6.70; C, 71.79%. Calcd for $C_{18}H_{20}O_4$: H, 6.71; C, 71.98%.

4-[(2,5-Diacetoxy-4-methylphenyl)methyl]benzaldehyde (9). The methyl ester derivative (see above) was converted to the corresponding aldehyde in two steps ($LiAlH_4$ in THF, 0 °C to r.t., 6.5 h, 89%; PCC in CH_2Cl_2, r.t., 3 h, 89%). This aldehyde (1.25 g, 4.6 mmol) was dissolved in 50 ml of acetonitrile (reagent grade), and a solution of cerium(IV) ammonium nitrate (5.5 g, 10.1 mmol) in 20 ml of water was dropwise added over 30 min. After 2 h, water (50 ml) was added to the bright yellow solution, and the mixture was extracted with CH_2Cl_2. The extract was washed with water and evaporated. The residual orange oil was purified by flash column chromatography (R_f=0.5, CH_2Cl_2). This product (826 mg, 3.4 mmol) was dissolved in 15 ml of acetic anhydride, and this solution was added dropwise to a suspension of zinc dust (530 mg, 8 mmol) and anhydrous sodium acetate (290 mg) in acetic anhydride (5 ml) at 0 °C (under N_2). The mixture was stirred overnight, filtered to remove inorganic salts. The solvent was removed in vacuo, and the residual white solid was dissolved in ethyl acetate, washed with water and brine, dried, and evaporated. Yield: 1.06 g (3.2 mmol, 96%). Mp 107—108 °C (EtOH). ^{1}H NMR δ=9.97 (1H, s), 7.79 (2H, d, J=8.3 Hz), 7.31 (2H, d, J=8.3 Hz), 6.96 (1H, s), 6.80 (1H, s), 3.92 (2H, s), 2.28 (3H, s) 2.17 (3H, s), 2.15 (3H, s). Found: H, 5.48; C, 69.31%. Calcd for $C_{19}H_{18}O_5$: H, 5.56; C, 69.93%.

***N*-Hexyl-*N*′-[(4-formylphenyl)methyl]-1,2:4,5-benzenebis(dicarboximide) (10).** A precursor of this compound, 4-(5,5-dimethyl-1,3-dioxan-2-yl)benzylamine was synthesized in 2 steps from 4-cyanobenzaldehyde: (1) protection of the formyl group (1.1 equiv of 2,2-dimethyl-1,3-propanediol, 0.1 equiv of *p*-toluenesulfonic acid, benzene, reflux 1.5 h, 98%), (2) reduction to the primary amine ($LiAlH_4$, ether/THF, 0 °C, 5 h, 96%). This amine (6.6 g, 30 mmol) and hexylamine (9.1 g, 90 mmol) was dissolved in 150 ml of DMF, and a solution of 1,2:4,5-benzenetetracarboxylic dianhydride (13.1 g, 60 mmol) in 80 ml of DMF was added. The mixture was heated to reflux overnight and cooled. The precipitates were collected by filtration. TLC showed three products (CH_2Cl_2), and the second one was collected by column chromatography. This product (2.2 g, 4.4 mmol, 15%) was treated with acid to hydrolyze the acetal protecting group ($CHCl_3$ 50 ml, trifluoroacetic acid 20 ml, 5% aqueous H_2SO_4 15 ml, r.t., overnight). The mixture was poured into water and the organic layer was separated, washed with $NaHCO_3$ solution and water, dried and evaporated. Yield: 1.4 g (3.2 mmol, 73%). Mp>300 °C (benzene). ^{1}H NMR δ=9.99 (1H, s), 8.28 (2H, m), 7.86 (2H, d, J=8.3 Hz), 7.59 (2H, d, J=8.0 Hz), 4.96 (2H, s), 3.73 (2H, t, J=7.4 Hz), 1.69 (2H, m), 1.31 (6H, m), 0.87 (3H, m). Found: H, 5.05; C, 68.86; N, 6.72%. Calcd for $C_{24}H_{22}N_2O_5$: H, 5.30; C, 68.89; N, 6.69%.

4′-(5,5-Dimethyl-1,3-dioxan-2-yl)-[1,1′-biphenyl]-4-methanamine. To a solution of the monoprotected aldehyde **6b** (445 mg, 1.5 mmol) in a mixture of ethanol (50 ml) and CH_2Cl_2 (10 ml) was added a solution of hydroxylamine hydrochloride (118 mg, 1.7 mmol) and sodium carbonate (95 mg, 0.9 mmol) in 2.5 ml of water. The solution became opaque and white precipitates appeared. The mixture was stirred overnight at room temperature, then poured into 100 ml of water, extracted with CH_2Cl_2, washed with water, dried, and evaporated. The white solid was washed with hexane and dried in vacuo to give an oxime (346 mg, 1.1 mmol, 74%). This oxime (1 mmol) was treated with $LiAlH_4$ (2 mmol) in 17 ml of THF (70 °C, 6 h). After cooling, 1 ml of water and 1 ml of 10% NaOH solution was added, the solid was removed by filtration (washed by ether), and the filtrate was washed with brine, dried, and evaporated. Yield: 240 mg (0.81 mmol, 81%). ^{1}H NMR δ=7.58 (6H, m), 7.37 (2H, d, J=8.3 Hz), 5.44 (1H, s), 3.90 (2H, s), 3.79 (2H, d, J=11.3 Hz), 3.67 (2H, d, J=10.7 Hz), 1.31 (3H, s), 0.81 (3H, s).

***N*-Hexyl-*N*′-[[4′-formyl-[1,1′-biphenyl]-4-yl]methyl]-1,2:4,5-benzenebis(dicarboximide) (11).** This compound was synthesized from the above-described amine (0.67 mmol), hexylamine (6.0 mmol) and 1,2:4,5-benzenetetracarboxylic dianhydride (6.7 mmol) in a similar manner as **10**. Yield: 144 mg (0.29 mmol, 43%). ^{1}H NMR δ=10.05 (1H, s), 8.28 (2H, s), 7.93 (2H, d, J=8.2 Hz), 7.71 (2H, d, J=8.5 Hz), 7.61 (2H, d, J=8.5 Hz), 7.56 (2H, d, J=8.3 Hz), 4.95 (2H, s), 3.73 (2H, t, J=7.3 Hz), 1.69 (2H, m), 1.31 (6H, m), 0.88 (3H, m).

Synthesis of Formyl Porphyrins. 5-[2,6-Bis(benzyloxy)phenyl]-15-(4-formylphenyl)-2,8,12,18-tetrahexyl-3,7,13,17-tetramethylporphine (8a). 2,6-Bis(benzyloxy)benzaldehyde (425 mg, 1.33 mmol), 4-(5,5-dimethyl-1,3-dioxan-2-yl)benzaldehyde **6a** (294 mg, 1.33 mmol), and bis(3-hexyl-4-methyl-2-pyrrolyl)methane **5** (913 mg, 2.67 mmol) were dissolved in 35 ml of acetonitrile. Trichloroacetic acid (131 mg, 0.80 mmol) was added, and the mixture was stirred overnight (room temperature, under nitrogen, in the dark). A solution of *p*-chloranil (1.0 g, 4.1 mmol) in a minimum amount of tetrahydrofuran was added, and the mixture was stirred for 5 h. The solvent was evaporated and the residue was taken up in chloroform, washed with saturated $NaHCO_3$ solution and water, and dried over Na_2SO_4. To this chloroform solution was added 5 ml of saturated solution of zinc acetate in methanol, and the mixture was heated to reflux for 2 h. After cooling, the reaction mixture was washed with water, dried over Na_2SO_4 and evaporated. TLC showed three products (R_f=0.8, 0.5, and 0.3, benzene) and the second was separated by column chromatography (benzene). Yield of **7a** (zinc complex): 612 mg (0.492 mmol, 37%).

The compound **7a** zinc complex (419 mg, 0.337 mmol) was dissolved in a mixture of trifluoroacetic acid (10 ml), acetic acid (20 ml) and 5% aqueous sulfuric acid (5 ml). After being heated at 100 °C for 1.5 hours, the mixture was poured into 150 ml of water and extracted with CH_2Cl_2. The organic phase was washed with saturated $NaHCO_3$ solution (effervescence!), dried over Na_2SO_4, and evaporated. The residue was triturated and washed in methanol and dried in vacuo. Yield of **8a**: 303 mg (0.277 mmol, 82%). Mp 163—167 °C. ^{1}H NMR δ=10.40 (1H, s, CHO), 10.22 (2H, s, meso), 3.97 (8H, m, hexyl-1), 2.57 (6H, s, Me), 2.46 (6H, s, Me), 2.19 (8H, m, hexyl-2), 1.73 (8H, m, hexyl-3), 1.46 (8H, m, hexyl-4), 1.37 (8H, m, hexyl-5), 0.90 (12H, m, hexyl-6), −2.2 (2H, br, NH); 5-Ph: 7.62 (1H, t, J=8.5 Hz), 7.00 (2H, d, J=8.8 Hz); 15-Ph: 8.28 (4H, AB quartet); benzyloxy: 6.85 (2H, t, J=7.3 Hz), 6.72 (4H, t, J=7.9 Hz), 6.58 (4H, d, J=7.3 Hz), 4.94 (4H, s).

The compounds **8b**, **8c**, and **8d** was prepared in the similar manner as **8a**. The compound data are listed below:

8b: Yield (2 steps) 24%. Mp. 195—200 °C. ^{1}H NMR δ=10.22 (2H, s, meso), 10.18 (1H, s, CHO), 3.99 (8H, m, hex-1), 2.57 (6H, s, Me), 2.56 (6H, s, Me), 2.20 (8H, m, hex-2), 1.74 (8H, m, hex-3), 1.48 (8H, m, hex-4), 1.35 (8H, m, hex-5), 0.90 (12H, m, hex-6), −2.3 to −2.5 (2H, br, NH); 5-Ph: 7.62 (1H, t, J=8.3 Hz), 7.01 (2H, d, J=8.8 Hz); biphenylylene: 8.20 (2H, d, J=8.3 Hz), 8.13 (4H, s), 7.61 (2H, d, J=8.3 Hz) benzyloxy: 6.85 (2H, t, J=7.8 Hz), 6.72 (4H, t, J=7.6 Hz), 6.58 (4H, d, J=7.3 Hz), 4.94 (4H, s).

8c: Yield (2 steps) 20%. Mp 181—185 °C. ^{1}H NMR δ=10.22 (2H, s, meso), 10.12 (1H, s, CHO), 4.00 (8H, m, hex-1), 2.58 (6H, s, Me), 2.57 (6H, s, Me), 2.21 (8H, m, hex-2), 1.74 (8H, m, hex-3), 1.48 (8H, m, hex-4), 1.38 (8H, m, hex-5), 0.90 (12H, m, hex-6), −2.15 (1H, s, NH), −2.26 (1H, s, NH); 5-Ph: 7.62 (1H, t, J=8.3 Hz), 7.01 (2H, d, J=8.3 Hz); terphenyl: 8.18 (2H, d, J=8.3 Hz), 8.10 (2H, d, J=8.3 Hz), 8.07 to 8.03 (4H, 2 doublets), 7.92 (2H, d, J=8.3 Hz), 7.90 (2H, d, J=8.3 Hz); benzyloxy: 6.85 (2H, t, J=7.3 Hz), 6.72 (4H, t, J=7.9 Hz), 6.58 (4H, d, J=7.3 Hz), 4.94 (4H, s).

8d: Yield (2 steps) 32%. Mp 52—58 °C. ^{1}H NMR δ=10.20 (2H, s, meso), 10.10 (1H, s, CHO), 3.98 (8H, m, hex-1), 2.57 (6H, s, Me), 2.51 (6H, s, Me), 2.19 (8H, m, hex-2), 1.74 (8H, m, hex-3), 1.46 (8H, m, hex-4), 1.36 (8H, m, hex-5), 0.90 12H, m, hex-6), −2.2 (2H, NH); 5-Ph: 7.62 (1H, t), 7.00 (2H, d, J=8.3 Hz); $PhCH_2Ph$: 8.02 (2H, d, J=7.8 Hz), 7.98 (2H, d, J=7.8 Hz), 7.62 (2H, d), 7.55 (2H, d, J=7.3 Hz), 4.44 (2H, s); benzyloxy: 6.84 (2H, t, J=7.3 Hz), 6.71 (4H, t, J=7.6 Hz), 6.57 (4H, d, J=7.8 Hz), 4.93 (4H, s).

Synthesis of Free-Base Diporphyrins. 15-[2,6-Bis(benzyloxy)phenyl]-15′-[4-[(2,5-diacetoxy-4-methylphenyl)methyl]phenyl]-5,5′-(1,4-phenylene)bis[2,8,12,18-tetrahexyl-3,7,13,17-tetramethylporphine] (1a). The formylporphyrin **8a** (147 mg, 0.13 mmol) was dissolved in 15 ml of acetonitrile containing 57 mg (0.35 mmol) of trichloroacetic acid. The aldehyde **9** (261 mg, 0.80 mmol) in 5 ml of CH_3CN and **5** (319 mg, 0.93 mmol) in 5 ml of CH_3CN were added, and the mixture was stirred overnight (room temperature, under N_2, dark). A solution of *p*-chloranil (344 mg, 1.4 mmol) in a minimum amount of tetrahydrofuran was added, and the mixture was stirred for additional 3 h. The reaction mixture was poured into 100 ml of water, extracted with CH_2Cl_2, washed with $NaHCO_3$ solution and dried over Na_2SO_4. This dichloromethane solution was treated with a saturated solution of zinc acetate in methanol (5 ml, 2 h reflux), washed with water, dried and evaporated. At this stage, all porphyrinic products were separated from tarry materials by column chromatography (CH_2Cl_2, R_f=0.8 to 1.0). This mixture of zinc porphyrins were dissolved in dichloromethane and shaken with two portions of 4 M (1 M=1 mol dm^{-3}) hydrochloric acid, neutralized with $NaHCO_3$ solution, dried and evaporated, to give a mixture of free-base porphyrins. The mixture was separated by column chromatography (CH_2Cl_2+Et_2O) to give two products (R_f=0.6 and 0.3, CH_2Cl_2/Et_2O (v/v)=100/5). The second fraction was the diporphyrin **1a**. Yield: 116 mg (56 mmol, 43%). Mp 134—140 °C. ^{1}H NMR δ=10.34 (2H, s, meso), 10.32 (2H, s, meso), 4.15 (8H, m, hex-1), 4.04 (8H, m, hex-1), 3.20 (12H, s, Me), 2.61 (6H, s, Me), 2.54 (6H, s, Me), 2.32 (8H, m, hex-2), 2.25 (8H, m, hex-2), 1.86 (8H, m, hex-3), 1.78 (8H, m, hex-3), 1.6—1.4 (m, hex-4 and hex-5), 1.0—0.9 (24H, m, hex-6); bridging phenylene: 8.58 (4H, s); 15-phenyl: 7.64 (1H, t, *J*=8.3 Hz), 7.03 (2H, d, *J*=8.8 Hz); benzyloxy: 6.88 (2H, t, *J*=7.3 Hz), 6.76 (4H, t, *J*=7.6 Hz), 6.62 (4H, d, *J*=7.3 Hz), 4.98 (4H, s); 15′-substituent: 8.02 (2H, d, *J*=8.3 Hz), 7.55 (2H, d, *J*=7.8 Hz), 7.12 (1H, s), 7.10 (1H, s), 4.24 (2H, s, benzylic), 2.44 (3H, s, acetyl), 2.43 (3H, s, acetyl), 2.27 (3H, s). MS *m*/*z* 2065 (M+H$^+$), 1032 (doubly charged ion).

The compounds **1b**, **1c**, and **1d** were prepared in the similar manner as **1a**. The compound data are listed below:

1b: Yield 69%. Mp 279—283 °C. ^{1}H NMR δ=10.29 (2H, s, meso), 10.27 (2H, s, meso), 4.0 (16H, m, hex-1), 2.75 (12H, s, Me), 2.60 (6H, s, Me), 2.53 (6H, s, Me), 2.24 (16H, m, hex-2), 1.77 (16H, m, hex-3), 1.5 (m, hex-4), 1.40 (m, hex-5), 0.93 (m, hex-6), −2.12 (1H, br, NH), −2.18 (1H, br, NH), −2.29 (1H, br, NH), −2.35 (1H, br, NH); bridging biphenylylene: 8.34 (8H, m); 15-phenyl: 7.64 (1H, t), 7.02 (2H, d, *J*=8.3 Hz); benzyloxy: 6.87 (2H, t, *J*=6.8 Hz), 6.74 (4H, t, *J*=7.8 Hz), 6.61 (4H, d, *J*=7.3 Hz), 4.96 (4H, s); 15′-substituent: 8.02 (2H, d, *J*=7.8 Hz), 7.54 (2H, d, *J*=7.8 Hz), 7.11 (1H, s), 7.09 (1H, s), 4.23 (2H, s, benzylic), 2.44 (3H, s, acetyl), 2.43 (3H, s, acetyl), 2.26 (3H, s). MS *m*/*z* 2141 (M+H$^+$).

1c: Yield 55%. Mp>300 °C. ^{1}H NMR δ=10.27 (2H, s, meso), 10.25 (2H, s, meso), 4.02 (16H, m, hex-1), 2.65 (12H, 2s, Me), 2.59 (6H, s, Me), 2.52 (6H, s, Me), 2.22 (16H, m, hex-2), 1.76 (16H, m, hex-3), 1.5 (m, hex-4), 1.39 (m, hex-5), 1.92 (m, hex-6), −2.2 (1H, br, NH), −2.3 (1H, br, NH), −2.4 (2H, br, NH); bridging terphenyl: 8.23 (12H, m); 15-phenyl: 7.63 (1H, t), 7.02 (2H, d, *J*=8.8 Hz); benzyloxy: 6.86 (2H, t, *J*=6.8 Hz), 6.73 (4H, t, *J*=7.6 Hz), 6.60 (4H, d, *J*=7.4 Hz), 4.95 (4H, s); 15′-substituent: 8.01 (2H, d, *J*=7.8 Hz), 7.54 (2H, d, *J*=7.8 Hz), 7.11 (1H, s), 7.08 (1H, s), 4.23 (2H, s, benzylic), 2.46 (3H, s, acetyl), 2.42 (3H, s, acetyl), 2.26 (3H, s, Me). MS *m*/*z* 2217 (M+H$^+$).

1d: Yield 76%. Mp 100—105 °C. ^{1}H NMR δ=10.26 (2H, s, meso), 10.24 (2H, s, meso), 4.00 (16H, m, hex-1), 2.64 (12H, s, Me), 2.59 (6H, s, Me), 2.52 (6H, s, Me), 2.20 (16H, m, hex-2), 1.75 (16H, m, hex-3), 1.49 (m, hex-4), 1.36 (16H, m, hex-5), 0.88 (m, hex-6), −2.1 to −2.4 (4H, br, NH); bridging group: 8.15 (4H, 2d), 7.85 (2H, 2d), 4.72 (2H, s); 15-phenyl: 7.63 (1H, t), 7.01 (2H, d, *J*=8.8 Hz); benzyloxy: 6.86 (2H, t, *J*=7.3 Hz), 6.73 (4H, t, *J*=7.8 Hz), 6.60 (4H, d, *J*=7.3 Hz), 4.95 (4H, s); 15′-substituent: 8.01 (2H, d, *J*=8.3 Hz), 7.54 (2H, d, *J*=8.3 Hz), 7.11 (1H, s), 7.08 (1H, s), 4.22 (2H, s, benzylic), 2.26 (3H, s, Me). MS *m*/*z* 2155 (M+H$^+$).

15-[2,6-Bis(benzyloxy)phenyl]-15′-[4-[(4-methyl-3,6-dioxo-1,4-cyclohexadienyl)methyl]phenyl]-5,5′-(1,4-phenylene)-bis-[2,8,12,18-tetrahexyl-3,7,13,17-tetramethylporphine] (2a). The diporphyrin **1a** (43 mg, 0.020 mmol) was dissolved in a mixture of 20 ml of methanol and 3 ml of concentrated hydrochloric acid. The mixture was heated under gentle reflux for 2.5 h (under N_2), poured into aqueous $NaHCO_3$ solution, extracted with CH_2Cl_2, dried and evaporated. The residue was dissolved again in CH_2Cl_2 (10 ml) and treated with 90 mg (0.38 mmol) of PbO_2 at room temperature for 2 h. The mixture was filtered through Celite to remove the inorganic material and evaporated. The crude product was purified as the dizinc complex (treatment with large excess of $Zn(OAc)_2$) by column chromatography (benzene). The free-base **2a** was recovered from the dizinc complex by treatment of the dichloromethane solution with 4 M hydrochloric acid. Yield: 30 mg (0.015 mmol, 75%). ^{1}H NMR δ=10.35 (2H, s, meso), 10.32 (2H, s, meso), 4.13 (8H, m, hex-1), 4.04 (8H, m, hex-1), 3.21 (12H, s, Me), 2.61 (6H, s, Me), 2.55 (6H, s, Me), 2.33 (8H, m, hex-2), 2.24 (8H, m, hex-2), 1.87 (8H, m, hex-3), 1.78 (8H, m, hex-3), 1.6 to 1.3 (m, hex-4 and hex-5), 0.98 to 0.90 (m, hex-6), −1.5 to −2.2 (br, NH); bridging phenylene: 8.57 (4H, s); 15-phenyl: 7.64 (1H, t), 7.03 (2H, d, *J*=8.3 Hz); benzyloxy: 6.88 (2H, t, *J*=7.8 Hz), 6.76 (4H, t, *J*=7.6 Hz), 6.62 (4H, d, *J*=7.3 Hz), 4.98 (4H, s); 15′-substituent: 8.08 (2H, d, *J*=7.8 Hz), 7.58 (2H, d, *J*=7.8 Hz), 6.79 (1H, s), 6.66 (1H, s), 4.13 (2H, s, benzylic), 2.17 (3H, s, Me). MS *m*/*z* 1981 ([M+3H]$^+$), 991 (doubly charged ion).

The compounds **2b**, **2c**, and **2d** were prepared in the similar manner as **2a**. The compound data are shown below:

2b: Yield 88%. Mp 290—295 °C. ^{1}H NMR δ=10.30 (2H, s, meso), 10.27 (2H, s, meso), 4.03 (16H, m, hex-1), 2.75 (12H, s, Me), 2.60 (6H, s, Me), 2.53 (6H, s, Me), 2.14 (16H, m, hex-2), 1.77 (16H, m, hex-3), 1.5 (m, hex-4), 1.40 (16H, m, hex-5), 0.9 (m, hex-6), −2.1 (1H, br, NH), −2.2 (1H, br, NH), −2.3 to −2.4 (2H, br, NH); bridging biphenylylene: 8.3 (8H, m); 15-phenyl: 7.64 (1H, t), 7.03 (2H, d, *J*=8.3 Hz) benzyloxy: 6.88 (2H, t, *J*=7.3 Hz), 6.75 (4H, t, *J*=7.8 Hz), 6.61 (4H, d, *J*=7.3 Hz), 7.55 (2H, d, *J*=7.8 Hz), 6.78 (1H, s), 6.65 (1H, s), 4.11 (2H, s, benzylic), 2.16 (3H, s, Me). MS *m*/*z* 2057 ([M+3H]$^+$), 1028 (doubly charged ion).

2c: Yield 90%. Mp 285—290 °C. ^{1}H NMR δ=10.28 (2H, s, meso), 10.25 (2H, s, meso), 4.02 (16H, m, hex-1), 2.65 (12H, s, Me), 2.59 (6H, s, Me), 2.53 (6H, s, Me), 2.23 (16H, m, hex-2), 1.77 (16H, m, hex-3), 1.51 (16H, m, hex-4), 1.38 (16H, m, hex-5), 0.93 (24H, m, hex-6), −2.1 (1H, br, NH), −2.26 (1H, br, NH), −2.35 (2H, br, NH); bridging terphenyl: 8.21 (8H, d and s), 8.15 (4H, 2 doublets); 15-phenyl: 7.63 (1H, t), 7.02 (2H, d, *J*=8.8 Hz); benzyloxy: 6.86 (2H, t), 2.74 (4H, t, *J*=7.6 Hz), 6.60 (4H, d, *J*=7.8 Hz), 4.96 (4H, s); 15′-substituent: 8.05 (2H, d, *J*=7.8 Hz), 7.55 (2H, d, *J*=7.8 Hz), 6.77 (1H, m, *J*<2 Hz), 6.64 (1H, s), 4.11 (2H, s, benzylic), 2.15 (3H, m, *J*<2 Hz). MS *m*/*z* 2133 ([M+3H]$^+$), 1066 (doubly charged ion).

2d: Yield 83%. Mp 143—148 °C. ^{1}H NMR δ=10.27 (2H, s, meso), 10.24 (2H, s, meso), 4.00 (16H, m, hex-1), 2.64 (12H, s, Me), 2.58 (6H, s, Me), 2.52 (6H, s, Me), 2.22 (16H, m, hex-2), 1.75 (16H, m, hex-3), 1.48 (16H, m, hex-4), 1.36 (16H, m, hex-5), 0.88 (m, hex-6), −2.15 (1H, br, NH), −2.26 (1H, m, NH), −2.35 (2H, br, NH); bridging group: 8.15 (4H, 2 doublets), 7.85 (4H, 2 doublets), 4.71 (2H, s, benzylic); 15-phenyl: 7.63 (1H, t), 7.01 (2H, d, *J*=8.8 Hz); benzyloxy: 6.86 (2H, t, *J*=7.3 Hz), 6.73 (4H, t, *J*=7.6 Hz), 6.59 (4H, d, *J*=7.3 Hz), 4.97 (4H, s); 15′-substituent: 8.06 (2H, d, *J*=7.8 Hz), 7.56 (2H, d,

J=8.3 Hz), 6.78 (1H, m, J<2 Hz), 6.65 (1H, m, J<2 Hz), 4.11 (2H, s, benzylic), 2.16 (3H, m, J<2 Hz, Me). MS m/z 2071 ($[M+3H]^+$).

15-[2,6-Bis(benzyloxy)phenyl]-15′-[4-(6-hexyl-1,3,5,7-tetrahydro-1,3,5,7-tetraoxobenzo[1,2-*c*:4,5-*c*′]dipyrrol-2-yl)phenyl]-5,5′-(1,4-phenylene)bis[2,8,12,18-tetrahexyl-3,7,13,17-tetramethylporphine] (3a). The formyl porphyrin **8a** (60 mg, 0.055 mmol) and the *N*-(formylphenyl)diimide **10** (161 mg, 0.385 mmol) were dissolved in a mixture of 10 ml of dry acetonitrile and 10 ml of dry benzene containing 33 mg (0.2 mmol) of trichloroacetic acid. To this solution, bis(3-hexyl-4-methyl-2-pyrrolyl)methane **5** (151 mg, 0.44 mmol) in 10 ml of acetonitrile was added, and the mixture was stirred for 5 h (dark, under N_2, room temperature). A solution of *p*-chloranil (162 mg, 0.66 mmol) in THF was added, and stirring was continued for 2 h. The solvent was removed by rotary evaporation, and the residue was taken up in dichloromethane and washed with aqueous $NaHCO_3$ solution. At this point, red precipitates appeared from the organic phase. Methanol was added to complete precipitation, and the solids were collected by filtration and washed with methanol. The red-violet solids were dissolved again in dichloromethane and treated with excess zinc acetate to give a mixture of zinc porphyrins, which was separated by column chromatography to give two products (R=0.6 and 0.4, CH_2Cl_2). The second fraction was the dizinc complex of **3a**, from which the free-base **3a** was obtained by successive treatment with 4 M hydrochloric acid and aqueous $NaHCO_3$. Yield 79 mg (0.036 mmol, 67%). ^{1}H NMR δ=10.33 (4H, s, meso), 4.17 (8H, m, hex-1), 4.03 (8H, m, hex-1), 3.21 (12H, s, Me), 2.62 (6H, s, Me), 2.46 (6H, s, Me), 2.34 (8H, m, hex-2), 2.25 (8H, m, hex-2), 1.88 (8H, m, hex-3), 1.60 (8H, m, hex-3), 1.6 to 1.3 (m, hex-4 and hex-5), 1.0 to 0.9 (m, hex-6), −1.82 (2H, br, NH), −1.91 (1H, br, NH), −2.09 (1H, br, NH); bridging phenylene: 8.59 (4H, s); 15-phenyl: 7.65 (1H, t), 7.04 (2H, d, J=8.8 Hz); benzyloxy: 6.89 (2H, t, J=7.3 Hz), 6.77 (4H, t, J=7.6 Hz), 6.64 (4H, d, J=6.8 Hz), 4.99 (4H, s); 15′-substituent: 8.2 (2H, br, imide-aromatic H), 8.08 (2H, d, J=7.8 Hz), 7.76 (2H, d, J=7.8 Hz), 5.21 (2H, s, benzylic), 3.74 (2H, t, hex-1), 1.7 (2H, m, hex-2), 1.3 (m, hex-3, 4, 5), 1.0 to 0.9 (m, hex-6). MS m/z 2157, 1078.

The compounds **3b**, **3c**, and **3d** were prepared in the similar manner as **3a**. The compound data are listed below:

3b: Yield 47%. ^{1}H NMR δ=10.28 (2H, s, meso), 10.27 (2H, s, meso), 4.1 to 4.0 (16H, m, hex-1), 2.75 (12H, s, Me), 2.60 (6H, s, Me), 2.45 (6H, s, Me), 2.3 to 2.2 (16H, m, hex-2), 1.8 to 1.7 (18H, m, hex-3 and imide-hex-2), 1.6 to 1.5 (m, hex-4), 1.5 to 1.3 (m, hex-5 and imide-hex-3, 4, and 5), 1.0 to 0.9 (m, hex-6 and imide-hex-6), −2.12 (1H, br, NH), −2.21 (1H, br, NH), −2.35 (1H, br, NH), −2 .38 (1H, br, NH); bridging biphenylylene: 8.33 (8H, m); 15-phenyl: 7.63 (1H, t), 7.03 (2H, d, J=8.8 Hz); benzyloxy: 6.88 (2H, t, J=7.8 Hz), 6.75 (4H, t, J=7.6 Hz), 6.62 (4H, d, J=7.8 Hz), 4.97 (4H, s); 15′-substituent: 8.26 (2H, br, imide-aromatic), 8.08 (2H, d, J=8.3 Hz), 7.76 (2H, d, J=7.8 Hz), 5.23 (2H, s, benzylic), 3.76 (2H, t, hex-1). MS m/z 2233, 1117.

3c: Yield 65%. Mp 116—121 °C. ^{1}H NMR δ=10.25 (4H, 2 singlets, meso), 4.0 (16H, m, hex-1), 2.66 (6H, s, Me), 2.65 (6H, s, Me), 2.60 (6H, s, Me), 2.44 (6H, s, Me), 2.23 (16H, m, hex-2), 1.77 (18H, m, hex-3 and imide-hex-2), 1.5 (m, hex-4), 1.4 (m, hex-5 and imide-hex-3,4,5), 0.9 (m, hex-6 and imide-hex-6), −2.14 (1H, s, NH), −2.26 (1H, s, NH), −2.39 (1H, s, NH), −2.42 (1H, s, NH); bridging terphenyl: 8.24 (10H, m, overlapping with imide-aromatic), 8.17 (4H, 2 doublets); 15-phenyl: 7.64 (1H, t), 7.02 (2H, d, J=8.8 Hz); benzyloxy: 6.87 (2H, t, J=7.3 Hz), 6.74 (2H, d, J=8.8 Hz), 6.87 (2H, t, J=7.3 Hz), 6.74 (t, J=7.8 Hz), 6.61 (4H, d, J=7.3 Hz), 4.96 (4H, s); 15′-substituent: 8.07 (2H, d, J=7.8 Hz), 7.75 (2H, d, J=7.8 Hz), 5.22 (2H, s, benzylic), 3.98 (2H, t, hex-1). MS m/z 2309, 1155.

3d: Yield 47%. Mp 140—145 °C. ^{1}H NMR δ=10.24 (4H, 2 singlets, meso), 4.0 (16H, m, hex-1), 2.65 (12H, s, Me), 2.59 (6H, s, Me), 2.43 (6H, s, Me), 2.2 (16H, m, hex-2), 1.8 (18H, hex-3 and imide-hex-2), 1.5 (m, hex-4), 1.3 (m, hex-5 and imide-hex-3,4,5), 0.9 (m, hex-6 and imide-hex-6), −2.16 (1H, s, NH), −2.28 (1H, s, NH), −2.41 (1H, s, NH), −2.44 (1H, s, NH); bridging group: 8.16 (6H, 2 doublets, overlapping with imide-aromatic), 7.86 (4H, 2 doublets), 4.72 (2H, s, benzylic); 15-phenyl: 7.63 (1H, t), 7.01 (2H, d, J=8.3 Hz); benzyloxy: 6.87 (2H, t, J=7.3 Hz), 6.74 (4H, t, J=7.6 Hz), 6.61 (4H, d, J=7.3 Hz), 4.96 (4H, s); 15′-substituent: 8.06 (2H, d, J=7.8 Hz), 7.74 (2H, d, J=7.8 Hz), 5.20 (2H, s, benzylic), 3.73 (2H, t, hex-1). MS m/z 2247, 1123.

15-[2,6-Bis(benzyloxy)phenyl]-15′-[4′-(6-hexyl-1,3,5,7-tetrahydro-1,3,5,7-tetraoxobenzo[1,2-*c*:4,5-*c*′-]dipyrrol-2-yl)[1,1′-biphenyl]-4-yl]-5,5′-(1,4-phenylene)bis[2,8,12,18-tetrahexyl-3,7,13,17-tetramethylporphine] (4). Synthesized from the formyl porphyrin **8a**, the aldehyde **11** and **5** in a similar manner as **3a**. Yield: 55%. Mp>300 °C, ^{1}H NMR δ=10.35 (2H, s, meso), 10.32 (2H, s, meso), 4.16 (8H, m, hex-1), 4.04 (8H, m, hex-1), 3.18 (12H, s, Me), 2.62 (6H, s, Me), 2.54 (6H, s, Me), 2.34 (8H, m, hex-2), 2.26 (8H, m, hex-2), 1.88 (8H, m, hex-3), 1.78 (8H, m, hex-3), 1.59 (8H, m, hex-4), 1.5 to 1.3 (m, hex-4,5 and imide-hex-3,4,5), 1.0 to 0.9 (m, hex-6 and imide-hex-6), −1.78 (2H, br, NH), −1.89 (1H, br, NH), −2.03 (1H, br, NH); bridging phenylene, biphenylylene and imide-aromatic: 8.50 (4H, m), 8.18 (2H, m), 8.10 (2H, m), 7.92 (4H, m), 7.67 (2H, d); 15-phenyl: 7.65 (1H, t, J=8.6 Hz), 7.04 (2H, d, J=8.8 Hz); benzyloxy: 6.88 (2H, t, J=7.3 Hz), 6.76 (4H, t, J=7.6 Hz), 6.62 (4H, d, J=7.3 Hz), 4.98 (4H, s); imide: 5.00 (2H, s, benzylic CH_2), 3.73 (2H, t, hex-1), 1.71 (2H, m, hex-2). MS m/z 2233, 1117.

5-(4-Methylphenyl)-15-[4-[(2,5-diacetoxy-4-methylphenyl)methyl]phenyl]-2,8,12,18-tetrahexyl-3,7,13,17-tetramethylporphine (12). Synthesized from the aldehyde **9**, *p*-tolualdehyde and **5** in a similar manner as **7a** (see the synthesis of **8a**). The zinc porphyrin was converted to the free-base **12** by treatment with 4 M hydrochloric acid. Yield: 32%. Mp 140—142 °C. ^{1}H NMR δ=10.22 (2H, s), 7.98 (2H, d, J=8.3 Hz), 7.92 (2H, d, J=7.8 Hz), 7.53 (2H, d, J=7.8 Hz), 7.52 (2H, d, J=7.8 Hz), 7.10 (1H, s), 7.07 (1H, s), 4.21 (2H, s), 3.97 (8H, t, J=7.8 Hz), 2.72 (3H, s), 2.503 (6H, s), 2.498 (6H, s), 2.42 (3H, s), 2.41 (3H, s), 2.25 (3H, s), 2.18 (8H, quint, J=7.4 Hz), 1.72 (8H, quint, J=7.5 Hz), 1.47 (8H, quint, J=7.2 Hz), 1.36 (8H, sext, J=7.3 Hz), 0.90 (12H, t, J=7.4 Hz), −2.41 (2H, s). MS m/z 1090.

The compound **14** (or **15**) was also synthesized from the aldehyde **10** (or **11**), *p*-tolualdehyde and **5** in a similar manner as **12**. The compound data are shown below:

14: Yield: 39% (solvent: $CH_3CN+C_6H_6$=2 : 1). Mp 120—124 °C. ^{1}H NMR δ=10.20 (2H, s), 8.31 (2H, s), 8.04 (2H, d, J=7.8 Hz), 7.92 (2H, d, J=7.8 Hz), 7.74 (2H, d, J=7.8 Hz), 7.54 (2H, d, J=7.8 Hz), 5.24 (2H, s), 3.95 (8H, m) 3.76 (2H, t, J=7.3 Hz), 2.72 (3H, s), 2.50 (6H, s), 2.41 (6H, s), 2.17 (8H, m), 1.72 (10H, m), 1.47 (8H, m), 1.35 (14H, m), 0.89 (15H, m), −2.46 (2H, s). MS m/z 1181.

15: Yield: 30% (solvent: $CH_3CN+CH_2Cl_2$=4:3). Mp 275—278 °C. ^{1}H NMR δ=10.22 (2H, s), 8.22 (2H, s), 8.12 (2H, d, J=7.8 Hz), 7.94 (6H, m), 7.68 (2H, d, J=8.3 Hz), 7.54 (2H, d, J=7.8 Hz), 5.01 (2H, s), 3.97 (8H, m), 3.73 (2H, t), 2.72 (3H, s), 2.52 (6H, s), 2.51 (6H, s), 2.17 (8H, m), 1.72 (10H, m), 1.53 (8H, m), 1.36 (14H, m), 0.89 (15H, m), −2.43 (2H, s). MS m/z 1257.

5-(4-Methylphenyl)-15-[4-[(3,6-dioxo-4-methyl-1,4-cyclohexadienyl)methyl]phenyl]-2,8,12,18-tetrahexyl-3,7,13,17-tetramethylporphine (13). Synthesized from the diacetoxyphenyl porphyrin **12** in a similar manner as **2a**. Yield: 91%. Mp 190—193 °C. ^{1}H NMR δ=10.27 (1H, s), 8.03 (2H, d, J=7.8 Hz), 7.96 (2H, d, J=7.3 Hz), 7.57 (2H, d, J=7.8 Hz), 7.50 (2H, d, J=7.8 Hz), 6.75 (1H, s), 6.59 (1H, s), 4.02 (10H, m, benzylic and hex-1), 2.76 (3H, s), 2.55 (6H, s), 2.52 (6H, s), 2.23 (8H, m), 2.15 (3H, s), 1.78 (8H, m), 1.53 (8H, m), 1.42 (m), 0.96 (12H, m), −2.35 (2H, s). MS m/z 1006 ($[M+3H]^+$).

Procedure for Selective Metallation. The free-base diporphyrin (0.015 mmol) was dissolved in 20 ml of CH_2Cl_2, and a 30 mM solution of zinc acetate in $MeOH/CH_2Cl_2$ (0.4 ml, 0.012 mmol) was added. The mixture was stirred at room temperature for 15 min, and washed with water and dilute $NaHCO_3$ solution, dried and evaporated. The residue was separated by column chromatography ($CH_2Cl_2+Et_2O$) to four fractions, and each was checked by UV-visible, MS and ^{1}H NMR spectra (see text). The (H_2, Zn) complex was obtained in 12—33% yield. Purity was checked by TLC and ^{1}H NMR spectra.

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7) In the case of the 1,4-phenylene bridged diporphyrins, the UV-visible absorption spectra were slightly (about 3 nm) red-shifted due to the exciton interaction between the two porphyrins.

8) The photophysics of the (H_2, Zn) diporphyrins are somewhat complicated because of the singlet energy transfer from the zinc porphyrin to the free-base porphyrin. When the acceptor moiety is present, the excited state of the zinc porphyrin (which is formed by absorption of the incident light; ε(free-base) : ε(zinc)=6.3 : 1 at 507—510 nm) should be also quenched by the acceptor. Therefore, decrease of the fluorescence intensity of the free-base porphyrin can be partly attributed to the quenching of the zinc porphyrin. Analysis of the photo-steady state led to the estimation that the free-base fluorescence would be decreased through this effect by a factor of $(\varepsilon_H+k_{EN}\varepsilon_Z/(k_{EN}+k_0+k_q))/(\varepsilon_H+k_{EN}\varepsilon_Z/(k_{EN}+k_0))$, where ε_H, ε_Z are extinction coefficients of free-base and zinc porphyrins, k_{EN} is the rate of energy transfer, k_0 is the decay rate constant of the zinc porphyrin, and k_q is the rate of electron transfer from the zinc porphyrin to the acceptor. Using the values of $k_0=6.3\times10^8$ s^{-1}, $k_q=7.1\times10^{10}$ s^{-1} (for **2**), 1.3×10^{10} s^{-1} (for **3**), 8.5×10^7 s^{-1} (for **4**), and the reported values of k_{EN} (Ref. 15), the factor was estimated to be in the range of 0.89 to 1.0. The values shown in Table 1 have been compensated by these factors, thus their deviation from unity can be ascribed simply to the interaction of the free-base and the acceptor moiety.

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