Synthesis and Intramolecular Electron- and Energy-Transfer Reactions of Polyyne- or Polyene-Bridged Diporphyrins

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A series of geometrically restricted polyyne- or polyene-bridged diporphyrins **1**–**7** has been prepared by a convenient, one-pot, double porphyrin cyclization reaction in acceptable yields from the corresponding dialdehydes **1–7CHO**. Polyene-bridged diporphyrins **8** and **9** were prepared by a double Horner–Emmons–Wadsworth reaction of formyl-substituted zinc–porphyrin monomer **12** with bis-phosphonate esters **13** and **14**, respectively. The diporphyrins **1-9** were transformed into zinc–free-base and zinc–ferric hybrid diporphyrins. Photoinduced intramolecular electron transfer in the zinc–ferric hybrid diporphyrins as well as intramolecular excitation energy transfer in the zinc–free-base hybrid diporphyrins have been studied by picosecond time-resolved fluorescence spectroscopy. Rate constants through the polyene-bridges are larger than those through the polyyne-bridges in both reactions. The distance dependence of the electron-transfer rate was found to be quite small: the attenuation factors were determined to be 0.08 and 0.1 Å^{-1} for the polyene- and polyyne-bridged diporphyrins, respectively. The distance dependence of the energy-transfer rate was quite similar to that of the electron transfer and was explained better by the Dexter mechanism rather than by the Förster mechanism. These results clearly demonstrate that the linear π-conjugated polyyne and polyene spacers enhance through-bond electronic coupling between the donor and acceptor.

Introduction

There has been an increasing interest in long-range charge separations in conformationally rigid donor–spacer–acceptor systems.[2] One way to achieve such charge separation is the use of a multi-step electron-transfer strategy as seen in the natural photosynthetic reaction centers.[2–4] Multi-step electron transfer is usually designed by introducing a series of electron relay molecules between the initial donor and the ultimate acceptor. The forward electron-transfer reactions consist of a series of exothermic steps, each of which can occur quickly and with high quantum yield. Another way may be the use of "molecular wire" that can facilitate rapid electron transfer over a long distance.[5–8] Several molecular systems in which redox centers are connected by "molecular wires" such as polyenes and polyynes have indeed realized efficient, long-distance electron and energy transfers.[7,8] However, systematic investigations on the distance dependence of the electron-transfer (ET) and energy-transfer (EN) reactions over conjugated π-electronic systems are very rare and still remain an important subject.

In our early work, we first prepared polyyne-linked porphyrins in order to examine the excited-state interactions between the polyynes and porphyrin.[9] Recently, considerable attention has been paid to polyyne-substituted porphyrins from the standpoints of tuning the porphyrin electronic excited states,[10] of convenient coupling sites for making architecturally rigid structures,[11] and of electronic and photonic communication.[12] In this paper, we report a series of polyyne- or polyene-bridged diporphyrins (Chart 1) as a novel donor–spacer–acceptor system designed for a study on the distance dependence of ET and EN reactions over these π-systems.[9] Starting from these diporphyrins, we have prepared two series of zinc porphyrin (ZnP)–free base porphyrin (HP) hybrid diporphyrins and ZnP–ferric porphyrin (FeP) hybrid diporphyrins. In the former, ZnP is a singlet excitation energy donor and HP is a singlet energy acceptor, while in the latter ZnP is an electron donor and FeP is an electron acceptor. In the two sets of diporphyrins, the

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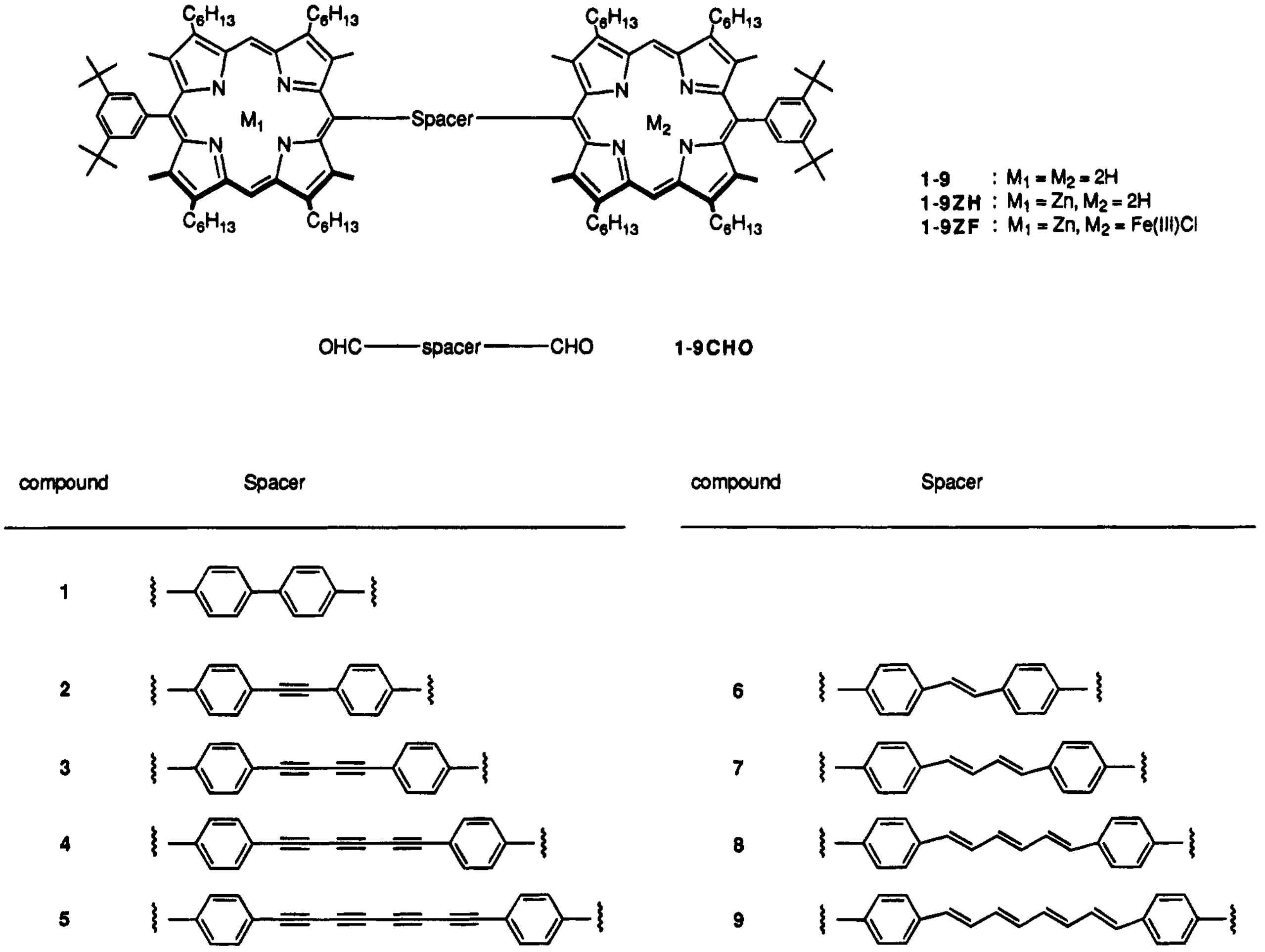
Chart 1. Structures of Polyyne- or Polyene-Bridged Diporphyrins 1–9 and Polyyne- or Polyene-Bridged Benzaldehydes 1-9CHO



rates of the ET and the EN have been determined by the picosecond time-resolved fluorescence spectroscopy. The center-to-center distances between the porphyrins are well defined in the polyyne-bridged system and are fairly precisely estimated in the polyene-bridged system. These structural features are suitable for investigation of the distance dependence of electron and energy transfers. The polyyne and polyene moieties are proposed to be highly polarizable and to work as efficient mediators for electron exchange interactions between donor and acceptor that will make possible long-distance ET and EN reactions.

Results and Discussion

Synthesis. Synthetic schemes to polyyne- and polyene-bridged diporphyrins are shown in Schemes 1 and 2.[13] A double porphyrin cyclization reaction of aldehyde **10**, dipyrrylmethane **11**, and dialdehydes **1–7CHO** was accomplished according to the method developed by Osuka,[14] where formation of polymeric byproducts was largely suppressed by using a large excess amount of terminating monoaldehyde **10**. By subsequent chromatographic purification, the desired diporphyrins were isolated as free-base forms **1–7** in acceptable yields (13–46% based on the dialdehyde used; not optimized). This one-pot synthetic procedure is very convenient and efficient compared to the method previously reported.[9b] The reaction conditions are mild enough not to affect the somewhat acid-sensitive polyyne and polyene moieties. Diporphyrins **8** and **9** were synthesized by a Horner–Emmons–Wadsworth olefination reaction.[5a,15] A double condensation reaction of formyl-substituted zinc–porphyrin monomer **12** with bis-phosphonate esters **13** and **14** followed by demetalation with HCl gave **8** and **9** in 15 and 22% yields, respectively. Free base diporphyrins **1–9** are fully characterized by 500 MHz ^{1}H-NMR spectra and high resolution FAB-mass spectra. Syntheses of the starting dialdehydes **2–5CHO** are described elsewhere,[9b,16] and the synthetic routes to **6–9CHO** are shown in Scheme 2.[5a,15]

Partial zinc metalation was done upon treatment of **1-9** with a small amount of $Zn(OAc)_2$/MeOH while the extent of the metalation was monitored by TLC. After suitable time, the metalation was stopped by addition of water and the products were separated by flash silica gel column chromatography, giving singly zinc-metalated diporphyrins (ZH diporphyrins) **1–9ZH** in 25–35% yields. By a subsequent ferric-ion insertion to **1–9ZH** with Fe-

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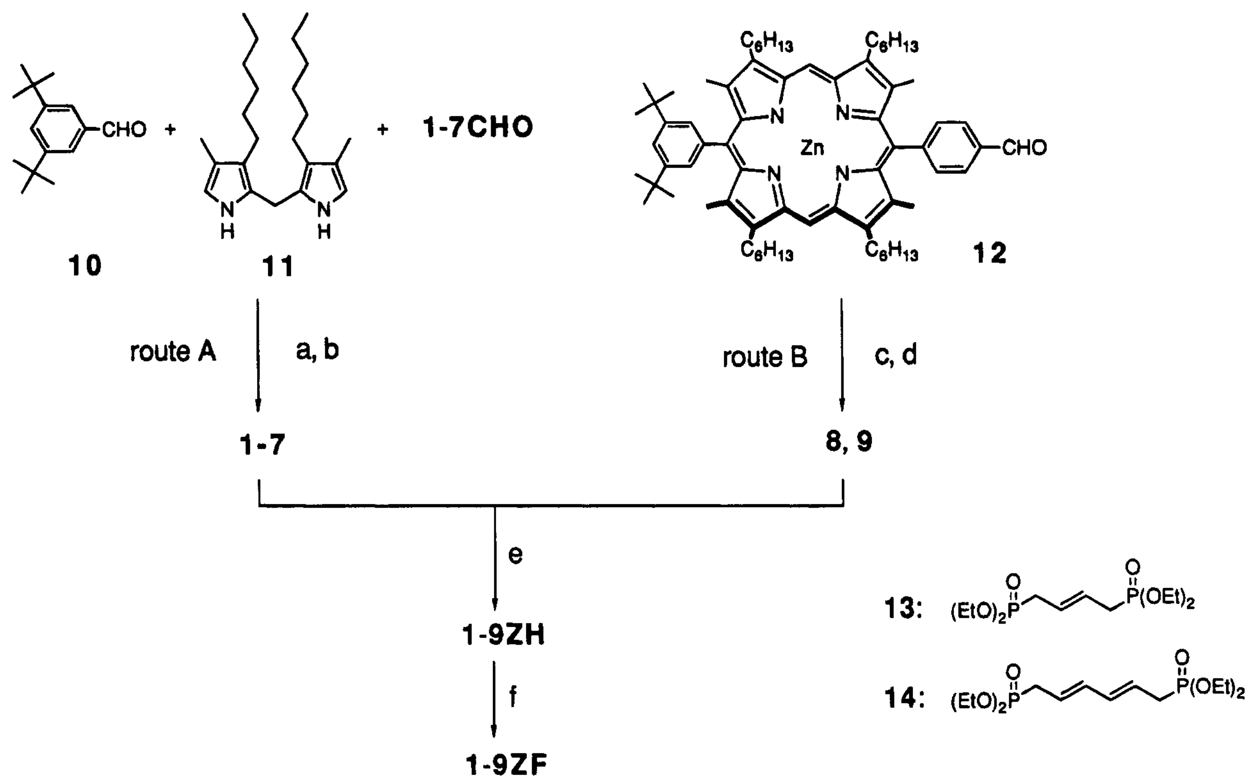
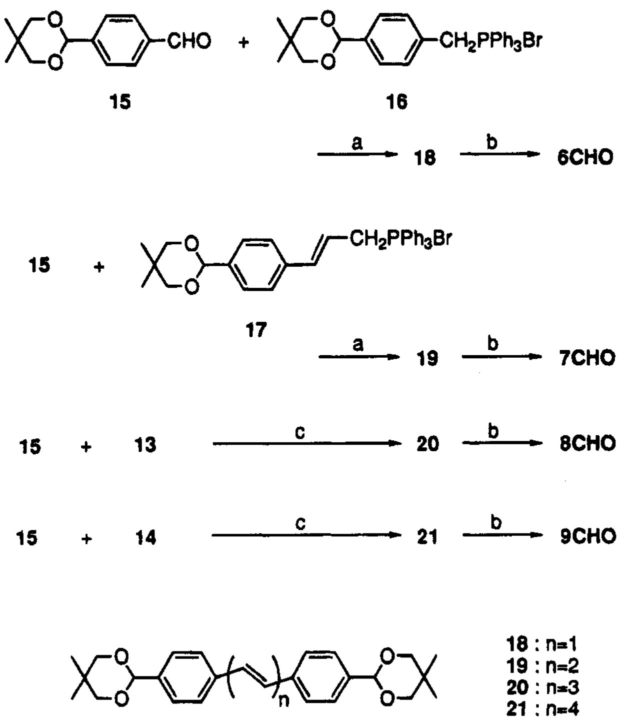
Scheme 1. Synthesis of Diporphyrins 1–9, 1–9ZH, and 1–9ZF[a]



[a] Key: (a) Trichloroacetic acid, CH_3CN/CH_2Cl_2; (b) *p*-chloranil/THF; (c) **13** or **14**, NaH, 15-crown-5, THF; (d) 2 M HCl, CH_2Cl_2; (e) $Zn(OAc)_2/MeOH$, CH_2Cl_2; (f) $Fe(CO)_5$, I_2, K_2CO_3, toluene.

Scheme 2. Synthesis of Polyene-Bridged Dialdehydes 6-9CHO[a]



[a] Key: (a) *n*-BuLi, THF; (b) TFA, H_2O, CH_2Cl_2; (c) NaH, 15-crown-5, THF.

$(CO)_5$ and I_2 in toluene, zinc–ferric hybrid diporphyrins (ZF diporphyrins) **1–9ZF** were prepared in 50–60% yields.

Optical Properties. Figure 1 shows the absorption spectra of **1–9ZH** in THF along with a reference spec-

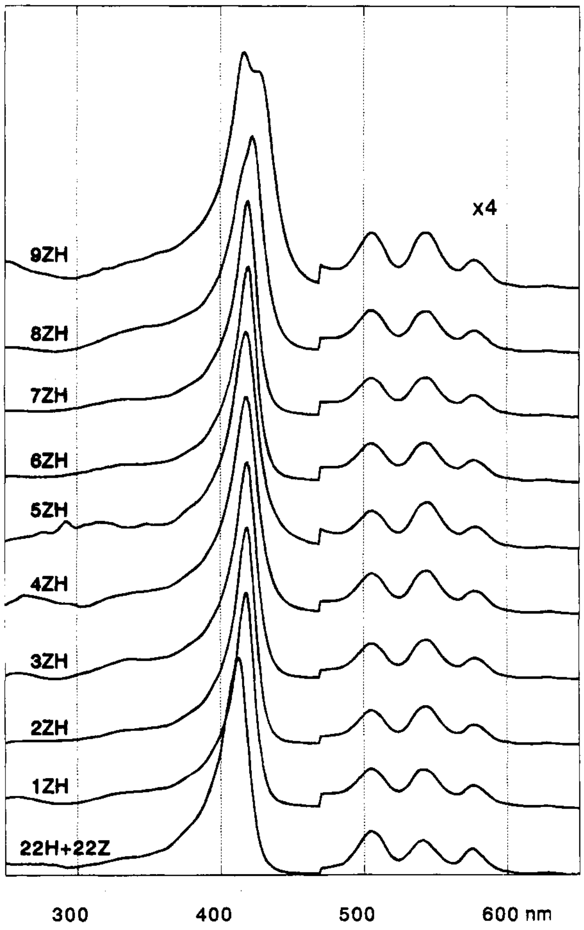


Figure 1. UV–vis absorption spectra of ZH diporphyrins in THF.

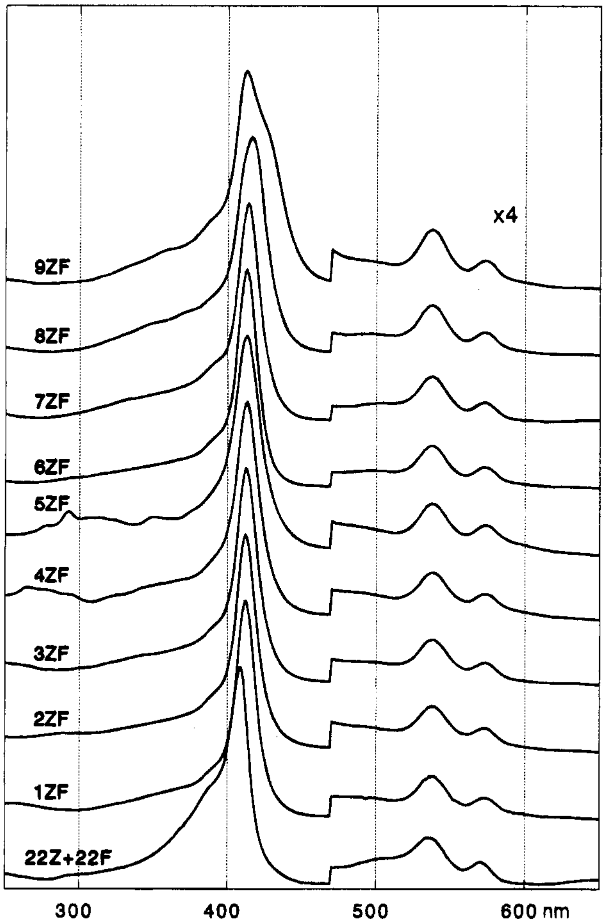
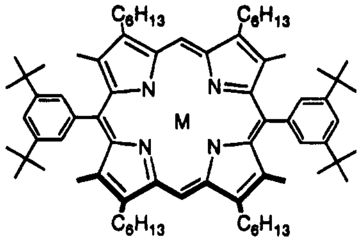


Figure 2. UV–vis absorption spectra of ZF diporphyrins in CH_2Cl_2.

Chart 2. Reference Porphyrin Monomers



22H : M = 2H
22Z : M = Zn
22F : M = Fe(III)Cl

trum of a 1:1 mixture of **22Z**[14a] and **22H** and Figure 2 shows the absorption spectra of **1–9ZF** in CH_2Cl_2 along with a reference spectrum of 1:1 mixture of **22Z** and **22F** (Chart 2). The absorption spectra of **1–9CHO** are also shown in Figure 3. The ZF diporphyrins were found to be extremely unstable under exposure to light in THF solutions; the absorbance decreased significantly within several minutes. Thus, the optical properties of the ZF diporphyrins were studied in CH_2Cl_2 solution. In the Q-band region, the absorption spectral shape is almost a simple sum of the reference spectra. The absorbances due to the spacer moiety become more visible in the Soret-band region for the diporphyrins having longer unsaturated bridges such as **9ZH** and **9ZF**.

In the fluorescence spectra (not shown), only the emission from the zinc porphyrin was observed for the ZF diporphyrins, while the emissions from both the zinc porphyrin and the free-base porphyrin were observed for the ZH diporphyrins. In the both cases, the fluorescence intensities of the zinc porphyrin at 580 and 630 nm are reduced, indicating the intramolecular quenching. In the case of the ZH series, the reduction is accompanied by an increase in the fluorescence intensity of the free-base subunit, in line with the intramolecular singlet–singlet energy transfer from the zinc porphyrin to the free-base porphyrin.

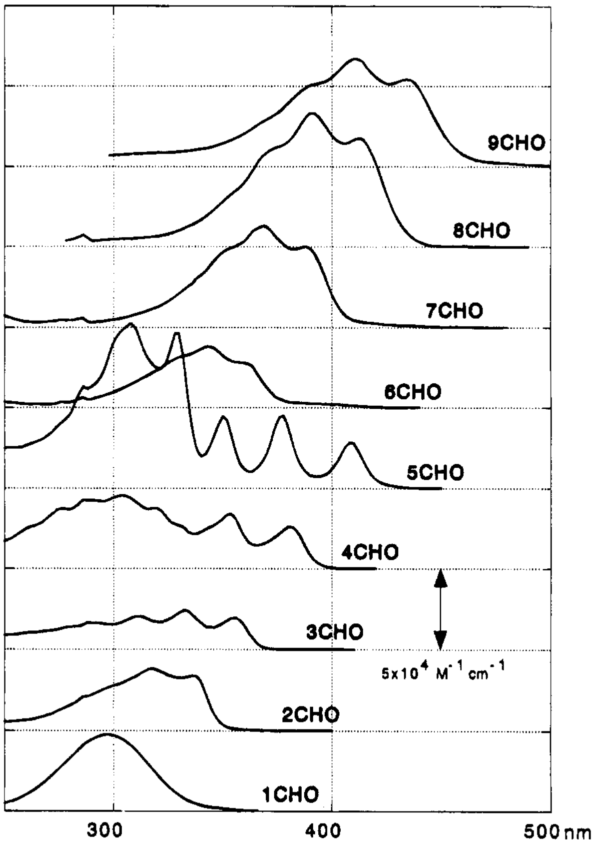


Figure 3. UV–vis absorption spectra of dialdehydes in THF.

Table 1. Estimated DA Distances (Center-to-Center) in Å on the Basis of CPK Models

compd	rotamers[a]	DA distances		
1		16.8		
2		19.4		
3		21.9		
4		24.5		
5		27.0		
6	1	19.4 (1)[b]		
7	2	22.2 (1)	21.7 (1)	
8	4	24.2 (1)	23.8 (3)	
9	8	26.6 (1)	26.2 (4)	26.1 (3)

[a] The number of possible rotamers. [b] The numbers in parentheses indicate the number of the related rotamers. The values for "*all s-trans*" conformer are indicated on the left.

Structure Considerations. At this point it may be appropriate to consider the molecular structures of these diporphyrin models. For the polyyne moiety, the molecular length is linear to the number of carbon–carbon triple bonds, and the donor-to-acceptor (DA) distance is well-defined for the series. For the polyene moiety, the rotation around a single bond can lead to variations in the DA distance. Listed in Table 1 are the DA distances estimated on the basis of CPK models for these rotational conformations of the polyene-bridged diporphyrins. In Figure 4 is presented a typical three double-bond case that corresponds to **8**. It can be seen that the influence

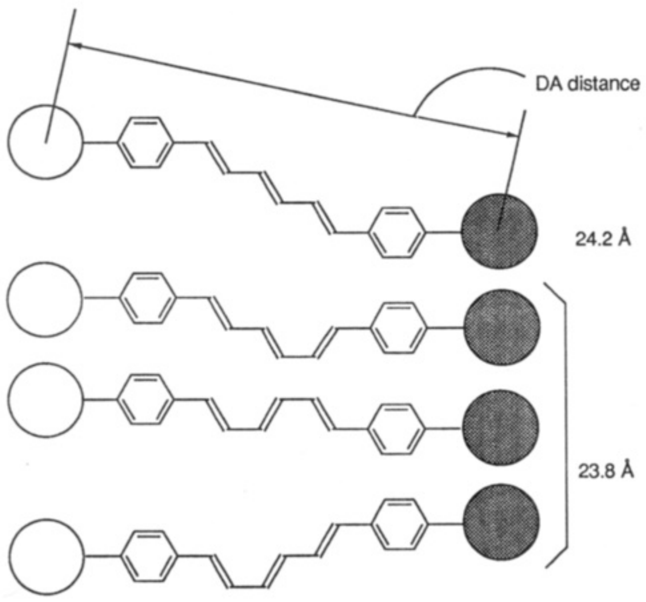


Figure 4. Possible rotamers in the three double-bond case. Open and filled circles represent respective porphyrin rings.

of these rotational conformers on the DA distance is rather small. Moreover, polyene systems have long been the subject of intensive studies in relation to their important roles in photobiology such as photosynthesis and vision,[18] and the previous theoretical studies suggested that the hypothetical s-*cis* conformer is higher in energy by 9.6–10.5 kJ/mol than the most stable s-*trans* conformer and the rotational barrier height amounts to 21–29 kJ/mol.[19,20] These results lead to a prediction that the majority of molecules are in their *all*-s-*trans* conformations at room temperature. Accordingly, we used the DA distance of *all-s-trans* conformer for analysis of electron and energy transfer reactions.

Estimation of Electron- and Energy-Transfer Rate Constants. Observed decreases in the fluorescence intensity of the ZnP in the ZF and ZH series can be considered as arising from the intramolecular ET and EN reactions by referring to the related systems, respectively.[21,22] Shown in Scheme 3a,b is simplified reaction schemes for the ZF diporphyrin and the ZH diporphyrin, respectively. For the singlet excited state of the acceptor-free ZnP, two representative decaying pathways with rate constants k_F and k_{NF} are considered. Specified by k_F is a rate of radiative decay by fluorescence emission. Other nonfluorescent decaying pathways, including intersystem crossing to the triplet state, non radiative decay to the ground state and so on, are treated as one imaginary path having a rate constant of k_{NF}. Under our dilute conditions (*ca.* 10^{-6} M), the intermolecular quenching can be neglected. Once an "acceptor" is attached to the donor ZnP, an additional decaying pathway is available for its singlet excited state. This new path is the intramolecular electron transfer in the ZF diporphyrin with a rate constant of k_{ET} and the intramolecular singlet energy transfer in the ZH diporphyrins with a rate constant of k_{EN}.

Table 2. Fluorescence Lifetimes τ (ps) and Intramolecular Rate Constants, k_{ET} (s^{-1}) for ZF Diporphyrins and k_{EN} (s^{-1}) for ZH Diporphyrins

	ZF forms		**ZH** forms	
parent	τ	$k_{ET}/10^9$	τ	$k_{EN}/10^9$
1	42.0	24	172	5.8
2	90.0	11	326	3.1
3	129	7.8	438	2.3
4	185	5.4	511	2.0
5	198	5.1	525	1.9
6	60	17	247	4.1
7	73	14	310	3.2
8	106	9.4	402	2.5
9	101	9.9	472	2.1

According to these reaction schemes, k_{ET} and k_{EN} values can be calculated by eqs 1 and 2, where τ(ZF), τ(ZH), and τ(Z) are the fluorescence lifetimes of the ^{1}(ZnP)* in ZF diporphyrins, those in ZH diporphyrins, and that of **22** (1.5 ns), respectively. Table 2 summarizes the fluorescence lifetimes and the estimated value of k_{ET} and k_{EN} rate constants.

$$k_{ET} = 1/\tau(\mathrm{ZF}) - 1/\tau(\mathrm{Z}) \qquad (1)$$

$$k_{EN} = 1/\tau(\mathrm{ZH}) - 1/\tau(\mathrm{Z}) \qquad (2)$$

In order to confirm the intramolecular electron transfer in the ZF diporphyrins, the transient absorption spectra have been measured in CH_2Cl_2 (supporting information). Although the decay times of the $S_1 \rightarrow S_n$ absorption of the zinc porphyrin parallel the fluorescence lifetimes, we could not detect the charge separated states clearly. Failure of the detection of the charge separated states may be ascribed to efficient charge recombination of such states to the ground states.

Electron-Transfer Rate Constants (k_{ET}). The magnitude of k_{ET} as 10^{10} s^{-1} found for **1ZF** is in line with the previous data.[21] Other notable facts are that (1) the rate constants are still larger than 10^9 s^{-1} in **5ZF** and **9ZF**, in which the center-to-center DA separations are 27 and 26.6 Å, respectively, providing a firm experimental confirmation for efficient long-distance ET over the linear π-conjugated systems, and (2) the electron transfer is ca. 2 times more efficient in the polyene-bridged diporphyrin than the corresponding polyyne-bridged diporphyrin.

It is widely accepted that the ET rate constant is dependent upon the DA distance in the weak-coupling limit since the electronic coupling term depends exponentially on the DA distance. A frequently used formula is eq 3 or 4 where R is the DA distance, A' and A are

$$k_{ET} = A' \exp(-\beta R) \qquad (3)$$

$$\ln k_{ET} = A - \beta R \qquad (4)$$

pre-exponential factors, and β is an attenuation factor related to the distance dependence. The β values reported are 0.4 Å^{-1} for aromatic hydrocarbon frameworks[21]

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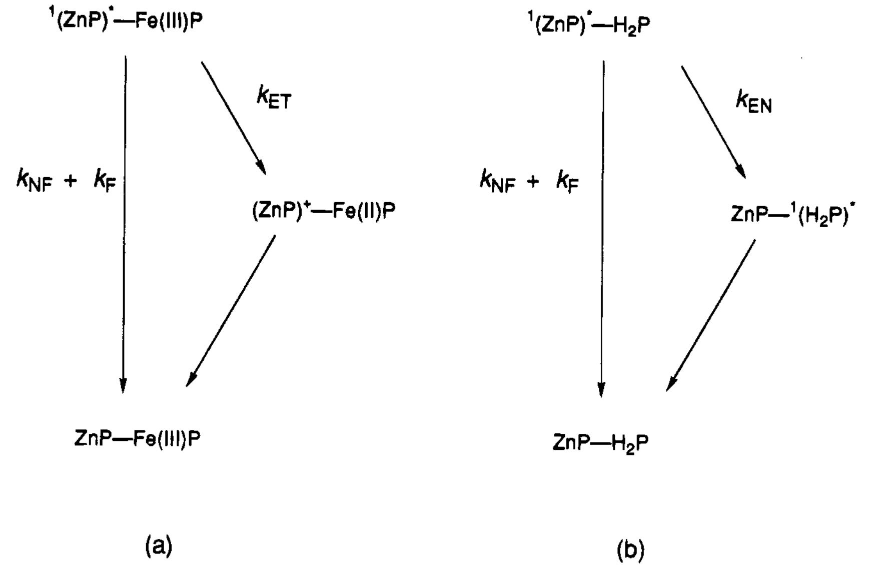
Scheme 3. Reaction Schemes for ZF (a) and ZH (b) Diporphyrins



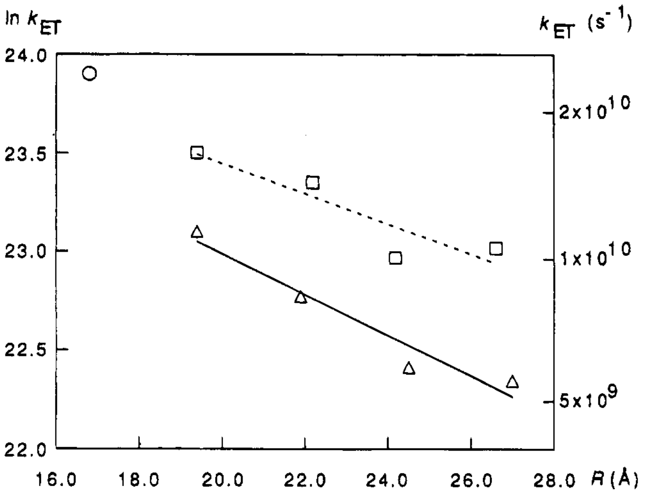


Figure 5. Semilogarithmic plot of obtained k_{ET} values versus DA distances: △ and solid line for **2-5ZF**, □ and dashed line for **6-9ZF**, and ○ for **1ZF**. The lines are theoretical best-fits to the experimental data.

and 0.8–1.0 Å^{-1} for saturated hydrocarbon backbones.[23] A semilogarithmic plot of the obtained k_{ET} values versus DA distance according to eq 4 is shown in Figure 5.

A good linearity is seen in both the series. This may indicate the validity of eqs 3 and 4. The calculated β values by linear fitting with the least-squares method are 0.08 and 0.1 Å^{-1} for the polyene and polyyne series, respectively. Quite similar β-values were obtained for the polyene and polyyne series, and these are much smaller than the value of 0.4 Å^{-1} reported for the aromatic spacers. Apparently, the electronic coupling between the donor and acceptor is efficiently mediated through these conjugated spacers.

The detailed mechanisms, i.e., why the electron transfer is ca. 2 times more efficient in the polyene-bridged diporphyrin than the corresponding polyyne-bridged one are now under investigation. One possible mechanism may be that the polyene moieties in the diporphyrins have lower S_1-energies in comparison to the corresponding polyyne moieties as seen in the absorption spectra of the ZF diporphyrins (Figure 2) and can work as a better mediator for electronic coupling of the donor and acceptor via superexchange interaction.[26] The decline in the through-space coupling upon elongation of unsaturated spacer may be offset partially by an extension of the spacer π-electronic system which leads to the decrease of the lowest excitation energy as well as the decrease of the one-electron oxidation and reduction potentials.

Energy-Transfer Rate Constants. The EN from the singlet excited state of the zinc porphyrin to the free-base porphyrin has been found to remain remarkably efficient even for the ZH diporphyrins having a large DA distance (Table 2).

As for the energy transfer reactions, two major mechanisms have been identified, *i.e.*, the Förster mechanism[24] and the Dexter mechanism.[25] The former operates via Coulombic interaction between transition dipole moments and therefore requires no direct contact between the energy donor and acceptor. The distance dependence of rate constant is formulated as in eq 5

$$\ln k_{EN} = A = 6 \ln R \qquad (5)$$

On the other hand, the Dexter mechanism depends on electron exchange, and the distance dependence is written as eq 6 where L is related to the average effective

$$\ln k_{EN} = A' - R/L \qquad (6)$$

Bohr radius. In general, the Dexter mechanism would operate only when the DA separation is sufficiently short, assuring significant electronic interactions between the energy donor and acceptor.

Equations 5 and 6 predict the different distance dependence of the energy-transfer rate. In other words, the distance dependence of the energy-transfer rate could be a good test for identification of the energy-transfer mechanism. Accordingly, the obtained k_{EN} values are plotted in a logarithmic or semilogarithmic manner against the DA distances in Figure 6. The experimental

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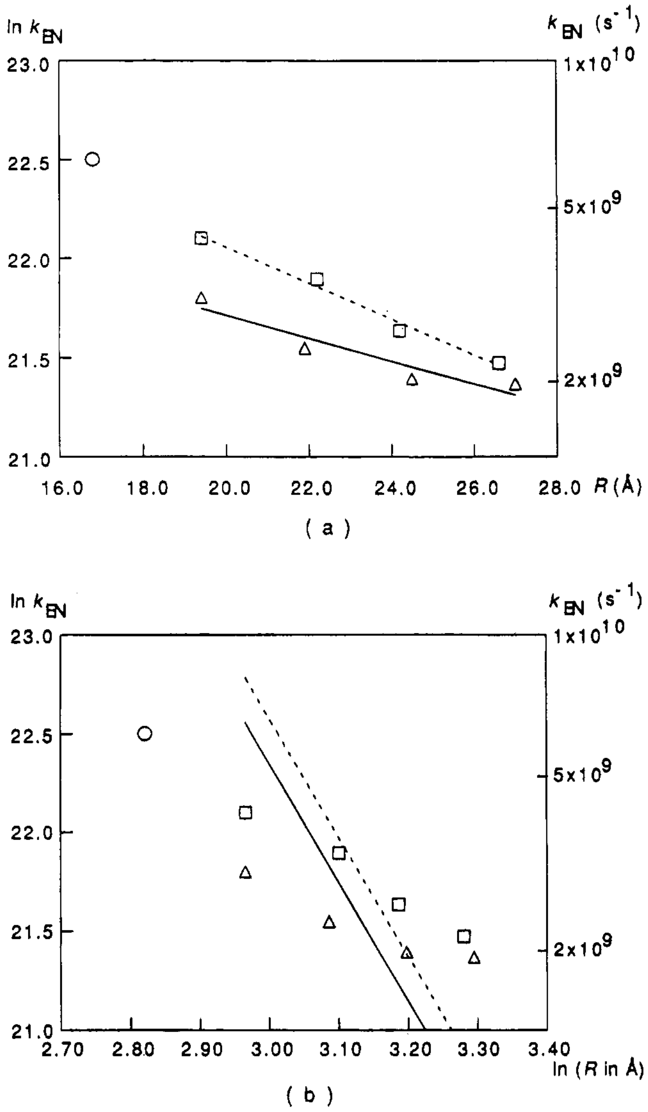

Figure 6. (a) Semilogarithmic (Dexter mechanism) and (b) logarithmic (Förster mechanism) plots of k_{EN} against measured DA distances: △ and solid line for **2-5ZF**, □ and dashed line for **6-9ZF**, and ○ for **1ZF**. The lines are theoretical best-fits to the experimental data.

results are well fitted to the Dexter mechanism in Figure 6a. With the Förster mechanism such an agreement is not achieved at all (Figure 6b). For the Dexter mechanism, the acceptable value of 11 and 17 Å has been obtained for L in the polyene and polyyne series, respectively. Thus, the Förster mechanism seems to be less appropriate in the singlet energy transfer in the ZH diporphyrins, which is consistent with the fact that electron–electron exchange interaction between the donor and the acceptor is mediated by the highly polarizable π-conjugated systems.

In summary, the polyyne- and polyene-bridged diporphyrins were synthesized by a one-pot, double cyclization reaction or by a double Horner–Emmons–Wadsworth olefination reaction. The distance dependencies of the electron transfer rate constants over polyyne and polyene were found to be quite similar and remarkably small. The distance dependencies of the energy transfer rate constants were also very small and quite similar to those found for the electron transfer, suggesting the applicability of the Dexter mechanism. The distance dependencies determined here will be very useful for future design of donor–acceptor systems bridged by these or even longer polyyne and polyene spacers.

Experimental Section

General. All general experimental procedures were as described previously.[27] Synthesis of zinc porphyrin monomer **12** will be described elsewhere.[31]

4,4′-Bis[15-(3,5-di-*tert*-butylphenyl)-2,8,12,18-tetrahexyl-3,7,13,17-tetramethyl-5-porphinyl]biphenyl (1). To a solution of 3,5-di-*tert*-butylbenz-aldehyde (**10**)[28] (0.8 mmol), 4,4′-diformylbiphenyl (**1CHO**) (0.1 mmol), and dipyrrylmethane **11**[29] (1.0 mmol) in a mixture of CH_3CN (5.5 mL) and CH_2Cl_2 (2.5 mL) was added trichloroacetic acid (0.3 mmol) dissolved in CH_3CN (2 mL). When the solubility of dialdehyde was not enough, the content of CH_2Cl_2 could be increased up to that of CH_3CN. After being stirred for 1 day under N_2 in the dark at rt, *p*-chloranil (1.6 mmol) dissolved in THF (20 mL) was added, and the mixture was stirred further for 1 day. After evaporation of the solvent, the residue was redissolved in a small amount of $CHCl_3$ and the solution was passed through a short activated alumina column (Wako, 200 mesh). The porphyrin product was purified by chromatography on silica gel (Merck, Kieselgel 7736; CH_2Cl_2/hexane to CH_2Cl_2 eluent) and was subsequently recrystallized from $CHCl_3$/MeOH to give 25–45 μmol (25–45% based on the amount of **1CHO** used) of **1** as violet crystals. ^{1}H-NMR: δ 10.29 (s, 4H), 8.35 (d, J = 8.0 Hz, 4H), 8.32 (d, J = 8.0 Hz, 4H), 7.95 (d, J = 2.0 Hz, 4H), 7.82 (t, J = 2.0 Hz, 2H), 4.02–4.10 (m, 16H), 2.75 (s, 12H), 2.49 (s, 12H), 2.20–2.29 (m, 16H), 1.74–1.82 (m, 16H), 1.53 (s, 36H), 1.47–1.55 (m, 16H), 1.35-1.46 (m, 16H), 0.93 (t, J = 7.3 Hz, 12H), 0.92 (t, J = 7.3 Hz, 12H), −2.32 (br, 4H). HRMS: found 1932.45(4), calcd 1932.4879 for $C_{136}H_{186}N_8$ + H.

Monozinc Complex of the Porphyrin Dimer (1ZH). To a solution of **1** (20 mg) in CH_2Cl_2 (10 mL) was added few drops of a saturated MeOH solution of $Zn(OAc)_2$. After a while, the solution was washed with water, dried with anhydrous Na_2SO_4, and concentrated *in vacuo*. Chromatography on silica gel (Merck, Kieselgel 7736; CH_2Cl_2/hexane to CH_2Cl_2 eluent) followed by recrystallization from $CHCl_3$/MeOH gave **1ZH** as sparkling violet crystals. Yield: 20–35%. MS: found 1995, calcd 1995 for $C_{136}H_{184}N_8Zn$.

Zinc–Ferric Hybrid Complex of the Porphyrin Dimer (1ZF). To a solution of **1ZH** (6 mg) in toluene (6 mL) was added anhydrous K_2CO_3 (200 mg), I_2 (45 mg) and $Fe(CO)_5$/toluene (30 μL in 1 mL). After vigorous stirring for 1 day in the air, the resulting solution was washed thoroughly with water followed by with brine and was dried with oven-dried NaCl. The chromatographic purification with $CHCl_3$ as an eluent followed by recrystallization led to **1ZF**. Yield was 30–40%. MS: found 2049, calcd 2049 for $C_{136}H_{182}N_8ZnFe$.

Acetylene-Bridged Dimer 2. The synthetic procedure was the same as for **1** except for dialdehyde. Isolated yield 26%. ^{1}H-NMR: δ 10.27 (s, 4H), 8.20 (d, J = 7.8 Hz, 4H), 8.11 (d, J = 7.8 Hz, 4H), 7.93 (d, J = 1.5 Hz, 4H),7.82 (t, J = 1.5 Hz, 2H), 3.98–4.08 (m, 16H), 2.64 (s, 12H), 2.48 (s, 12H), 2.17–2.27 (m, 16H), 1.74–1.82 (m, 16H), 1.52 (s, 36H), 1.46–1.58 (m, 16H), 1.33-1.43 (m, 16H), 0.93 (t, J = 7.3 Hz, 12H), 0.92 (t, J = 7.3 Hz, 12H), −2.36 (br, 4H). HRMS: found 1956.43(2), calcd 1956.4879 for $C_{138}H_{186}N_8$ + H. MS: (**ZH**) found 2019, calcd 2019 for $C_{138}H_{184}N_8Zn$; (**ZF**) found 2073, calcd 2073 for $C_{138}H_{182}N_8ZnFe$.

Butadiyne-Bridged Dimer 3. The synthetic procedure was the same as for **1** except for dialdehyde. Isolated yield: 28%. ^{1}H-NMR: δ 10.26 (s, 4H), 8.15 (d, J = 7.8 Hz, 4H), 8.02 (d, J = 7.8 Hz, 4H), 7.93 (d, J = 1.6 Hz, 4H),7.81 (t, J = 1.6 Hz, 2H), 3.98–4.04 (m, 16H), 2.58 (s, 12H), 2.47 (s, 12H), 2.17–2.25 (m, 16H), 1.72–1.79 (m, 16H), 1.51 (s, 36H), 1.45–1.53 (m, 16H), 1.33-1.43 (m, 16H), 0.92 (t, J = 7.1 Hz, 12H), 0.91

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(t, J = 7.2 Hz, 12H), −2.39 (br, 4H). HRMS: found 1980.44(1), calcd 1980.4879 for $C_{140}H_{186}N_8$ + H. MS: (**ZH**) found 2043, calcd 2043 for $C_{140}H_{184}N_8Zn$; (**ZF**) found 2097, calcd 2097 for $C_{140}H_{182}N_8ZnFe$.

Hexatriyne-Bridged Dimer 4. The synthetic procedure was the same as for **1** except for dialdehyde. Isolated yield: 30%. ^{1}H-NMR: δ 10.25 (s, 4H), 8.10 (d, J = 8.0 Hz, 4H), 7.97 (d, J = 8.0 Hz, 4H), 7.93 (d, J = 1.8 Hz, 4H),7.81 (t, J = 1.8 Hz, 2H), 3.96−4.02 (m, 16H), 2.52 (s, 12H), 2.47 (s, 12H), 2.16−2.24 (m, 16H), 1.71−1.78 (m, 16H), 1.51 (s, 36H), 1.45−1.52 (m, 16H), 1.34-1.40 (m, 16H), 0.92 (t, J = 7.3 Hz, 12H), 0.91 (t, J = 7.3 Hz, 12H), −2.39 (br, 4H). HRMS: found 2004.49(3), calcd 2004.4879 for $C_{142}H_{186}N_8$ + H. MS: (**ZH**) found 2067, calcd 2067 for $C_{142}H_{184}N_8Zn$; (**ZF**) found 2121, calcd 2121 for $C_{142}H_{182}N_8ZnFe$.

Octatetrayne-Bridged Dimer 5. The synthetic procedure was the same as for **1** except for dialdehyde. Isolated yield: 46%. ^{1}H-NMR: δ 10.24 (s, 4H), 8.11 (d, J = 7.8 Hz, 4H), 7.96 (d, J = 7.8 Hz, 4H), 7.92 (d, J = 1.5 Hz, 4H), 7.81 (t, J = 1.5 Hz, 2H), 3.95−4.03 (m, 16H), 2.51 (s, 12H), 2.46 (s, 12H), 2.05−2.25 (m, 16H), 1.70−1.78 (m, 16H), 1.51 (s, 36H), 1.43−1.53 (m, 16H), 1.35-1.42 (m, 16H), 0.91 (t, J = 7.3 Hz, 24H), −2.39 (br, 2H), −2.42 (br, 2H). HRMS: found 2028.52(3), calcd 2028.4879 for $C_{144}H_{186}N_8$ + H. MS: (**ZH**) found 2091, calcd 2091 for $C_{144}H_{184}N_8Zn$; (**ZF**) found 2145, calcd 2145 for $C_{144}H_{182}N_8ZnFe$.

Ethylene-Bridged Dimer 6. The synthetic procedure was the same as for **1** except for dialdehyde. Isolated yield: 10%. ^{1}H-NMR: 10.27 (s, 4H), 8.19 (d, J = 7.6 Hz, 4H), 8.10 (d, J = 7.6 Hz, 4H), 7.93 (d, J = 1.7 Hz, 4H), 7.83 (s, 2H), 7.81 (t, J = 1.7 Hz, 2H), 4.06−3.99 (m, 16H), 2.66 (s, 12H), 2.48 (s, 12H), 2.26−2.19 (m, 16H), 1.81−1.73 (m, 16H), 1.59−1.47 (m, 32H), 1.52 (s, 36H), 1.43−1.35 (m, 16H), 0.93 (t, J = 7.1 Hz, 12H), 0.92 (t, J = 7.3 Hz, 12H), −2.35 (br, 4H). HRMS: found 1958.53(1), calcd 1958.5035 for $C_{138}H_{188}N_8$+H. MS: (**ZH**) found 2022, calcd 2021 for $C_{138}H_{186}N_8Zn$; (**ZF**) found 2075, calcd 2075 for $C_{138}H_{184}N_8ZnFe$.

Butadiene-Bridged Dimer 7. The synthetic procedure was the same as for **1** except for dialdehyde. Isolated yield was 13%. ^{1}H-NMR: δ 10.26 (s, 4H), 8.11 (d, J = 7.6 Hz, 4H), 7.94 (d, J = 7.6 Hz, 4H), 7.93 (d, J = 1.9 Hz, 4H), 7.81 (t, J = 1.9 Hz, 2H), 7.49 (d, J = 14.9 Hz, 2H), 7.18 (d, J = 14.9 Hz, 2H), 4.04−3.98 (m, 16H), 2.63 (s, 12H), 2.47 (s, 12H), 2.24−2.18 (m, 16H), 1.79−1.72 (m, 16H), 1.57−1.47 (m, 32H), 1.51 (s, 36H), 1.42−1.34 (m, 16H), 0.92 (t, J = 7.3 Hz, 12H), 0.91 (t, J = 7.4 Hz, 12H), −2.36 (br, 4H). HRMS: found 1984.55(2), calcd 1984.5192 for $C_{140}H_{190}N_8$ + H. MS: (**ZH**) found 2048, calcd 2047 for $C_{140}H_{188}N_8Zn$; (**ZF**) found 2101, calcd 2101 for $C_{140}H_{186}N_8ZnFe$.

Hexatriene-Bridged Dimer 8. To a solution of 5-(3,5-di-*tert*-butylphenyl)-15-(4-formylphenyl)-2,8,12,18-tetrahexyl-3,7,-13,17-tetramethylporphinatozinc(II) **12** (0.24 mmol), tetraethyl (2*E*)-butene-1,4-diphosphonate (**13**)[15] (0.12 mmol), and a small amount of 15-crown-5 in THF (100 mL) was added NaH (1.5 equiv). The mixture was stirred for 2 h at room temperature and then refluxed for 3 h and stirred overnight again at room temperature. Water was added, and the products were extracted with CH_2Cl_2. The desired porphyrin dimer **8ZZ** (bis-zinc form) was obtained in 15% yield after purification with chromatography on silica gel (benzene eluent) followed by recrystallization. **8ZZ** was stirred in CH_2Cl_2 solution with 2 M HCl for 5 min and then was washed with water, dried with anhydrous Na_2SO_4, evaporated, and recrystallized to finally give **8** in quantitative yield. ^{1}H-NMR: δ 10.25 (s, 4H), 8.07 (d, J = 7.9 Hz, 4H), 7.92 (d, J = 1.8 Hz, 4H), 7.87 (d, J = 7.9 Hz, 4H), 7.81 (t, J = 1.9 Hz, 2H), 7.34 (ddd, J = 3.0, 6.8 and 15.0 Hz, 2H), 7.05 (d, J = 15.0 Hz, 2H), 6.88 (dd, J = 3.0 and 6.8 Hz, 2H), 4.02−3.96 (m, 16H), 2.60 (s, 12H), 2.47 (s, 12H), 2.24−2.17 (m, 16H), 1.78−1.71 (m, 16H), 1.51 (s, 36H), 1.50−1.45 (m, 32H), 1.41−1.34 (m, 16H), 0.92 (t, J = 7.3 Hz, 12H), 0.91 (t, J = 7.3 Hz, 12H), −2.36 (br, 4H). HRMS: found 2010.52(3), calcd 2010.5348 for $C_{142}H_{192}N_8$+H. MS: (**ZH**) found 2074, calcd 2073 for $C_{142}H_{190}N_8Zn$; (**ZF**) found 2127, calcd 2127 for $C_{142}H_{188}N_8ZnFe$.

Octatetraene-Bridged Dimer 9. This was synthesized by the same methods as **8** using tetraethyl hexa-2(*E*),4(*E*)-diene-1,6-diphosphonate (**14**)[15] instead of **13**. Yield of the double condensation: 22% . ^{1}H-NMR: δ 10.24 (s, 4H), 8.06 (d, J = 8.0 Hz, 4H), 7.92 (d, J = 1.8 Hz, 4H), 7.84 (d, J = 7.9 Hz, 4H), 7.81 (t, J = 1.8 Hz, 2H), 7.00 (d, J = 6.1 Hz, 2H), 6.73 (m, 4H), 4.02−3.97 (m, 16H), 2.58 (s, 12H), 2.46 (s, 12H), 2.23−2.17 (m, 16H), 1.77−1.71 (m, 16H), 1.51 (s, 36H), 1.50−1.46 (m, 32H), 1.41−1.34 (m, 16H), 0.91 (t, J = 7.3 Hz, 24H), −2.38 (br, 4H). HRMS: found 2036.56(3), calcd 2036.5505 for $C_{144}H_{194}N_8$+H. MS: (**ZH**) found 2100, calcd 2099 for $C_{144}H_{192}N_8Zn$; (**ZF**) found 2153, calcd 2153 for $C_{144}H_{190}N_8ZnFe$.

1,2-Bis[4-(4,4-dimethyl-2,6-dioxan-1-yl)phenyl]-(*E*)-ethene (18). To a solution of [4-(4,4-dimethyl-2,6-dioxan-1-yl)benzyl]triphenylphosphonium bromide (**16**: 5.47 g, 10 mmol) in THF (40 mL) was added *n*-BuLi in hexane (1.6 M solution, 1.1 equiv), and the mixture was stirred for 30 min at 0 °C. Then 4-(4,4-dimethyl-2,6-dioxan-1-yl)benzaldehyde (**15**; 2.20 g, 10 mmol) in THF (10 mL) was added, and the mixture was stirred for 4 days at room temperature. Water was added, and following extraction with benzene and recrystallization from CH_2Cl_2/hexane a *cis-trans* mixture was obtained in 61% yield as pale yellow crystals. This was used in the following step of deprotection without further separations. Mp: 175−176 °C. ^{1}H-NMR (*trans* isomer): δ 7.52 (d, J = 8.30 Hz, 4H), 7.49 (d, J = 8.30 Hz, 4H), 7.10 (s, 2H), 5.39 (s, 2H), 3.78 (d, J = 11.2 Hz, 4H), 3.66 (d, J = 10.3 Hz, 4H), 1.30 (s, 6H), 0.81 (s, 6H): IR (KBr) 2951 (s), 2868 (m), 1472 (m), 1385 (s), 1103 (s), 1020 (s), 994 (m), and 831 (m) cm^{-1}. HRMS: found 408.2314, calcd 408.2301 for $C_{26}H_{32}O_4$. Anal. Calcd for $C_{26}H_{32}O_4$: C, 76.44; H, 7.89. Found: C, 76.49; H, 7.85.

1,2-Bis-(4-formylphenyl)-(*E*)-ethene (6CHO). A solution of **18** (2.0 g, 5 mmol) in CH_2Cl_2 (100 mL) was stirred overnight with 50% TFA (100 mL) at 0 °C. The solution was washed with saturated $NaHCO_3$ solution and evaporated. Product was recrystallized from CH_2Cl_2/hexane. **6CHO** was preferentially precipitated from the reaction mixture as yellow crystals. Yield: 12% (*cis* isomer was 54%). Mp: 170 °C. ^{1}H-NMR: δ 10.02 (s, 2H), 7.91 (d, J = 8.3 Hz, 4H), 7.70 (d, J = 7.8 Hz, 4H), 7.30 (s, 2H). IR (KBr) 1694 (vs), 1603 (s), 1570 (m), 1210 (s), 1165 (s), 824 (s), 789 (s), and 527 (s) cm^{-1}. HRMS: found 236.0844, calcd 236.0837 for $C_{16}H_{12}O_2$. Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.38. Found: C, 81.26; H, 5.42.

1,4-Bis[4-(4,4-dimethyl-2,6-dioxan-1-yl)phenyl]buta-1(*E*),3(*E*)-diene (19). To a solution of [4-(4,4-dimethyl-2,6-dioxan-1-yl)cinnamyl]triphenylphosphonium bromide (**17**) (5.73 g, 10 mmol) in THF (40 mL) was added *n*-BuLi in hexane (1.6 M solution, 1.1 equiv), and the mixture was stirred for 30 min at 0 °C. Then **15** (1.80 g, 10 mmol) in THF (10 mL) was added, and the mixture was stirred for 4 days at room temperature. Water was added, and the mixture was extracted with benzene. The product was purified by chromatography on silica gel (5% AcOEt/benzene eluent). The second fraction is all-*trans* isomer **19**. The first fraction (*cis*−*trans* mixture) was dissolved in benzene (100 mL), and a trace amount of I_2 was added.[30] The resulting solution was refluxed for 3 h, evaporated, and recrystallized from CH_2Cl_2/hexane to provide **19** as pale yellow crystals. A combined yield was 81%. Mp: 248 °C. ^{1}H-NMR: δ 7.47 (d, J = 8.3 Hz, 4H), 7.44 (d, J = 8.8 Hz, 4H), 6.95 (d, J = 14.7 Hz, 2H), 6.67 (d, J = 14.7 Hz, 2H), 5.39 (s, 2H), 3.78 (d, J = 10.7 Hz, 4H), 3.65 (d, J = 10.7 Hz, 4H), 1.30 (s, 6H), 0.81 (s, 6H). IR (KBr) 2951 (s), 2869 (m), 1466 (m), 1387 (s), 1101 (s), 1019 (s), 986 (s), 841 (m), 795 (m), and 781 (m) cm^{-1}. HRMS: found 434.2455, calcd 434.2457 for $C_{28}H_{34}O_4$. Anal. Calcd for $C_{28}H_{34}O_4$: C, 77.39; H, 7.89. Found: C, 77.43; H, 7.84.

1,4-Bis(4-formylphenyl)buta-1(*E*),3(*E*)-diene (7CHO). This was obtained in a similar manner as for **6CHO**. Yield: 75%. Mp: 200 °C. ^{1}H-NMR: δ 10.00 (s, 2H), 7.87 (d, J = 8.3 Hz, 4H), 7.12 (dd, J = 14.7 and 2.9 Hz, 2H), 6.80 (dd, J = 14.7 and 2.9 Hz, 2H). IR (KBr) 1694 (vs), 1599 (s), 1561 (m), 1213 (s), 1169 (s), 986 (s), 851 (m), and 799 (s) cm^{-1}. HRMS: found 262.1012, calcd 262.0994 for $C_{18}H_{14}O_2$. Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.36; H, 5.40.

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1,6-Bis[4-(4,4-dimethyl-2,6-dioxan-1-yl)phenyl]hexa-1(*E*),3(*E*),5(*E*)-triene (20). To a solution of **15** (4.41 g, 20 mmol), tetraethyl (2*E*)-butene-1,4-diphosphonate (**13**; 3.28 g, 10 mmol),[15] and 15-crown-5 (0.1 g) in THF (200 mL) was added NaH (1.1 equiv). The mixture was refluxed overnight and then cooled to room temperature. Water was added, and the precipitate (*all-trans* isomer **20**) was filtered off. The filtrate was extracted with ether and evaporated. These solids were combined and recrystallized from CH_2Cl_2/EtOH to provide pure **20** as yellow crystals. Yield: 15%. Mp: 256 °C. ^{1}H-NMR: δ 7.45 (d, J = 8.3 Hz, 4H), 7.42 (d, J = 8.3 Hz, 4H), 6.92–6.85 (m, 2H), 6.58 (d, J = 16 Hz, 2H), 6.52–6.50 (m, 2H), 5.38 (s, 2H), 3.77 (d, J = 10.7 Hz, 4H), 3.65 (d, J = 11.2 Hz, 4H), 1.30 (s, 6H), 0.81 (s, 6H). IR (KBr) 2951 (s), 2869 (m), 1468 (m), 1387 (s), 1103 (s), 1019 (s), 995 (s), 808 (m), and 642 (m) cm^{-1}. HRMS: found 460.2560, calcd 460.2614 for $C_{30}H_{36}O_4$. Anal. Calcd for $C_{30}H_{36}O_4$: C, 78.23; H, 7.88. Found: C, 78.28; H, 7.86.

1,6-Bis(4-formylphenyl)hexa-1(*E*),3(*E*),5(*E*)-triene (8CHO). This was obtained in a similar manner as for **6CHO**. Yield: 88%. Mp: 220 °C. ^{1}H-NMR: δ 9.98 (s, 2H), 7.85 (d, J = 8.3 Hz, 4H), 7.57 (d, J = 8.3 Hz, 4H), 7.08–7.02 (m, 2H), 6.69 (d, J = 15.6 Hz, 2H), 6.65–6.62 (dd, J = 7.1 and 3.2 Hz, 2H). IR (KBr) 1686 (vs), 1599 (s), 1566 (m), 1213 (s), 1159 (s), 999 (s), 874 (m), 810 (s), and 519 (s) cm^{-1}. HRMS: found 288.1137, calcd 288.1150 for $C_{20}H_{16}O_2$. Anal. Calcd for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.36; H, 5.56.

1,8-Bis[4-(4,4-dimethyl-2,6-dioxan-1-yl)phenyl]octa-1(*E*),3(*E*),5(*E*),7(*E*)-tetraene (21). To a solution of **15** (4.41 g, 20 mmol), tetraethyl hexa-2(*E*),4(*E*)-diene-1,6-diphosphonate (**14**; 3.54 g, 10 mmol),[15] and 15-crown-5 (0.1 g) in THF (200 mL) was added NaH (1.1 equiv). The mixture was refluxed overnight and then cooled to room temperature. Water was added, and the precipitate (all-*trans* isomer **21**) was filtered off. The filtrate was extracted with ether. The extract was evaporated and redissolved in chloroform (140 mL), and a trace amount of I_2 was added. This mixture was then refluxed for 3 h and evaporated. The residue and the previous precipitate were combined and recrystallized from CH_2Cl_2/MeOH to provide pure **21** as yellow crystals. Yield: 40%. Mp: 176 °C. ^{1}H-NMR: δ 7.45 (d, J = 8.3 Hz, 4H), 7.40 (d, J = 8.3 Hz, 4H), 6.90–6.83 (m, 2H), 6.57 (d, J = 15.6 Hz, 2H), 6.47–6.41 (m, 4H), 5.37 (s, 2H), 3.77 (d, J = 10.8 Hz, 4H), 3.65 (d, J = 11.2 Hz, 4H), 1.30 (s, 6H), 0.80 (s, 6H). IR (KBr) 2953 (s), 2869 (s), 1470 (m), 1387 (s), 1100 (s), 1019 (s), 994 (s), 803 (m), and 635 (m) cm^{-1}. HRMS: found 486.2781, calcd 486.2770 for $C_{32}H_{38}O_4$. Anal. Calcd for $C_{32}H_{38}O_4$: C, 78.98; H, 7.87. Found: C, 78.95; H, 7.86.

1,8-Bis(4-formylphenyl)octa-1(*E*),3(*E*),5(*E*),7(*E*)-tetraene (9CHO). This was obtained in a similar manner as for **6CHO**. Yield: 91%. Mp: 248 °C. ^{1}H-NMR: 9.97 (s, 2H), 7.83 (d, J = 8.30 Hz, 4H), 7.55 (d, J = 8.30 Hz, 4H), 7.07–7.00 (m, 2H), 6.65 (d, J = 14.7 Hz, 2H), 6.57–6.53 (m, 4H). IR (KBr) 2361 (m), 1686 (vs), 1595 (s), 1211 (s), 1159 (s), 1003 (s), and 801 (s) cm^{-1}. HRMS: found 314.1336, calcd 314.1307 for $C_{22}H_{18}O_2$. Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 84.06; H, 5.75.

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Supporting Information Available: Supporting spectral data and spectra (11 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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