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Energy and Electron Transfer Properties of Methyl Pheophorbide-*a* in Zinc Porphyrin–Pheophorbide Dyads

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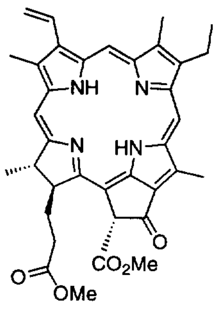
Abstract: *A series of ortho-, meta- and para-substituted zinc porphyrin–pheophorbide dyads were synthesized directly from methyl pheophorbide-a by trans-esterification of β-keto methyl ester with hydroxymethyl substituted porphyrins. Quantitative energy transfer occurred from the excited zinc porphyrin to the pheophorbide. The excited state of the pheophorbide was quenched by an electron transfer reaction from the zinc porphyrin that was found to depend both on the distance between chromophores and the polarity of solvent.* © 1997 Elsevier Science Ltd.

Photoinduced electron transfer is the primary reaction in photosynthesis converting light energy to chemical energy. In the reaction centers of photosynthetic plants, chlorophylls and pheophytins participate in the relay of photons and electrons.[1] These photochemical reactions have been modeled with artificial systems[2] in which porphyrins and metalloporphyrins have been commonly used because they have similar structures and properties to those of chlorophylls, and are easy to be built up into an array of oligomers.[3] Photo-induced electron transfer reactions triggered by light absorption of porphyrins have been widely studied in various covalently linked donor-acceptor model systems.[4] Recently much attention has been directed toward the electron transfer between two tetrapyrrole pigments[5] because the primary reaction in the reaction center starts with the fast electron transfer from the special pair (chlorophyll dimer) to pheophytin (free-base form of chlorophyll). To regulate electron transfer in porphyrin-porphyrin compounds, a charge-separated state must be stabilized to an energy level lower than the S_1-state of the porphyrins. Usually this has been achieved by employment of different porphyrin subunits so as to leave enough $-\Delta G^0$ for the electron transfer process.[6]

An effective approach is to use porphyrin-chlorin hybrid molecules, since chlorins differ from porphyrins in the key properties of excitation energy level and redox potential.[7-9] Chlorin-porphyrin hybrid compounds have been successfully prepared from synthetically derived chlorins and characterized photochemically.[7] A more convenient way is to employ chlorophyll-*a* which can be easily obtained on a large scale from plants and bacteria.[9] Since chlorophyll-*a* itself has few functional groups to be usable for the covalent linkage with another pigment, some modifications have usually been needed at the peripheral functional groups.[5a, 10]

We recently found[11] an ester-exchange reaction of methyl pheophorbide-*a* (**1**) which allows the attachment of various primary and secondary alcohols to **1** without affecting the pheophorbide chromophore.



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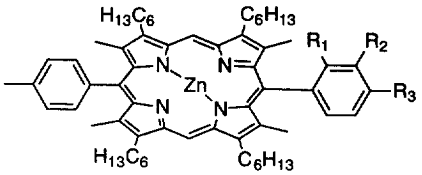
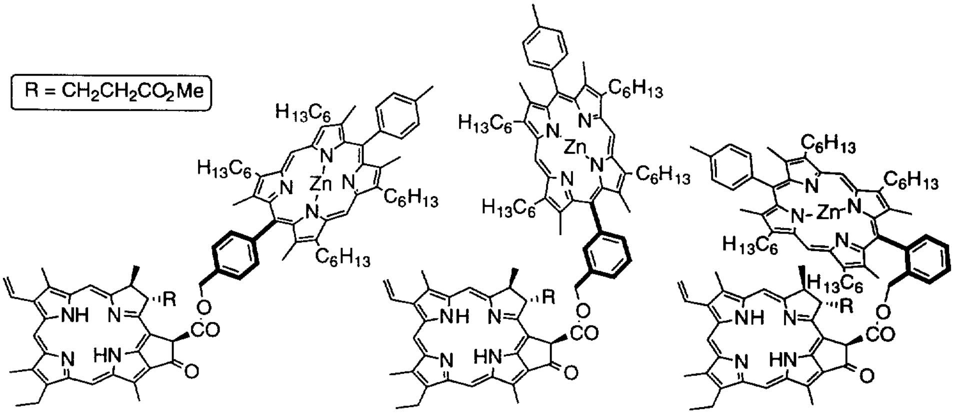


2 $R_1 = R_2 = H, R_3 = CH_3$

4a $R_1 = R_2 = H, R_3 = CH_2OH$
4b $R_1 = R_3 = H, R_2 = CH_2OH$
4c $R_2 = R_3 = H, R_1 = CH_2OH$



3a (para) **3b** (meta) **3c** (ortho)

In this paper, three kinds of porphyrin-pheophorbide dyads **3a-c** were directly synthesized from 1 and hydroxymethyl substituted porphyrins **4a-c**. By changing the substitution pattern of the linkage phenyl group (bold lines on the chart), two chromophores in the dyads were separated by different distances in time-averaged conformations. Intramolecular energy transfer from zinc porphyrin to pheophorbide followed by an electron transfer from the zinc porphyrin to the excited-state pheophorbide was observed at their excited states which was strongly dependent on the distance between the chromophores and the polarity of solvent. Here we report the synthesis and interesting relationship between the structure and photochemical properties of these porphyrin-pheophorbide systems.

RESULTS AND DISCUSSION

Synthesis

Pheophorbide-porphyrin dyads **3a-c** were prepared by trans-esterification of β-keto methyl ester of methyl pheophorbide-*a* (**1**) with *ortho-*, *meta-* and *para*-hydroxymethyl substituted porphyrins (**4a-c**)[12], respectively. This reaction is analogous to the trans-esterification reaction of β-keto methyl esters reported by

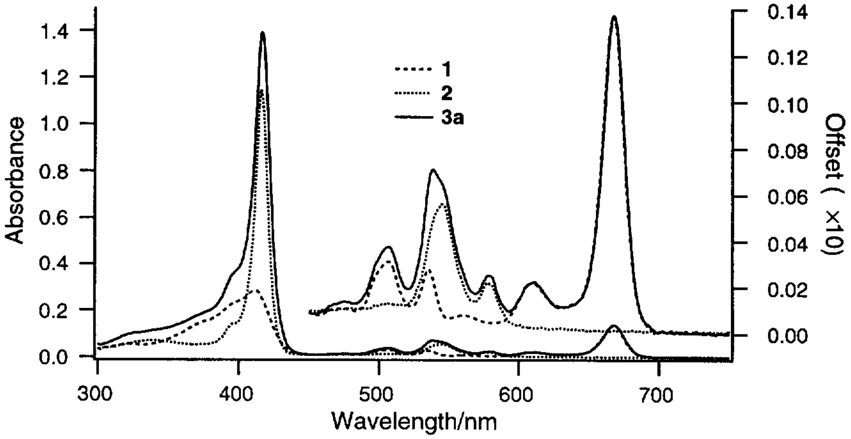


Figure 1. Steady-state absorption spectra of dyad **3a** (solid line), and references **1** (dashed line) and **2** (dotted line) in THF solutions at room temperature. Absorbance of **1** and **2** were adjusted so that the sum of their absorbance corresponded with that of **3a**.

Taber *et al.*[13] In our case, however, the reaction did not proceed without 3-chloro-1-methylpyridinium iodide, while 4-dimethylaminopyridine could be replaced by other bases such as triethylamine without a reduction in the product yield. The dyad products were easily separated by flash column chromatography over silica gel.[14] Our reaction conditions were found to have wide applicability to alcohol substrates such as sterols and thymidine derivatives.[11] Although the yield was moderate, **3b** and **3c** were obtained in lower yields than **3a**, which might be due to the steric hindrance of the products.

The porphyrin moiety was then metallated with zinc(II) to raise its S_1 energy level and lower its oxidation potential.[15] Metallation proceeded selectively and quantitatively at the porphyrin by stirring a CH_2Cl_2 solution of the dyad with a little excess of zinc acetate for 5 minutes at room temperature. The completeness of metallation was confirmed by the disappearance of the proton NMR signal of internal pyrrole NH.

In ^1H NMR spectra of **3b** and **3c**, it was remarkable that one of the two *meso*-protons of the porphyrin ring showed a much larger upfield shift than the other; the differences ($\Delta\delta$) were 0.30 ppm for **3b** and 0.59 ppm for **3c**. Ring current effects by the opposite tetrapyrrole ring were seen in the dyads and were more obvious in the order of **3c** > **3b** > **3a**, which indicated the averaged distances between zinc porphyrin and pheophorbide decreased in the order of **3c** < **3b** < **3a**.

Optical and electrochemical properties

Spectroscopic measurements were done in three solvents with different dielectric constants: DMF, THF and benzene. The ground-state absorption spectra of dyads **3a-c** were almost the same and could be analyzed as a superposition of the spectra of **1** and **2** (Figure 1). The absorption maxima in the Qy-band region of the pheophorbides were only slightly red-shifted (< 1 nm) from **1**. Thus, ground-state interaction between the two chromophores was thought to be very weak, allowing treatment of them as independent chromophores. The linkage bond containing a few single bonds could prevent the through-bond π–π interaction that was preferable

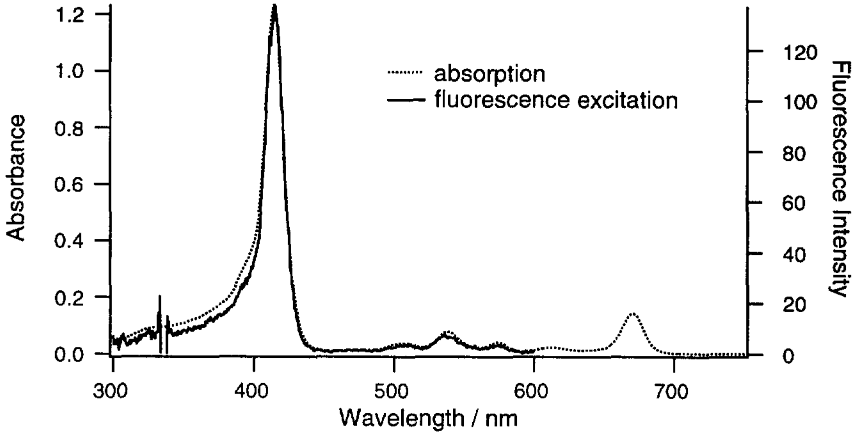


Figure 2. Steady-state corrected fluorescence excitation spectrum (solid line) and absorption spectrum (dotted line) of **3a** in benzene. The fluorescence of the pheophorbide was monitored at 668 nm. Both spectra have been normalized at 410 nm.

for the investigation of intact pheophorbide properties. Energy levels of the locally excited states of the chromophores were determined from the average wavelength of their Qy absorption and emission maxima (Table 1). The S_1 energy of the zinc porphyrin was 0.29 eV higher than that of the pheophorbide. At a wavelength longer than 600 nm, there was only an absorption of the pheophorbide, which permitted the selective excitation of the pheophorbide moiety in this region.

The fluorescence spectrum of the zinc porphyrin effectively overlapped with the absorption of the pheophorbide. This seemed preferable for singlet-singlet energy transfer from the porphyrin to the pheophorbide. Actually, emission from the porphyrin moiety was hardly seen in the steady-state fluorescence spectra of all the dyads even when the porphyrin moiety was excited. To estimate the efficiency of energy transfer, the steady-state corrected fluorescence excitation spectra were measured by monitoring the fluorescence from the pheophorbide. In the case of **3a** in benzene (Figure 2), the excitation spectrum was consistent with the absorption spectrum, suggesting that singlet energy transfer occurred quantitatively from the porphyrin to the pheophorbide. The energy transfer was indeed found quantitative for **3b** and **3c** in all the solvents used in this study.

Table 1. Energy Levels of the First Singlet Excited-States and Redox Potentials of Reference Compounds

		E_{S1}/eV		$E^{0'}/V^a$	
Compd	Benzene	THF	DMF	Ered	Eox
1	1.84	1.85	1.86	-1.30	0.42
2	2.15	2.14	2.13	–[b]	0.41

[a] Half wave potentials vs Ag/AgCl in CH_2Cl_2 with 0.1M Bu_4NPF_6 as supporting electrolyte. [b] Reduction peak was observed in the scan range of 0 –> -2.0 V.

Table 2. Estimated Energy Level (E_{CS})[a] of the Charge-Separated State and Free-Energy Gap ($-\Delta G^0$)[b] for Electron Transfer Reaction

	Benzene		THF		DMF	
r_C/Å	E_{CS}/eV	$-\Delta G^0$/eV	E_{CS}/eV	$-\Delta G^0$/eV	E_{CS}/eV	$-\Delta G^0$/eV
10	2.02	-0.18	1.59	0.26	1.43	0.43
7.5	1.81	0.03	1.52	0.33	1.42	0.44
5	1.39	0.45	1.39	0.46	1.39	0.47

[a] E_{CS} values were estimated from the redox potentials (Table 1) and r_C (a proper distance between the centers of two macrocycles) using the Born equation. Ion radii were assumed to be 5 Å for both porphyrin and pheophorbide.
[b] $-\Delta G^0 = E_{S1}$(pheophorbide)$-E_{CS}$.

Redox potentials of reference compounds **1** and **2** were measured in CH_2Cl_2 by cyclic voltammetry, and standard potential (E_0') was determined from half value of the oxidative and reductive peak maxima (Table 1). The energy levels of the charge separated states in three solvents were estimated (Table 2) according to the Born equation.[16] It was found that the energy levels of the charge-separated states (porphyrin)$^+$–(chlorin)$^-$ were low enough to drive electron transfer from the locally excited state of the pheophorbide except for the case in non-polar benzene solution with a long distance (10 Å).

Fluorescence quenching

The facts that the fluorescence from the zinc porphyrin was strongly quenched and the fluorescence excitation spectrum recorded by monitoring the fluorescence of the pheophorbide coincided with the absorption spectrum indicated the efficient singlet-singlet excitation energy transfer from the zinc porphyrin to the pheophorbide. The rate constant of the energy transfer was obtained by measuring the fluorescence lifetime. Measurements were done by excitation at 532 nm monitoring the fluorescence emission of zinc porphyrin at 590 nm. In all cases, the decay curves were fit with bi-exponential function and a short lifetime component ($\tau < 20$ ps) was always the predominant one contributing > 95% of the initial amplitude. The lifetimes of these components are listed in Table 3. The rate of the energy transfer was calculated by equation 1,

$$r_E = \frac{1}{\tau} - \frac{1}{\tau_0} \qquad \text{(eq 1)}$$

where τ and τ_0 are the fluorescence lifetimes of porphyrin moieties of **3a-c** and reference **2**, respectively. The excitation energy transfer was quite independent of the solvent polarity and was slightly faster in the most closed model **3c** than in **3a** or **3b**. The rapid energy transfer, which has also been reported in other porphyrin-chlorin hybrid molecules, suggested a dipole-dipole interacting Förster mechanism, since in **3a-c** the spectral overlap of the donor fluorescence and the acceptor absorption was indeed relatively large.[17]

The fluorescence intensity of the pheophorbide in **3a-c**, on the other hand, varied with the distance between chromophores and the polarity of solvent (Figure 3). These intensities decreased in the order of **3a** > **3c** > **3b** in benzene and **3a** > **3b** > **3c** in THF and DMF. The reference molecule **1** decayed in a single-exponential manner with τ = ca. 5 ns, while the fluorescence decays of the pheophorbide in the dyads could not

Table 3. Fluorescence Lifetimes of the Zinc Porphyrin in Dyads (ps)[a]

compd	Benzene τ_{por}/ps	Benzene $r_E/10^{10}s^{-1}$	THF τ_{por}/ps	THF $r_E/10^{10}s^{-1}$	DMF τ_{por}/ps	DMF $r_E/10^{10}s^{-1}$
2	1.6×10^3		1.5×10^3		1.4×10^3	
3a	22 (0.95)[b]	4.5	19 (0.99)	5.3	18 (0.99)	5.6
	84 (0.04)		110 (0.01)		130 (0.01)	
3b	20 (0.94)	5.0	19 (0.96)	5.3	18 (0.97)	5.6
	94 (0.05)		110 (0.03)		130 (0.02)	
3c	14 (0.95)	7.1	13 (0.99)	7.7	13 (0.99)	7.7
	62 (0.04)		220 (0.01)		180 (0.01)	

[a] Both the porphyrin and pheophrobide were excited at 532 nm and the fluorescence was monitored at 590 nm. Decay curve was fit with tri-exponentials. [b] Values in parentheses are the relative values of the initial (t=0) amplitude of decay component.

be fit with a single exponential function. Thus, the fluorescence decays were analyzed in terms of bi-exponential function and the resultant lifetimes are summarized in Table 4. These values were smaller than 5 ns and proportional to the steady-state fluorescence quenching experiments.

Since the S_1-state of the pheophorbide was confirmed to be the lowest excited state in the dyads **3a-c**, the electron transfer was the most probable mechanism for the quenching, because in these solvents the charge

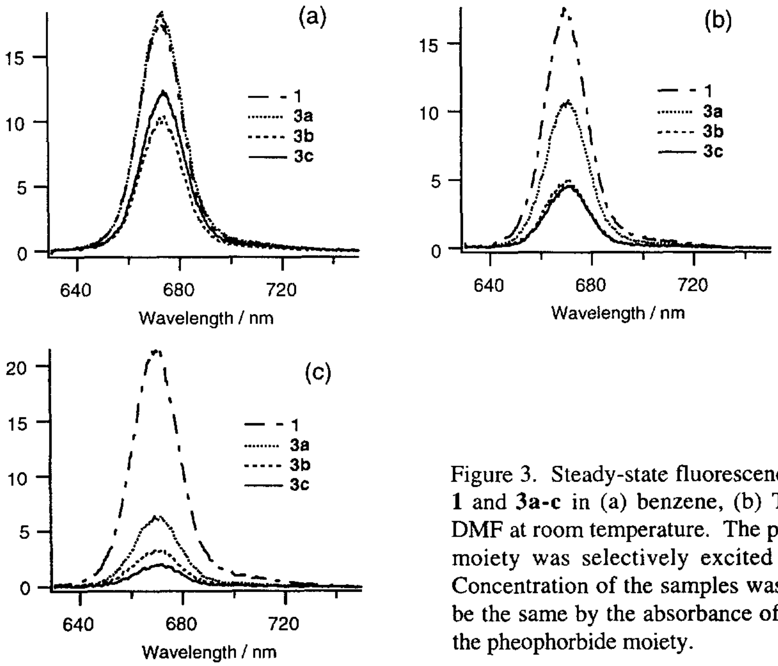


Figure 3. Steady-state fluorescence spectra of **1** and **3a-c** in (a) benzene, (b) THF and (c) DMF at room temperature. The pheophorbide moiety was selectively excited at 610 nm. Concentration of the samples was adjusted to be the same by the absorbance of Qy band of the pheophorbide moiety.

Table 4. Fluorescence Lifetimes of the Pheophorbide in Dyads (ns)[a]

Compd	solvent		
	Benzene	THF	DMF
1	5.1	5.2	5.1
3a	5.9 (1)[b]	3.9 (0.89) 1.3 (0.11)	2.5 (0.71) 0.82 (0.29)
3b	5.0 (0.80) 1.1 (0.20)	2.7 (0.84) 0.64 (0.16)	1.9 (0.68) 0.45 (0.32)
3c	5.1 (1)	2.4 (0.79) 0.69 (0.21)	1.1 (0.61) 0.28 (0.35)

[a] Pheophorbide moiety was selectively excited at 610 nm and the fluorescence was monitored at 690 nm. [b] Values in parentheses are the relative values of the initial (t=0) amplitude of each decay component.

separated states, (zinc porphyrin)$^+$–(pheophrobide)$^-$, were calculated to be lying energetically lower than the S_1-state of the pheophorbide. The solvent-polarity effects were quite analogous to those found for the electron transfer between tetrapyrrolic pigments.[7a] Reasons for the observed bi-exponential behaviors of the fluorescence decays are not clear at the present stage. One plausible explanation might be that **3a-c** existed in two or more stable conformations and had a different electron transfer rate constant in each conformation. Confirmation of the electron transfer will be established only after pertinent time-resolved transient absorption spectroscopy measurements.

CONCLUSION

Pheophorbide-*a* and hydroxymethyl substituted porphyrin were built up to a photoactive donor-acceptor system by one-pot trans-esterification reaction. In the hybrid dyads, a rapid excitation energy transfer resulted in the quantitative formation of the pheophorbide excited state, which could act as an electron acceptor toward the zinc porphyrin ground state. Incorporation of these dyad moieties into further elaborated photosynthetic models and further application of this synthetic strategy to the connection of other photoactive entities such as quinones, steroids and carotenoids are being conducted in our laboratory.

EXPERIMENTAL

Spectroscopic Measurements. All the optical measurements were done at room temperature. UV-Vis absorption spectra were recorded on a Hitachi UV-3500T spectrometer. Steady-state fluorescence and excitation spectra were recorded on a Hitachi F-3010 spectrofluorometer. Fluorescence lifetimes were determined by the previously reported method.[18] Cyclic voltammetry was carried out with a BAS CV-50W voltammetric analyzer and all measurements were performed in CH_2Cl_2 containing 0.1 M Bu_4NPF_6 as supporting electrolytes with a Pt working electrode and a Ag/AgCl counter electrode. Halfwave potential of ferrocene/ferrocenium appeared at 0.22 V under these conditions. In the fluorescence quenching experiments, concentration of a sample was adjusted so that the Qy absorption band of pheophorbide had the same absorbance around 0.2 and pheophorbide moiety was selectively excited at the $Qy_{0\text{-}1}$ absorption band (610 nm). Relative fluorescence quantum yields of the pheophorbide moieties were determined from the intensity at the maximum intensity wavelength.

Synthesis. Toluene was distilled twice over calcium hydride under N_2 atmosphere. DMF, THF and benzene (spectroscopic grade) used for spectroscopic measurements were purchased from Nacalai Tesque and used as received. All other reagents were used without further purification. Flash column chromatography was performed using silica gel 60 H (Art. 7736) as purchased from Merck. Melting points were determined using a Yanagimoto melting point apparatus and were uncorrected. NMR spectra were recorded on a JEOL LAMBDA-300 operating at 300 MHz. High resolution FAB mass spectra were recorded on a JEOL HX-110 using *m*-nitrobenzyl alcohol as a matrix.

Preparation of dyads. A 10 ml round-bottom flask was charged with 10 mg (16 µmol) of **4a**, 11 mg (12 µmol) of **1**, 10 mg (39 µmol) of 2-chloro-1-methylpyridinium iodide, 9 mg (0.07 mmol) of *N,N*-dimethylaminopyridine and 10 ml of toluene. Toluene was deaerated with N_2 before use. This flask was equipped with a reflux condenser and refluxed for 3 h under N_2 atmosphere. After cooling to room temperature, the reaction mixture was washed with water and dried over Na_2SO_4. Toluene was removed by a rotary evaporator and the resulting material was dissolved in CH_2Cl_2 (20 ml). To this solution was added 2.6 mg (12 µmol) of $Zn(OAc)_2{\bullet}2H_2O$ dissolved in MeOH (1 ml). After stirring for 10 min, the reaction mixture was washed with water to remove excess zinc salts and dried over Na_2SO_4 and the solvent was removed by a rotary evaporator. The resulting material was purified by flash chromatography (CH_2Cl_2) followed by recrystallization from CH_2Cl_2-hexane to give 6.0 mg (4 µmol, 30%) of **3a**.

3a (*para*). m.p. 133-135°C (decomp.). UV (λmax/nm, THF) 417 (1), 507 (0.027), 539 (0.051), 579 (0.018), 611 (0.016), and 668 (0.098). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.14 (s, 2H), 9.60 (s, 1H), 9.43 (s, 1H), 8.58 (s, 1H), 8.01 (dd, 1H), 7.96 (d, 2H), 7.93 (d, 2H), 7.69 (d, 2H), 7.54 (d, 2H), 6.49 (s, 1H), 6.30 (d, 1H), 6.19 (d, 1H), 5.77 (s, 2H), 4.48 (m, 2H), 3.95 (t, 4H), 3.9-3.8 (4H), 3.77 (s, 3H), 3.73 (q, 2H), 3.57 (s, 3H), 3.39 (s, 3H), 3.26 (s, 3H), 2.73 (s, 3H), 2.47 (s, 6H), 2.26 (s, 6H), 2.16 (m, 4H), 2.07 (m, 4H), 1.91 (d, 3H), 1.73 (m, 4H), 1.72 (t, 3H), 1.62 (m, 4H), 1.5-1.3 (16H), 0.91 (t, 6H), 0.87 (t, 6H), 0.62 (s, 1H), and -1.56 (s, 1H). HRMS *m/z* 1534.824 (M^+), $C_{97}H_{114}N_8O_5Zn$ = 1534.820.

3b (*meta*). Yield 3%. m.p. 134-136°C (decomp.). UV (λmax/nm, THF) 417 (1), 507 (0.030), 539 (0.054), 579 (0.020), 611 (0.018), and 668 (0.104). ^{1}H NMR ($CDCl_3$, 300 MHz) δ10.02 (s, 1H), 9.72 (s, 1H), 9.32 (s, 1H), 8.99 (s, 1H), 8.09 (d, 1H), 7.89 (d, 1H), 8.0-7.6 (5H), 7.54 (d, 1H), 7.50 (d, 1H), 7.43 (t, 1H), 6.25 (s, 1H), 6.08 (d, 1H), 6.05 (d, 1H), 5.84 (d, 1H), 5.52 (d, 1H), 4.20 (m, 1H), 4.02 (m, 4H), 3.90 (m, 1H), 3.63 (s, 3H), 3.48 (s, 3H), 3.21 (s, 3H), 3.07 (s, 3H), 2.76 (s, 3H), 2.61 (s, 3H), 2.53 (s, 3H), 2.52 (s, 3H), 1.94 (s, 3H), 1.65 (t, 3H), 1.27 (d, 3H), 1.0-0.8 (12H), 0.25 (s, 1H), and -2.33 (s, 1H). HRMS *m/z* 1534.820 (M^+), $C_{97}H_{114}N_8O_5Zn$ = 1534.820.

3c (*ortho*). Yield 7%. m.p. 137-139°C (decomp.). UV (λmax/nm, THF) 417 (1), 507 (0.029), 539 (0.054), 580 (0.020), 611 (0.017), 669 (0.103). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.07 (s, 1H), 9.52 (s, 1H), 9.48 (s, 1H), 9.43 (s, 1H), 8.07 (s, 1H), 8.04 (1H), 8.02 (1H), 7.93 (1H), 7.85 (1H), 7.83 (1H), 7.69 (1H), 7.60 (1H), 7.57 (ddd, 1H), 7.54 (1H), 6.32 (d, 1H), 6.21 (d, 1H), 5.75 (s, 1H), 5.11 (s, 2H), 3.96 (m, 1H), 3.82 (m, 1H), 3.74 (2H), 3.50 (s, 3H), 3.31 (s, 3H), 3.28 (s, 3H), 3.10 (s, 3H), 2.75 (s, 3H), 2.50 (s, 3H), 2.48 (s, 3H), 2.24 (s, 3H), 1.94 (s, 3H), 1.74 (t, 3H), 0.90 (t, 3H), 0.85 (t, 3H), 0.79 (t, 3H), 0.73 (t, 3H), 0.45 (d, 3H), 0.44 (s, 1H), and -1.70 (s, 1H). HRMS *m/z* 1534.820 (M^+), $C_{97}H_{114}N_8O_5Zn$ = 1534.820.

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14. Although an epimerization at the 13^2-position of the chlorin could occur during the trans-esterification, only one epimeric isomer was actually obtained by column chromatography. The stereochemistry at the 13^2-position was probably maintained, but it have not been fully determined yet.
15. 5,15-Diaryloctaalkyl substituted zinc porphyrin is known to be more easily oxidized than the corresponding free-base porphyrin by ca. 0.2 V. The former has 0.15 eV higher S_1 energy than the latter. Asahi, T.; Ohkohchi, M.; Matsusaka, R.; Mataga, N.; Zhang, R. P.; Osuka, A.; Maruyama, K. *J. Am. Chem. Soc.* **1993**, *115*, 5665-5674.
16. The energy level of a charge separated state (E_{cs}, eV) in a given solvent was estimated from the redox potential by the commonly used Born equation:

$$E_{CS} = E^0_{OX} - E^0_{RED} + \frac{14.40}{2}\left(\frac{1}{\varepsilon_{solvent}} - \frac{1}{\varepsilon_{CH_2Cl_2}}\right)\left(\frac{1}{r_+} + \frac{1}{r_-}\right) - \frac{14.40}{r_C\varepsilon_{solvent}}$$

where r_+ and r_- are the ion radii of porphyrin and pheophorbide separated by a distance r_C (in Å) and ε is a dielectric constant of the solvent. Both radii r_+ and r_- were assumed to be 5 Å for estimation.

17. The spectral overlap (Ω, $cm^{-6}mol^{-1}$) between porphyrin fluorescence and pheophorbide absorption spectra in each solvent was calculated to be 4.34, 5.73 and 6.79×10^{-11} in benzene, THF and DMF, respectively:

$$\Omega = \int f(\nu)\varepsilon(\nu)d\nu$$

where $f(\nu)$ is the fluorescence intensity normalized to integrate to 1, $\varepsilon(\nu)$ (in cm^2mol^{-1}) is the extinction coefficient of the pheophorbide, and ν is wavenumber (cm^{-1}).

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