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Energy and Electron Transfer in Synthetic Oligoproline-Bridged Porphyrin Donor–Acceptor Molecules

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Oligo-L-proline-bridged bis(porphyrin) compounds were synthesized. The protected oligoprolines in ethanol might take a fairly stable helical conformation at an oligomerization number ≥ 4. An intramolecular singlet energy transfer occurred in ethanol from a photoexcited zinc porphyrin moiety in the *N*-terminal to a metal-free porphyrin moiety in the *C*-terminal at the same efficiency as from the zinc porphyrin moiety in the *C*-terminal to the metal-free porphyrin moiety in the *N*-terminal. A photoinduced electron transfer also occurred in ethanol from the zinc(II) porphyrin to the iron(III) porphyrin in the molecule, which was independent of the direction of the spacer as well as the energy transfer. A weak change in the intramolecular electron-transfer efficiency with the distance between the zinc and iron porphyrins suggested that electrons should move through the amide bonds in the oligoproline linkage.

Protein-mediated long-range energy and electron transfer is of biological importance. Naturally occurring protein-bridged and modified protein-bridged donor–acceptor systems have been investigated.[1,2] These natural proteins, however, are so complex in the molecules that a desired modification of their supramolecular structures is difficult to achieve. In contrast, synthetic donor–acceptor molecules with a linkage of known oligopeptides provide a decisive means for a systematic elucidation of the energy- and electron-transfer mechanism.[3—8] These systems are based on the use of electronically excited states produced by a photoirradiation or pulse-radiolysis technique as well as on the direct and/or indirect detection of the excited states and/or the successively produced charge separation states. Some experiments[4—6] in oligo-L-proline-bridged donor–acceptor molecules have been proven to be useful for studying rapid energy and electron transfer processes, because the oligo-L-proline spacers take a fairly stable helical conformation and the intramolecular energy and electron transfer can be readily monitored by various emission and absorption techniques. We report here on the synthesis of molecules having a series of oligo-L-proline spacers to separate the energy or electron donor and acceptor pair. The system described herein utilizes a photoexcited zinc(II) porphyrin as an energy and electron donor, and a metal-free porphyrin and an iron(III) porphyrin as an energy and electron acceptor, respectively (see Fig. 1). In this paper, we also describe the role of the oligo-L-proline linkage in the intramolecular energy and electron transfer. This is the first example, to our knowledge, that the same synthetic oligopeptide spacers and structurally similar donor–acceptor pairs have been used for both energy and electron transfer under the same conditions.

Results and Discussion

Porphyrins are known to aggregate easily via a π–π interaction in solution. In the present study, porphyrin moieties with *t*-butyl groups on the *meso*-phenyl groups were used, which suppressed the intra- and intermolecular interaction of the porphyrin moieties by a steric repulsion.[9] To avoid any conjugation of the porphyrins with the oligo-L-prolines spacer, a methylene group[7] was inserted between the *meso*-phenyl and amido groups. The general strategy for synthesizing bis(porphyrin) donor–acceptor molecules separated by oligoprolines is based upon techniques used for standard peptide synthesis.[8] The synthetic route is shown in Schemes 1 and 2.[10] The detailed synthetic procedures and spectral data are described in the Experimental Section.

The UV-vis spectra of all synthetic **Z-*n*-H**, **H-*n*-Z** (n=0—8), and a 1 : 1 mixture of 5,10,15,20-tetrakis(3,5-di-*t*-butylphenyl)porphyrin (H_2TDBPP) and its zinc complex (ZnTDBPP) in ethanol showed no significant shape change or peak shift (Soret band: 424(±1) nm; Q-bands: 514(±2), 557(±2), 597(±2), and 648(±2) nm), indicating that there is no appreciable interaction among the three moieties, two porphyrin chromophores and oligoproline spacer, in the synthetic donor–acceptor molecule.

The fluorescence spectra of **Z-*n*-H** and **H-*n*-Z** in ethanol at room temperature (excited at the Soret band) gave three peaks at 604(±1), 650(±2), and 716(±1) nm. The 604-nm band is emitted from the singlet excited state of the zinc porphyrin moiety in the molecule and the 716-nm band is mainly emitted from that of metal-free porphyrin, whose assignments were made by a comparison with the emission maxima of H_2TDBPP (650 and 715 nm) and ZnTDBPP (604 and 657 nm). The fluorescence intensities at the 604-nm band were reduced, and the intensities at the 716-nm band were concomitantly increased. Considering the low concen-

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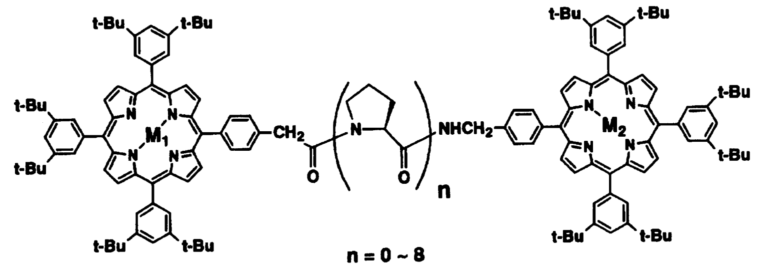
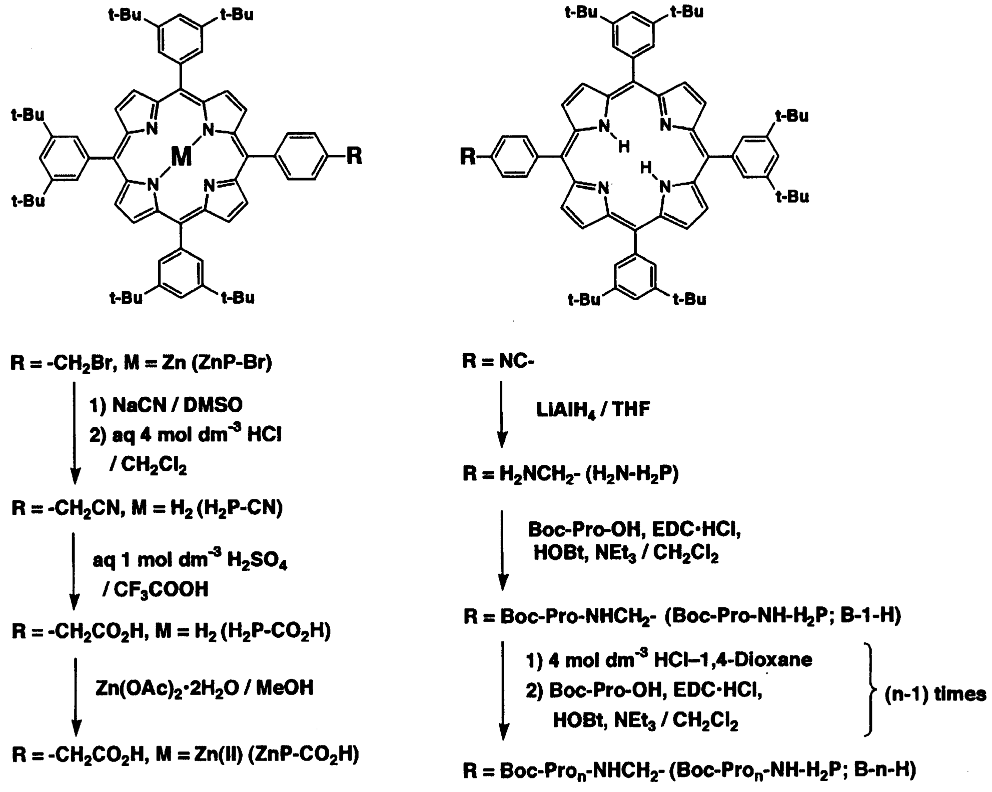


		M_1	M_2
ZnP-CO-Pro$_n$-NH-H_2P	(Z-n-H)	Zn(II)	H_2
H_2P-CO-Pro$_n$-NH-ZnP	(H-n-Z)	H_2	Zn(II)
ZnP-CO-Pro$_n$-NH-FeP	(Z-n-F)	Zn(II)	Fe(III)Cl
FeP-CO-Pro$_n$-NH-ZnP	(F-n-Z)	Fe(III)Cl	Zn(II)

Fig. 1. Synthetic oligo-L-proline-bridged porphyrin donor–acceptor molecules.



Scheme 1. Synthesis of 5-aryl-10,15,20-tris(3,5-di-*t*-butylphenyl)porphyrin.

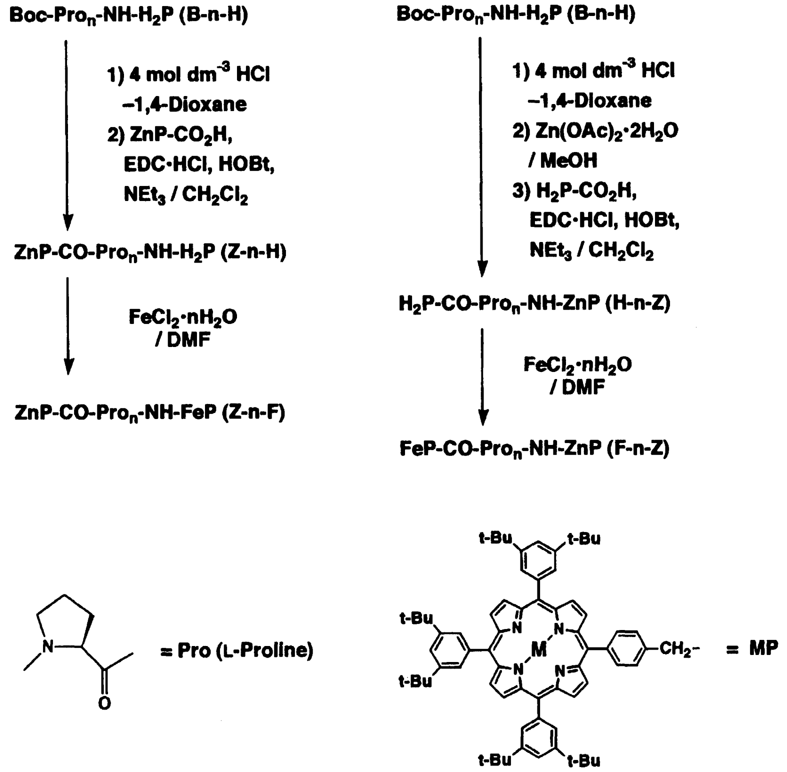
tration of the solutions (2×10^{-6} mol dm^{-3}), it is reasonable that the change in the fluorescence intensity is due to an intramolecular quenching of the photoexcited zinc porphyrin moiety by the metal-free porphyrin moiety,[8] i.e. a singlet energy transfer occurred from the zinc to metal-free porphyrin moiety in the molecule.

The relative fluorescence intensities ($I_{\mathrm{rel}}=I_{\mathrm{H}}/I_0$) at the 604-nm band were calculated by division of the intensities (I_{H}) in **Z-*n*-H** or **H-*n*-Z** by the standard I_0 in a 1 : 1 mixture of H_2TDBPP and ZnTDBPP, which were all measured under the same conditions (solvent, concentration, temperature, etc.). In both the series of the donor–acceptor molecules, I_{rel} increased with an increase in the number (n) of proline units in the spacer, and quenching via an energy transfer was reduced in concomitance with the increase in n, suggesting that the average spatial distance between both chromophores in the molecule should increase with an increase in n.

The singlet energy transfer rate (k_{energy}) can be estimated from the steady-state of fluorescence spectra[8] using

$$k_{\mathrm{energy}} = (I_0/I_{\mathrm{H}} - 1)/\tau_0, \qquad (1)$$

where τ_0 is the fluorescence lifetime in the absence of a metal-free porphyrin as an intramolecular quencher, i.e. the lifetime of ZnTDBPP. It is known that the singlet energy should migrate from the zinc-porphyrin to the metal-free one via an interaction between these transi-



Scheme 2. Synthesis of oligo-L-proline-bridged porphyrin donor–acceptor molecules.

tion dipoles.[8] Therefore, k_{energy} can also be expressed (Förster type[11]) as functions of the refractive index of the medium between the donor and acceptor (k), the orientation factor (κ), the fluorescence decay rate (k_0) and the quantum yield (Φ_0) of the donor in the absence of an acceptor, the spectral overlap integral of the donor fluorescence with acceptor absorption (J), and the center-to-center distance between donor and acceptor (R_{DA}),

$$k_{\text{energy}} = k\kappa^2 k_0 \Phi_0 J / R_{\text{DA}}^6. \tag{2}$$

In **Z-*n*-H** and **H-*n*-Z**, R_{DA} can be described as

$$R_{\text{DA}} = dn + R_0, \tag{3}$$

where d is the additional distance between the donor and acceptor per proline residue and R_0 is the donor–acceptor distance in a directly linked molecule (n=0), as **Z-0-H** or **H-0-Z**. R_0 can be estimated as 21 Å from an MM2 calculation by the CAChe system. In this study of the energy transfer, k is constant under the measurement conditions, κ^2 is 2/3 (determined from the random distribution of both dipoles of terminal porphyrin moieties because of free rotation through phenyl–CH$_2$–CO (or NH) bonds), $k_0=1/\tau_0$, and Φ_0 and J are assumed to be constant because the visible absorption and fluorescence emission spectra of the porphyrin moiety were not affected by the bridged oligoprolines, as the spacer and another porphyrin moiety in the opposite terminal (vide supra). The above three equations (Eqs. 1, 2, and 3) lead to the following equation:

$$I_0/I_{\text{H}} - 1 = 2k\Phi_0 J/3(dn+R_0)^6. \tag{4}$$

Then, the d-value can be readily obtained by fitting the experimental data to the following equation (c: constant):

$$(I_0/I_{\text{H}} - 1)^{-1/6} = cdn + cR_0. \tag{5}$$

In **Z-*n*-H**, a nearly straight line is obtained at $n \geq 4$, as shown in Fig. 2A. A least-squares fit to the line gives a slope (cd) and intercept (cR_0) of 0.072 and 0.47$_5$, respectively; thus d=3.2 Å/residue by using R_0=21 Å. The estimated d-value is in agreement with the value[6] ($d\approx$3.1 Å/residue) for a trans helix of poly-L-proline. The helix in **Z-*n*-H** might be stable for $n \geq 4$. These explanations are supported by a previous result[6] in which the protected oligoprolines at both terminals took a fairly stable trans helix for $n \geq 5$ in ethanol. Similarly, Fig. 2B shows that the isomeric **H-*n*-Z** molecules for $n \geq 4$ in ethanol might easily take the same helical conformation (d=3.1 Å/residue).

The fluorescence spectra of **Z-*n*-F** and **F-*n*-Z** in ethanol at room temperature gave two peaks at 603(±1) and 657(±1) nm. Iron(III) porphyrin is a nonfluorescent chromophore, and the two bands are assigned to the emission of the zinc porphyrin moiety in the donor–acceptor molecule. The fluorescence intensities at the 603- and 657-nm band increase along with an increase in the number (n) of proline units in the spacer. Considering the low concentration of the

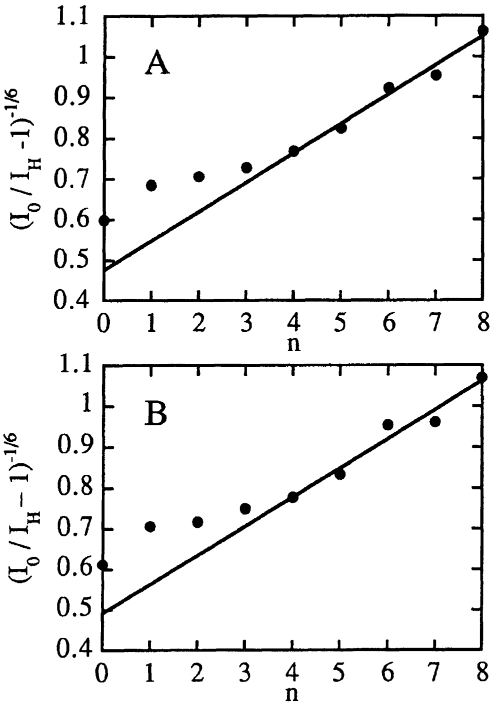


Fig. 2. The dependence of $(I_0/I_\mathrm{H}-1)^{-1/6}$ on the oligomerization number n in (A) **Z-*n*-H** and (B) **H-*n*-Z**.

solutions (2×10^{-6} mol dm^{-3}), the change in the fluorescence intensity might be described as being an intramolecular quenching of the photoexcited zinc porphyrin moiety by the iron porphyrin moiety. The iron(III) porphyrin is known to quench the singlet excited state of the zinc(II) porphyrin via an electron transfer to produce the iron(II) porphyrin and the cation radical of the zinc(II) porphyrin.[12] In **Z-*n*-F** and **F-*n*-Z**, the intramolecular fluorescence quenching must be due to a similar electron-transfer process.

Similar to Eq. 1, the electron-transfer rate (k_electron) is experimentally estimated based on the steady-state of fluorescence spectra,[7]

$$k_\mathrm{electron} = (I'_0/I_\mathrm{F} - 1)/\tau_0, \qquad (6)$$

where I_F and I'_0 are the fluorescence intensities of **Z-*n*-F** or **F-*n*-Z** and a 1 : 1 mixture of Zn(II)TDBPP and Fe(III)ClTDBPP under the same conditions respectively, and τ_0 is the fluorescence lifetime of ZnTDBPP (vide supra). On the other hand, k_electron is theoretically expressed[13] as a function of the edge-to-edge donor-acceptor distance (r_DA), and expressed as

$$k_\mathrm{electron} = k^\mathrm{max}\exp(-\beta r_\mathrm{DA}), \qquad (7)$$

where

$$r_\mathrm{DA} = dn + r_0 \qquad (8)$$

and k^max is the largest rate constant, β is an attenuation factor, d is the donor–acceptor distance separated by each one proline residue (vide supra), n is the number of proline residues in the peptide spacer (vide supra) and r_0 is the edge-to-edge donor–acceptor distance at $n=0$ (**Z-0-F** or **F-0-Z**). The above-three equations (Eqs. 6, 7, and 8) lead to

$$(I'_0/I_\mathrm{F} - 1)/\tau_0 = k^\mathrm{max}\exp[-\beta(dn + r_0)]. \qquad (9)$$

Then, the β-value can be readily obtained by fitting the experimental data to the following equation (c': constant):

$$\ln(I'_0/I_\mathrm{F} - 1) = -\beta dn + c'. \qquad (10)$$

In **Z-*n*-F**, a nearly straight line is obtained for $n\geq4$, as shown in Fig. 3A. A least-squares fit of the line gives a slope $(-\beta d) = -0.53$ residue^{-1}. Based on the assumption that **Z-*n*-F** ($n\geq4$) takes the same helical conformation as does **Z-*n*-H** in ethanol, β was estimated to be 0.16 Å^{-1} by using $d=3.2$ Å/residue. Upon a similar assumption, the β-value of the isomeric **F-*n*-Z** ($n\geq4$) was estimated to be 0.16 Å^{-1} (see Fig. 3B), which is the same as that of **Z-*n*-F**. This agreement shows that any intramolecular electron transfer in synthetic donor–acceptor molecules should be independent of the direction of the oligoproline as the linked spacer,[14] and dependent on the oligomerization number (n).

Normally, the β-factor was estimated by both theoretical and experimental studies[1] over the range of $\beta=$ 0.7—1.4 Å^{-1}. The usual values are larger than those estimated based on the donor–acceptor model compounds reported here. In a previous paper,[7] we reported that the β-value for a photoinduced electron transfer in

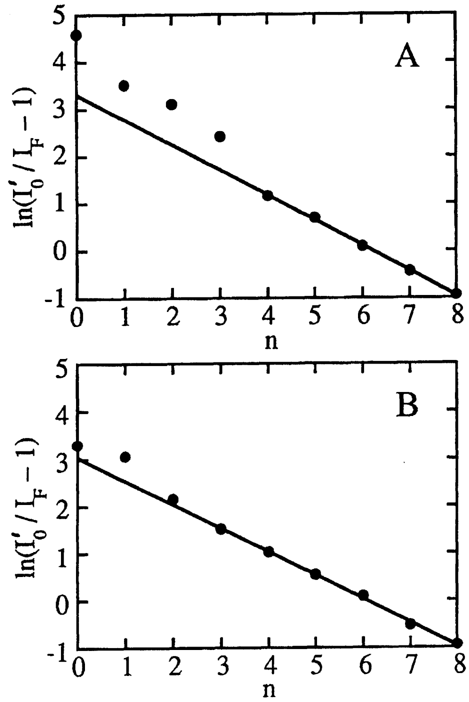


Fig. 3. The dependence of ln $(I'_0/I_\mathrm{F}-1)$ on the oligomerization number n in (A) **Z-*n*-F** and (B) **F-*n*-Z**.

oligopeptide-bridged donor–acceptor molecules might be crucially small, 0.1—0.2 Å^{-1}. Others[4,5] have also claimed that β in helical oligoproline bridged electron donor–acceptor systems$=$0.2—1.0 Å^{-1}. Therefore, a photoinduced intramolecular electron-transfer in **Z-*n*-F** and **F-*n*-Z** ($n \geq 4$) should be effected by the bridged oligoproline spacer, compared with the system possessing aliphatic hydrocarbon spacers investigated so for ($\beta \approx 1$ Å^{-1}).[1] From the above consideration, electrons in the presently reported system might move through the amide bonds, and the direction of the bonds should not be important in a bond-mediated electron-transfer process.

Experimental

General. All of the apparatus used was the same as that discussed in our previous report.[8] CH_2Cl_2, DMF, and DMSO were distilled from CaH_2 and stored over molecular sieves before use. Boc–L-Pro–OH[15] and ZnP–Br[9] were synthesized according to a procedure discussed in the literature. All of the new porphyrins reported here were synthesized as follows (see also Schemes 1 and 2). The other reagents and solvents were commrecially available and were used without purification. All of the reactions were carried out under N_2 in the dark. All of the porphyrins were purified by flash column chromatography on silica gel (Merck Kieselgel 60H 7736 or Wakogel FC-40) with CH_2Cl_2–MeOH used as eluants and recrystallization from CH_2Cl_2–MeOH and given as a purple solid; the mp of the new porphyrins was >300°C, except for **B-*n*-N** (n=1—8), specially mentioned below. The general procedures for metallation, deprotection, and coupling were as follows.

(a) Zinc-Metallation: A MeOH (30 ml) solution of a metal-free porphyrin (0.2 mmol) and a large excess Zn(OAc)$\cdot$2H_2O was stirred for 1 h at room temperature and washed with aq 5% $KHSO_4$, aq 4% $NaHCO_3$, and brine, dried over Na_2SO_4 and concentrated in vacuo. Purification of the residue gave the zinc(II) complex (>90%).

(b) Iron-Metallation: A DMF (30 ml) solution of a metal-free porphyrin (5 μmol) and a large excess $FeCl_2 \cdot nH_2O$ was gently refluxed for 30 min and washed with aq 2% HCl and brine, dried over NaCl and concentrated in vacuo. Recrystallization from CH_2Cl_2–MeOH gave the iron(III) complex with a chloride anion as a dark-purple solid.

(c) Deprotection of Boc-Group: An ice-chilled 4 mol dm^{-3} HCl–1,4-dioxane (20 ml) solution of a Boc-protected peptide-porphyrin (0.6 mmol) was stirred for 1 h and concentrated in vacuo. Recrystallization from CH_2Cl_2–hexane gave the 3HCl salt of the amine–porphyrin as a green solid quantitatively.

(d) Peptide-Bonding (Coupling): An ice-chilled CH_2Cl_2 (30 ml) solution of acid (0.6 mmol), free amine (0.6 mmol; produced by addition of 1.8 mmol NEt_3 to 3HCl salt of 0.6 mmol amine–porphyrin), EDC (0.6 mmol; produced by addition of 0.6 mmol NEt_3 to 0.6 mmol EDC$\cdot$HCl), and HOBt (0.6 mmol) was stirred overnight and washed with aq 5% $KHSO_4$, aq 4% $NaHCO_3$, and brine, dried over Na_2SO_4 and concentrated in vacuo. Purification of the residue gave the peptide. In the cases of n=5—8 [–(Pro)$_n$–], deactivated silica gel (10% H_2O containing) with AcOEt–MeOH as eluants was used for flash column chromatography.

5-(4-Cyanomethylphenyl)-10,15,20-tris(3,5-di-*t*-butylphenyl)porphyrin (H_2P–CN). A DMF (100 ml) solution of ZnP–Br (550 mg, 0.497 mmol) and NaCN (25 mg, 0.51 mmol) was stirred at room temperature for 1 h and washed with aq 4 mol dm^{-3} HCl and aq 10% Na_2CO_3, dried over Na_2SO_4, and concentrated in vacuo. Purification of the residue gave H_2P–CN (76%); IR (KBr) 3317 (NH), 2954, 2870 (C(CH_3)$_3$), and 2252 cm^{-1} (C≡N); ^{1}H NMR ($CDCl_3$) $\delta=-2.75$ (2H, s), 1.48 (54H, s), 4.12 (2H, s), 7.68 (2H, d, J=9 Hz), 7.75 (3H, s), 7.88 (6H, s), 8.18 (2H, d, J=8 Hz), 8.75 (2H, d, J=4 Hz), 8.84 (2H, d, J=4 Hz), and 8.85 (4H, s); MS (FAB) m/z 990 (MH$^+$).

5-(4-Carboxymethylphenyl)-10,15,20-tris(3,5-di-*t*-butylphenyl)porphyrin (H_2P–COOH). After refluxing overnight aq 1 mol dm^{-3} H_2SO_4–tirfluoroacetic acid (1 : 1, 100 ml) of H_2P-CN (330 mg, 0.334 mmol), the solution was washed with water until the green color changed to red, and was then dried over Na_2SO_4 and concentrated in vacuo. Purification of the residue gave H_2P–COOH (73%); IR (KBr) 3317 (NH), 2954, 2908, 2870 (C(CH_3)$_3$), and 1712 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) $\delta=-2.68$ (2H, s), 1.54 (54H, s), 4.07 (2H, s), 7.73 (2H, d, J=8 Hz), 7.81 (3H, t, J=2 Hz), 8.10 (2H, d, J=2 Hz), 8.11 (4H, d, J=2 Hz), 8.25 (2H, d, J=8 Hz), 8.89 (2H, d, J=3 Hz), 8.91 (2H, d, J=3 Hz), and 8.92 (4H, s); MS (FAB) m/z 1009 (MH$^+$).

Zinc 5-(4-Carboxymethylphenyl)-10,15,20-tris(3,5-di-*t*-butylphenyl)porphyrin (ZnP–COOH). 85% (prepared by zinc-metallation of H_2P–COOH without washing with aq 4% $NaHCO_3$); IR (KBr) 2962, 2908, 2870 (C(CH_3)$_3$), and 1712 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=1.53 (54H, s), 4.09 (2H, s), 7.72 (2H, d, J=8 Hz), 7.80 (3H, t, J=2 Hz), 8.08 (2H, d J=2 Hz), 8.09 (4H, d, J=2 Hz), 8.26 (2H, d, J=8 Hz), 8.99 (2H, d, J=3 Hz), 9.01 (2H, d, J=3 Hz), and 9.02 (4H, s); MS (FAB) m/z 1071 (MH$^+$, for ^{64}Zn).

5-(4-Cyanophenyl)-10,15,20-tris(3,5-di-*t*-butylphenyl)porphyrin. According to similar procedures as those previously reported,[9] refluxing a C_2H_5COOH solution of 4-cyanobenzaldehyde (1 eq), 3,5-di-*t*-butylbenzaldehyde (3 eq), and pyrrole (4 eq) gave the title porphyrin (5.5%); IR (KBr) 3317 (NH), 2962, 2908, 2870 (C(CH_3)$_3$), and 2225 cm^{-1} (C≡N); ^{1}H NMR ($CDCl_3$) $\delta=-2.71$ (2H, s), 1.53 (54H, s), 7.80 (3H, t, J=2 Hz), 8.05 (2H, d J=8 Hz), 8.06 (2H, d, J=2 Hz), 8.08 (4H, d, J=2 Hz), 8.36 (2H, d, J=8 Hz), 8.72 (2H, d, J=5 Hz), 8.91 (4H, s), and 8.92 (2H, d, J=5 Hz); MS (FAB) m/z 976 (MH$^+$).

5-(4-Aminomethylphenyl)-10,15,20-tris(3,5-di-*t*-butylphenyl)porphyrin (H_2N–H_2P). According to similar procedures as those previously reported,[9] a $LiAlH_4$-reduction of the above nitrile gave H_2N–H_2P (87%); IR (KBr) 3317 (NH), 2962, 2908, and 2870 cm^{-1} (C(CH_3)$_3$); ^{1}H NMR ($CDCl_3$) $\delta=-2.66$ (2H, s), 1.55 (54H, s), 1.87 (2H, br-s), 4.24 (2H, s), 7.70 (2H, d, J=8 Hz), 7.82 (3H, t, J=2 Hz), 8.11 (2H, d, J=2 Hz), 8.12 (4H, d, J=2 Hz), 8.22 (2H, d, J=8 Hz), 8.87 (2H, d, J=5 Hz), 8.91 (2H, d, J=5 Hz), and 8.93(4H, s); MS (FAB) m/z 980 (MH$^+$).

Boc–Pro–NH–H_2P (B-1-H). 85%, mp 195—197 °C (decomp); IR (KBr) 3317 (NH), 2962, 2908, 2870 (C(CH_3)$_3$), and 1689 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) $\delta=-2.69$ (2H, s), 1.51 (9H, s), 1.54 (54H, s), 2.05 (2H, m), 2.32 (1H, m), 2.53 (1H, m), 3.57 (2H, m), 3.56 (2H, s), 4.48 (1H, m), 6.73 (1H, br-s), 7.66 (2H, d, J=8 Hz), 7.80 (3H, t, J=1 Hz), 8.09 (2H, d, J=1 Hz), 8.10 (4H, d, J=1 Hz), 8.20 (2H, d,

J=8 Hz), 8.82 (2H, d, J=4 Hz), 8.89 (2H, d, J=4 Hz), and 8.91 (4H, s); MS (FAB) m/z 1177 (MH^+).

Boc–Pro_2–NH–H_2P (B-2-H). 82%, mp 189—192 °C (decomp); IR (KBr) 3317 (NH), 2962, 2877 ($C(CH_3)_3$), and 1689 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=−2.77 (2H, s), 1.51 (9H, s), 1.54 (54H, s), 1.80—2.35 (8H, m), 3.75—3.82 (4H, m), 4.33—4.68 (2H, m), 4.71—5.04 (2H, m), 6.13 (1H, br-s), 7.60 (2H, d, J=8 Hz), 7.80 (3H, s), 8.07 (2H, s), 8.09 (4H, s), 8.16 (2H, d, J=8 Hz), 8.83 (2H, d, J=2 Hz), 8.86 (2H, d, J=2 Hz), and 8.89 (4H, s); MS (FAB) m/z 1274 (MH^+).

Boc–Pro_3–NH–H_2P (B-3-H). 95%, mp 195—198 °C (decomp); IR (KBr) 3317 (NH), 2962, 2908, 2877 ($C(CH_3)_3$), and 1651 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=−2.70 (2H, s), 1.51 (9H, s), 1.53 (54H, s), 1.80—2.29 (12H, m), 3.67—3.95 (6H, m), 4.23—4.70 (3H, m), 4.80 (2H, br-d), 6.50 (1H, br-s), 7.67 (2H, d, J=8 Hz), 7.97 (3H,s), 8.06 (2H, s), 8.08 (4H,s), 8.18 (2H, d, J=8 Hz), 8.80 (2H, d, J=2 Hz), 8.86 (2H, d, J=2Hz), and 8.90 (4H, s); MS (FAB) m/z 1371 (MH^+).

Boc–Pro_4–NH–H_2P (B-4-H). 78%, mp 188—189 °C (decomp); IR (KBr) 3317 (NH), 2962, 2877 ($C(CH_3)_3$), and 1643 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=−2.70 (2H, s), 1.51 (9H, s), 1.53 (54H, s), 1.80—2.30 (16H, m), 3.24—3.90 (8H, m), 4.25—4.58 (4H, m), 4.73—4.90 (2H, m), 5.99 (1H, br-s), 7.62 (2H, d, J=8 Hz), 7.80 (3H, t, J=2 Hz), 8.07 (2H, d, J=2 Hz), 8.08 (4H, d, J=2 Hz), 8.17 (2H, d, J=8 Hz), 8.81 (2H, d, J=2 Hz), 8.87 (2H, d, J=2 Hz), and 8.89 (4H, s); MS (FAB) m/z 1468 (MH^+).

Boc–Pro_5–NH–H_2P (B-5-H). 85%, mp 188—189 °C (decomp); IR (KBr) 3317 (NH), 2962, 2870 ($C(CH_3)_3$), and 1643 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=−2.70 (2H, s), 1.51 (9H, s), 1.53 (54H, s), 1.85—2.28 (20H, m), 3.30—3.88 (10H, m), 4.20—4.60 (5H, m), 4.68—4.90 (2H, m), 6.60 (1H, br-s), 7.58 (2H, d, J=8 Hz), 7.78 (3H, t, J=2 Hz), 8.04 (2H, d, J=2 Hz), 8.06 (4H, d, J=2 Hz), 8.16 (2H, d, J=8 Hz), 8.80 (2H, d, J=2 Hz), 8.87 (2H, d, J=2 Hz), and 8.90 (4H, s); MS (FAB) m/z 1565 (MH^+).

Boc–Pro_6–NH–H_2P (B-6-H). 78%, mp 188—189 °C (decomp); IR (KBr) 3317 (NH), 2962, 2908, 2870 ($C(CH_3)_3$), and 1712 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=−2.70 (2H, s), 1.51 (9H, s), 1.53 (54H, s), 1.80—2.32 (24H, m), 3.55—3.82 (12H, m), 4.22—4.58 (6H, m), 4.68—4.78 (2H, m), 6.71 (1H, br-s), 7.58 (2H, d, J=8 Hz), 7.78 (3H, t, J=2 Hz), 8.06 (2H, d, J=2 Hz), 8.08 (4H, d, J=2 Hz), 8.15 (2H, d, J=8 Hz), 8.78 (2H, d, J=2 Hz), 8.88 (2H, d, J=2 Hz), and 8.99 (4H, s); MS (FAB) m/z 1662 (MH^+).

Boc–Pro_7–NH–H_2P (B-7-H). 72%, mp 233—237 °C (decomp); IR (KBr) 3317 (NH), 2962, 2877 ($C(CH_3)_3$), and 1643 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=−2.69 (2H, s), 1.53 (9H, s), 1.54 (54H, s), 1.85—2.29 (28H, m), 3.56—3.80 (14H, m), 4.25—4.60 (7H, m), 4.65—4.72 (2H, m), 6.32 (1H, br-s), 7.61 (2H, d, J=8 Hz), 7.82 (3H, t, J=2 Hz), 8.07 (2H, d, J=2 Hz), 8.09 (4H, d, J=2 Hz), 8.17 (2H, d, J=8 Hz), 8.81 (2H, d, J=2 Hz), 8.87 (2H, d, J=2 Hz), and 8.90 (4H, s); MS (FAB) m/z 1759 (MH^+).

Boc–Pro_8–NH–H_2P (B-8-H). 68%, mp 274—276 °C (decomp); IR (KBr) 3317 (NH), 2962, 2877 ($C(CH_3)_3$), and 1643 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=−2.70 (2H, s), 1.52 (9H, s), 1.54 (54H, s), 1.83—2.31 (32H, m), 3.55—3.82 (16H, m), 4.26—4.59 (8H, m), 4.66—4.70 (2H, m), 6.85 (1H, br-s), 7.62 (2H, d, J=8 Hz), 7.84 (3H, t, J=2 Hz), 8.09 (2H, d, J=2 Hz), 8.12 (4H, d, J=2 Hz), 8.15 (2H, d, J=8 Hz), 8.83 (2H, d, J=2 Hz), 8.90 (2H, d, J=2 Hz), and 8.91 (4H, s); MS (FAB) m/z 1856 (MH^+).

ZnP–CO–NH–H_2P (Z-0-H). 63%; UV (EtOH) 425, 514, 555, 597, and 647 nm; Fluorescence (EtOH) 605, 650, and 715 nm; IR (KBr) 3317 (NH), 2954, 2893 ($C(CH_3)_3$), and 1674 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=−2.70 (2H, s), 1.53 (108H, s), 4.00 (2H, s), 4.88 (1H, dd, J=5 and 16 Hz), 4.96 (1H, dd, J=6 and 16 Hz), 6.42 (1H, br-s), 7.71 (2H, d, J=8 Hz) 7.78 (2H, d, J=8 Hz), 7.79 (6H, t, J=2 Hz), 8.09 (6H, d, J=2 Hz), 8.11 (6H, d, J=2 Hz), 8.28 (2H, d, J=8 Hz), 8.32 (2H, d, J=8 Hz), 8.89 (2H, d, J=4 Hz), 8.90 (2H, d, J=4 Hz), 8.93 (4H, s), 9.02 (2H, d, J=5 Hz), 9.05 (2H, d, J=5 Hz), and 9.06 (4H, s); MS (FAB) m/z 2033 (MH^+, for ^{64}Zn). Found: m/z 2033.1851. Calcd for $C_{139}H_{158}N_9O^{64}Zn$: MH^+, 2033.1881.

ZnP–CO–Pro–NH–H_2P (Z-1-H). 85%; UV (EtOH) 424, 515, 558, 597, and 649 nm; Fluorescence (EtOH) 603, 650, and 716 nm; IR (KBr) 3309 (NH), 2954, 2870 ($C(CH_3)_3$) 1681, and 1643 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=−2.69 (2H, s), 1.53 (108H, s), 2.04 (1H, m), 2.16 (1H, m), 2.47 (1H, m), 2.63 (1H, m), 3.77 (1H, m), 3.89 (1H, m), 4.04 (2H, s), 4.64 (1H, dd, J=5 and 16 Hz), 4.84 (1H, m), 4.94 (1H, dd, J=6 and 16 Hz), 6.64 (1H, br-s), 7.66 (2H, d, J=8 Hz) 7.68 (2H, d, J=8 Hz), 7.77 (3H, t, J=2 Hz), 7.79 (3H, t, J=2 Hz), 8.07 (6H, d, J=2 Hz), 8.09 (6H, d, J=2 Hz), 8.23 (2H, d, J=8 Hz), 8.28 (2H, d, J=8 Hz), 8.86 (2H, d, J=4 Hz), 8.87 (2H, d, J=4 Hz), 8.88 (4H,s), 8.97 (2H, d, J=5 Hz), 8.98 (2H, d, J=5 Hz), and 9.02 (4H, s); MS (FAB) m/z 2130 (MH^+, for ^{64}Zn). Found: m/z 2130.2440. Calcd for $C_{144}H_{165}N_{10}O_2{}^{64}Zn$: MH^+, 2130.2408.

ZnP–CO–Pro_2–NH–H_2P (Z-2-H). 85%; UV (EtOH) 424, 514, 556, 596, and 650 nm; Fluorescence (EtOH) 603, 650, and 716 nm; IR (KBr) 3317 (NH), 2954, 2870 ($C(CH_3)_3$), and 1643 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=−2.70 (2H, s), 1.52 (108H, s), 1.88—2.40 (8H, m), 3.45 (2H, m), 3.66 (2H, m), 4.02 (2H, s), 4.71 (2H, m), 4.83 (2H, br-dd), 6.55 (1H, br-s), 7.64 (2H, d, J=8 Hz), 7.66 (2H, d, J=8 Hz), 7.78 (3H, t, J=2 Hz), 7.79 (3H, t, J=2 Hz), 8.09 (4H, d, J=2 Hz), 8.11 (8H, d, J=2 Hz), 8.20 (2H, d, J=8 Hz), 8.23 (2H, d, J=8 Hz), 8.84 (2H, d, J=4 Hz), 8.89 (2H, d, J=4 Hz), 8.89 (4H, s), 8.97(2H, d, J=4 Hz), 9.01 (2H, d, J=4 Hz), and 9.01 (4H, s); MS (FAB) m/z 2227 (MH^+, for ^{64}Zn). Found: m/z 2227.2875. Calcd for $C_{149}H_{172}N_{11}O_3{}^{64}Zn$: MH^+, 2227.2936.

ZnP–CO–Pro_3–NH–H_2P (Z-3-H). 74%; UV (EtOH) 424, 515, 557, 595, and 649 nm; Fluorescence (EtOH) 604, 651, and 717 nm; IR (KBr) 3309 (NH), 2954, 2870 ($C(CH_3)_3$), and 1643 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=−2.70 (2H, s), 1.53 (108H, s), 1.90—2.40 (12H, m), 3.61—4.03 (6H, m), 4.05 (2H, s), 4.45 (1H, m), 4.67 (2H, m), 4.86 (2H, m), 5.37 (1H, br-s), 7.60 (2H, d, J=8 Hz), 7.76 (2H, d, J=8 Hz), 7.78 (6H, t, J=2 Hz), 8.04 (4H, d, J=2 Hz), 8.07 (8H, d, J=2 Hz), 8.18 (2H, d, J=8 Hz), 8.17 (2H, d, J=8 Hz), 8.82 (2H, d, J=4 Hz), 8.87 (2H, d, J=4 Hz), 8.89 (4H, s), 8.96 (2H, d, J=5 Hz), 8.97 (2H, d, J=5 Hz), and 9.00 (4H, s); MS (FAB) m/z 2324 (MH^+, for ^{64}Zn). Found: m/z 2324.3459. Calcd for $C_{154}H_{179}N_{12}O_4{}^{64}Zn$: MH^+, 2324.3464.

ZnP–CO–Pro_4–NH–H_2P (Z-4-H). 60%; UV (EtOH) 424, 516, 555, 595, and 649 nm; Fluorescence (EtOH) 603, 650, and 717 nm; IR (KBr) 3317 (NH), 2960, 2870 ($C(CH_3)_3$), and 1644 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=−2.71 (2H, s), 1.51 (108H, s), 1.82—2.33 (16H, m), 3.45—3.87 (8H, m), 3.95 (2H, s), 4.63—4.92 (4H, m), 4.80 (2H, d, $J=5$ Hz), 4.87 (1H, br), 7.58 (2H, d, $J=8$ Hz), 7.63 (2H, d, $J=8$ Hz), 7.76 (6H, t, $J=2$ Hz), 8.06 (6H, d, $J=1$ Hz), 8.07 (6H, d, $J=1$ Hz), 8.14 (2H, d, $J=8$ Hz), 8.18 (2H, d, $J=8$ Hz), 8.80 (2H, d, $J=4$ Hz), 8.83 (2H, d, $J=4$ Hz), 8.89 (4H, s), 8.93 (2H, d, $J=4$ Hz), 8.96 (2H, d, $J=4$ Hz), and 8.99 (4H, s); MS (FAB) m/z 2421 (MH$^+$, for ^{64}Zn). Found: m/z 2421.4021. Calcd for $C_{159}H_{186}N_{13}O_5{}^{64}Zn$: MH$^+$, 2421.3992.

ZnP–CO–Pro$_5$–NH–H$_2$P (Z-5-H). 65%; UV (EtOH) 424, 513, 556, 596, and 648 nm; Fluorescence (EtOH) 604, 651, and 717 nm; IR (KBr) 3320 (NH), 2962, 2870 (C-$(CH_3)_3$), and 1643 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) $\delta=-2.70$ (2H, s), 1.53 (108H, s), 1.82—2.28 (20H, m), 3.61—3.95 (10H, m), 4.01 (1H, br-d), 4.03 (1H, br-d), 4.47—4.88 (5H, m), 4.77 (2H, br-d), 6.23 (1H, br-s), 7.58 (2H, d, $J=8$ Hz), 7.64 (2H, d, $J=8$ Hz), 7.77 (3H, t, $J=2$ Hz), 7.78 (3H, t, $J=2$ Hz), 8.07 (4H, d, $J=2$ Hz), 8.08 (8H, d, $J=2$ Hz), 8.14 (2H, d, $J=8$ Hz), 8.15 (2H, d, $J=8$ Hz), 8.80 (2H, d, $J=5$ Hz), 8.88 (2H, d, $J=5$ Hz), 8.89 (4H, s), 8.96 (2H+2H, d, $J=4$ Hz), and 9.01 (2H, d, $J=4$ Hz); MS (FAB) m/z 2518 (MH$^+$, for ^{64}Zn).

ZnP–CO–Pro$_6$–NH–H$_2$P (Z-6-H). 74%; UV (EtOH) 424, 515, 555, 596, and 649 nm; Fluorescence (EtOH) 604, 651, and 716 nm; IR (KBr) 3317 (NH), 2954, 2870 (C-$(CH_3)_3$), and 1643 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) $\delta=-2.70$ (2H, s), 1.52 (108H, s), 1.84—2.33 (24H, m), 3.42—3.98 (12H, m), 4.01 (1H, br-d), 4.04(1H, br-d), 4.52—4.88 (6H, m), 4.77 (2H, d, $J=5$ Hz), 5.12 (1H, br-s), 7.58 (2H, d, $J=8$ Hz), 7.65 (2H, d, $J=8$ Hz), 7.76 (3H, t, $J=2$ Hz), 7.78 (3H, t, $J=2$ Hz), 8.07 (4H, d, $J=2$ Hz), 8.08 (8H, d, $J=2$ Hz), 8.16 (2H, d, $J=8$ Hz), 8.17 (2H, d, $J=8$ Hz), 8.88 (2H, d, $J=4$ Hz), 8.87 (2H, d, $J=4$ Hz), 8.89 (4H, s), 8.96 (2H, d, $J=5$ Hz), 8.97 (2H, d, $J=5$ Hz), and 8.99 (4H, s); MS (FAB) m/z 2615 (MH$^+$, for ^{64}Zn).

ZnP–CO–Pro$_7$–NH–H$_2$P (Z-7-H). 72%; UV (EtOH) 424, 514, 556, 597, and 649 nm; Fluorescence (EtOH) 604, 651, and 716 nm; IR (KBr) 3317 (NH), 2954, 2870 (C-$(CH_3)_3$), and 1643 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) $\delta=-2.70$ (2H, s), 1.52 (108H, s), 1.81—2.28 (28H, m), 3.57—3.96 (14H, m), 4.01 (2H, s), 4.61—4.85 (7H, m), 4.74 (2H, d, $J=7$ Hz), 6.63 (1H, br-s), 7.57 (2H, d, $J=8$ Hz), 7.64 (2H, d, $J=8$ Hz), 7.78 (4H, t, $J=2$ Hz), 7.79 (2H, t, $J=2$ Hz), 8.07 (12H, d, $J=2$ Hz), 8.15 (2H, d, $J=8$ Hz), 8.16 (2H, d, $J=8$ Hz), 8.79 (2H, d, $J=4$ Hz), 8.87 (2H, d, $J=4$ Hz), 8.88 (4H, s), 8.97 (2H, d, $J=5$ Hz), 8.98 (2H, d, $J=5$ Hz), and 8.99 (4H, s); MS (FAB) m/z 2712 (MH$^+$, for ^{64}Zn).

ZnP–CO–Pro$_8$–NH–H$_2$P (Z-8-H). 68%; UV (EtOH) 424, 514, 556, 597, and 648 nm; Fluorescence (EtOH) 604, 652, and 716 nm; IR (KBr) 3317 (NH), 2954, 2870 (C-$(CH_3)_3$), and 1643 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) $\delta=-2.70$ (2H, s), 1.52 (108H, s), 1.80—2.28 (32H, m), 3.55—3.95 (16H, m), 4.10 (2H, s), 4.60—4.85 (8H, m), 4.72 (2H, d, $J=7$ Hz), 6.75 (1H, br-s), 7.55 (2H, d, $J=8$ Hz), 7.63 (2H, d, $J=8$ Hz), 7.76 (4H, t, $J=2$ Hz), 7.78 (2H, t, $J=2$ Hz), 8.06 (12H, d, $J=2$ Hz), 8.15 (2H, d, $J=8$ Hz), 8.16 (2H, d, $J=8$ Hz), 8.79 (2H, d, $J=4$ Hz), 8.88 (2H, d, $J=4$ Hz), 8.89 (4H, s), 8.97 (2H, d, $J=5$ Hz), 8.99 (2H, d, $J=5$ Hz), and 9.00 (4H, s); MS (FAB) m/z 2809 (MH$^+$, for ^{64}Zn).

H$_2$P–CO–NH–ZnP (H-0-Z). 78%; UV (EtOH) 425, 513, 557, 599, and 649 nm; Fluorescence (EtOH) 604, 651, and 717 nm; IR (KBr) 3317 (NH), 2954, 2908, 2870 (C-$(CH_3)_3$), and 1689 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) $\delta=-2.68$ (2H, s), 1.51 (108H, s), 4.02 (2H, s), 4.89(2H, br-s), 6.39 (1H, br-s), 7.73 (2H, d, $J=8$ Hz), 7.77 (6H, t, $J=2$ Hz), 7.78 (2H, d, $J=8$ Hz), 8.08 (6H, d, $J=2$ Hz), 8.10 (6H, d, $J=2$ Hz), 8.26 (2H, d, $J=8$ Hz), 8.31 (2H, d, $J=8$ Hz), 8.87 (2H, d, $J=4$ Hz), 8.88 (2H, d, $J=4$ Hz), 8.91 (4H, s), 8.99 (2H, d, $J=4$ Hz), 9.02 (2H, d, $J=4$ Hz), and 9.03 (4H, s); MS (FAB) m/z 2033 (MH$^+$, for ^{64}Zn). Found: m/z 2033.1820. Calcd for $C_{139}H_{158}N_9O{}^{64}Zn$: MH$^+$, 2033.1881.

H$_2$P–CO–Pro–NH–ZnP (H-1-Z). 73%; UV (EtOH) 424, 513, 557, 595, and 648 nm; Fluorescence (EtOH) 604, 650, and 716 nm; IR (KBr) 3317 (NH), 2954, 2870 (C-$(CH_3)_3$) 1681, and 1635 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) $\delta=-2.70$ (2H, s), 1.52 (108H, s), 2.03 (1H, m), 2.15 (1H, m), 2.45 (1H, m), 2.60 (1H, m), 3.75 (1H, m), 3.88 (1H, m), 4.01 (2H, s), 4.62 (1H, dd, $J=5$ and 16 Hz), 4.82 (1H, m), 4.90 (1H, dd, $J=6$ and 16 Hz), 5.64 (1H, br-s), 7.65 (2H, d, $J=8$ Hz), 7.68 (2H, d, $J=8$ Hz), 7.77 (3H, t, $J=2$ Hz), 7.78 (3H, t, $J=2$ Hz), 8.06 (6H, d, $J=2$ Hz), 8.09 (6H, d, $J=2$ Hz), 8.22 (2H, d, $J=8$ Hz), 8.26 (2H, d, $J=8$ Hz), 8.85 (2H, d, $J=4$ Hz), 8.86 (2H, d, $J=4$ Hz), 8.87 (4H, s), 8.96 (2H, d, $J=5$ Hz), 8.98 (2H, d, $J=5$ Hz), and 9.00 (4H, s); MS (FAB) m/z 2130 (MH$^+$, for ^{64}Zn). Found: m/z 2130.2424. Calcd for $C_{144}H_{165}N_{10}O_2{}^{64}Zn$: MH$^+$, 2130.2408.

H$_2$P–CO–Pro$_2$–NH–ZnP (H-2-Z). 83%; UV (EtOH) 424, 514, 556, 597, and 648 nm; Fluorescence (EtOH) 604, 650, and 716 nm; IR (KBr) 3325 (NH), 2962, 2870 (C-$(CH_3)_3$), and 1643 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) $\delta=-2.70$ (2H, s), 1.53 (108H, s), 1.89—2.42 (8H, m), 3.48 (2H, m), 3.64 (2H, m), 4.05 (2H, s), 4.71 (2H, m), 4.83 (2H, br-dd), 6.64 (1H, br-s), 7.62 (2H, d, $J=8$ Hz), 7.64 (2H, d, $J=8$ Hz), 7.77 (3H, t, $J=2$ Hz), 7.78 (3H, t, $J=2$ Hz), 8.08 (4H, d, $J=2$ Hz), 8.09 (8H, d, $J=2$ Hz), 8.18 (2H, d, $J=8$ Hz), 8.21 (2H, d, $J=8$ Hz), 8.84 (2H, d, $J=4$ Hz), 8.88 (2H, d, $J=4$ Hz), 8.89 (4H, s), 8.96 (2H, d, $J=4$ Hz), 8.99 (4H, s), and 9.00 (2H, d, $J=4$ Hz); MS (FAB) m/z 2227 (MH$^+$, for ^{64}Zn). Found: m/z 2227.2814. Calcd for $C_{149}H_{172}N_{11}O_3{}^{64}Zn$: MH$^+$, 2227.2936.

H$_2$P–CO–Pro$_3$–NH–ZnP (H-3-Z). 85%; UV (EtOH) 424, 514, 557, 597, and 647 nm; Fluorescence (EtOH) 604, 651, and 717 nm; IR (KBr) 3309 (NH), 2954, 2908, 2870 (C-$(CH_3)_3$), and 1643 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) $\delta=-2.70$ (2H, s), 1.53 (108H, s), 1.80—2.25 (12H, m), 3.35—3.73 (6H, m), 4.17 (2H, s) 4.28—4.88 (3H, m), 4.70 (1H, d, $J=8$ Hz), 4.73 (1H, d, $J=8$ Hz), 6.83 (1H, br-s), 7.57 (2H, d, $J=8$ Hz), 7.66 (2H, d, $J=8$ Hz), 7.78 (6H, t, $J=2$ Hz), 8.08 (6H, d, $J=2$ Hz), 8.09 (6H, d, $J=2$ Hz), 8.13 (2H, d, $J=8$ Hz), 8.15 (2H, d, $J=8$ Hz), 8.88 (4H, s), 8.90 (4H, s), 8.96 (2H, d, $J=4$ Hz), 8.98 (2H, d, $J=4$ Hz), and 9.00 (4H, s); MS (FAB) m/z 2324 (MH$^+$, for ^{64}Zn). Found: m/z 2324.3367. Calcd for $C_{154}H_{179}N_{12}O_4{}^{64}Zn$: MH$^+$, 2324.3464.

H$_2$P–CO–Pro$_4$–NH–ZnP (H-4-Z). 67%; UV (EtOH) 424, 516, 557, 599, and 648 nm; Fluorescence (EtOH) 603, 650, and 716 nm; IR (KBr) 3310 (NH), 2962, 2870 (C-$(CH_3)_3$), and 1643 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) $\delta=-2.71$ (2H, s), 1.51 (108H, s), 1.82—2.35 (16H, m), 3.55—3.95 (8H, m), 4.02 (2H, s) 4.30—4.88 (6H, m), 5.75 (1H, br-s), 7.58 (2H, d, $J=8$ Hz), 7.64 (2H, d, $J=8$ Hz), 7.77 (6H, t, $J=2$ Hz), 8.05 (6H, d, $J=2$ Hz), 8.07 (6H, d, $J=2$ Hz), 8.12 (2H, d, $J=8$ Hz), 8.18 (2H, d, $J=8$ Hz), 8.83 (4H, s), 8.88 (4H, s), 8.90 (2H, d, $J=4$ Hz), 8.97 (2H, d, $J=4$ Hz), 8.98 (2H, d, $J=4$ Hz), and 8.99 (2H, d, $J=4$ Hz); MS (FAB) m/z 2421 (MH$^+$, for ^{64}Zn). Found: m/z 2421.4007. Calcd for

$C_{159}H_{186}N_{13}O_5{}^{64}Zn$: MH^+, 2421.3992.

H_2P–CO–Pro_5–NH–ZnP (H-5-Z). 68%; UV (EtOH) 424, 514, 558, 599, and 648 nm; Fluorescence (EtOH) 604, 650, and 717 nm; IR (KBr) 3310 (NH), 2962, 2870 ($C(CH_3)_3$), and 1643 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) $\delta=-2.73$ (2H, s), 1.53 (108H, s), 1.82—2.28 (20H, m), 3.53—3.96 (10H, m), 4.03 (2H, s) 4.42—4.89 (7H, m), 5.08 (1H, br-s), 7.57 (2H, d, $J=8$ Hz), 7.64 (2H, d, $J=8$ Hz), 7.78 (6H, t, $J=2$ Hz), 8.07 (6H, d, $J=2$ Hz), 8.08 (6H, d, $J=2$ Hz), 8.14 (2H, d, $J=8$ Hz), 8.17 (2H, d, $J=8$ Hz), 8.86 (4H, s), 8.88 (4H, s), 8.94 (2H, d, $J=4$ Hz), 8.97 (2H, d, $J=4$ Hz), and 9.00 (4H, s); MS (FAB) m/z 2518 (MH^+, for ^{64}Zn).

H_2P–CO–Pro_6–NH–ZnP (H-6-Z). 68%; UV (EtOH) 424, 515, 558, 598, and 649 nm; Fluorescence (EtOH) 604, 651, and 717 nm; IR (KBr) 3317 (NH), 2954, 2870 ($C(CH_3)_3$), and 1643 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) $\delta=-2.71$ (2H, s), 1.53 (108H, s), 1.82—2.35 (24H, m), 3.55—3.95 (12H, m), 4.02 (1H, br-d), 4.05 (1H, br-d), 4.50—4.90 (6H, m), 4.77 (2H, d, $J=5$ Hz), 5.55 (1H, br-s), 7.58 (2H, d, $J=8$ Hz), 7.64 (2H, d, $J=8$ Hz), 7.76 (3H, t, $J=2$ Hz), 7.78 (3H, t, $J=2$ Hz), 8.05 (4H, d, $J=2$ Hz), 8.07 (8H, d, $J=2$ Hz), 8.16 (2H, d, $J=8$ Hz), 8.17 (2H, d, $J=8$ Hz), 8.88 (2H, d, $J=4$ Hz), 8.87 (2H, d, $J=4$ Hz), 8.90 (4H, s), 8.96 (2H, d, $J=5$ Hz), 8.97 (2H, d, $J=5$ Hz), and 9.00 (4H, s); MS (FAB) m/z 2615 (MH^+, for ^{64}Zn).

H_2P–CO–Pro_7–NH–ZnP (H-7-Z). 66%; UV (EtOH) 424, 514, 557, 598, and 649 nm; Fluorescence (EtOH) 604, 650, and 716 nm; IR (KBr) 3310 (NH), 2962, 2870 ($C(CH_3)_3$), and 1643 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) $\delta=-2.71$ (2H, s), 1.52 (108H, s), 1.82—2.37 (28H, m), 3.45—3.98 (14H, m), 4.02 (1H, br-d), 4.03 (1H, br-d), 4.63—4.88 (9H, m), 5.14 (1H, br-s), 7.57 (2H, d, $J=8$ Hz), 7.66 (2H, d, $J=8$ Hz), 7.78 (6H, m), 8.08 (12H, m), 8.17 (2H, d, $J=8$ Hz), 8.18 (2H, d, $J=8$ Hz), 8.85 (4H, s), 8.87 (4H, s), 8.91 (2H, d, $J=4$ Hz), 8.97 (4H, s), and 9.00 (2H, d, $J=4$ Hz); MS (FAB) m/z 2712 (MH^+, for ^{64}Zn).

H_2P–CO–Pro_8–NH–ZnP (H-8-Z). 57%; UV (EtOH) 424, 514, 558, 599, and 648 nm; Fluorescence (EtOH) 604, 652, and 716 nm; IR (KBr) 3310 (NH), 2954, 2870 ($C(CH_3)_3$), and 1643 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) $\delta=-2.70$ (2H, s), 1.53 (108H, s), 1.82—2.28 (32H, m), 3.57—3.95 (16H, m), 4.12 (2H, s), 4.62—4.86 (8H, m), 4.75 (2H, d, $J=7$ Hz), 6.72 (1H, br-s), 7.57 (2H, d, $J=8$ Hz), 7.65 (2H, d, $J=8$ Hz), 7.77 (4H, t, $J=2$ Hz), 7.78 (2H, t, $J=2$ Hz), 8.05 (4H, d, $J=2$ Hz), 8.06 (8H, d, $J=2$ Hz), 8.16 (2H, d, $J=8$ Hz), 8.17 (2H, d, $J=8$ Hz), 8.80 (2H, d, $J=4$ Hz), 8.87(2H, d, $J=4$ Hz), 8.89 (4H, s), 8.96 (2H, d, $J=5$ Hz), 8.99 (2H, d, $J=5$ Hz), and 9.01 (4H, s); MS (FAB) m/z 2809 (MH^+, for ^{64}Zn).

ZnP–CO–NH–FeP (Z-0-F). 84%; Fluorescence (EtOH) 604 and 658 nm; IR (KBr) 3433 (NH), 2954, 2908, 2870 ($C(CH_3)_3$), and 1689 cm^{-1} (C=O); MS (FAB) m/z 2086 ($[M-Cl]^+$, for ^{56}Fe and ^{64}Zn).

ZnP–CO–Pro–NH–FeP (Z-1-F). 80%; Fluorescence (EtOH) 603 and 658 nm; IR (KBr) 2962, 2870 ($C(CH_3)_3$), and 1681 cm^{-1} (C=O); MS (FAB) m/z 2183 ($[M-Cl]^+$, for ^{56}Fe and ^{64}Zn).

ZnP–CO–Pro_2–NH–FeP (Z-2-F). 87%; Fluorescence (EtOH) 603 and 657 nm; IR (KBr) 2954, 2870 ($C(CH_3)_3$), and 1643 cm^{-1} (C=O); MS (FAB) m/z 2280 ($[M-Cl]^+$, for ^{56}Fe and ^{64}Zn).

ZnP–CO–Pro_3–NH–FeP (Z-3-F). 82%; Fluorescence (EtOH) 603 and 657 nm; IR (KBr) 2954, 2870 ($C(CH_3)_3$), and 1643 cm^{-1} (C=O); MS (FAB) m/z 2377 ($[M-Cl]^+$, for ^{56}Fe and ^{64}Zn).

ZnP–CO–Pro_4–NH–FeP (Z-4-F). 85%; Fluorescence (EtOH) 603 and 658 nm; IR (KBr) 2962, 2870 ($C(CH_3)_3$), and 1643 cm^{-1} (C=O); MS (FAB) m/z 2474 ($[M-Cl]^+$, for ^{56}Fe and ^{64}Zn).

ZnP–CO–Pro_5–NH–FeP (Z-5-F). 88%; Fluorescence (EtOH) 603 and 658 nm; IR (KBr) 2954, 2870 ($C(CH_3)_3$), and 1651 cm^{-1} (C=O); MS (FAB) m/z 2571 ($[M-Cl]^+$, for ^{56}Fe and ^{64}Zn).

ZnP–CO–Pro_6–NH–FeP (Z-6-F). 80%; Fluorescence (EtOH) 604 and 657 nm; IR (KBr) 2954, 2870 ($C(CH_3)_3$), and 1643 cm^{-1} (C=O); MS (FAB) m/z 2668 ($[M-Cl]^+$, for ^{56}Fe and ^{64}Zn).

ZnP–CO–Pro_7–NH–FeP (Z-7-F). 75%; Fluorescence (EtOH) 603 and 657 nm; IR (KBr) 2954, 2931, 2861 ($C(CH_3)_3$), and 1643 cm^{-1} (C=O); MS (FAB) m/z 2765 ($[M-Cl]^+$, for ^{56}Fe and ^{64}Zn).

ZnP–CO–Pro_8–NH–FeP (Z-8-F). 80%; Fluorescence (EtOH) 603 and 658 nm; IR (KBr) 2954, 2870 ($C(CH_3)_3$), and 1643 cm^{-1} (C=O); MS (FAB) m/z 2862 ($[M-Cl]^+$, for ^{56}Fe and ^{64}Zn).

FeP–CO–NH–ZnP (F-0-Z). 77%; Fluorescence (EtOH) 603 and 658 nm; IR (KBr) 2962, 2870 ($C(CH_3)_3$), and 1666 cm^{-1} (C=O); MS (FAB) m/z 2086 ($[M-Cl]^+$, for ^{56}Fe and ^{64}Zn).

FeP–CO–Pro–NH–ZnP (F-1-Z). 88%; Fluorescence (EtOH) 603 and 657 nm; IR (KBr) 2954, 2870 ($C(CH_3)_3$), and 1643 cm^{-1} (C=O); MS (FAB) m/z 2183 ($[M-Cl]^+$, for ^{56}Fe and ^{64}Zn).

FeP–CO–Pro_2–NH–ZnP (F-2-Z). 85%; Fluorescence (EtOH) 603 and 656 nm; IR (KBr) 2954, 2870 ($C(CH_3)_3$), and 1643 cm^{-1} (C=O); MS (FAB) m/z 2280 ($[M-Cl]^+$, for ^{56}Fe and ^{64}Zn).

FeP–CO–Pro_3–NH–ZnP (F-3-Z). 81%; Fluorescence (EtOH) 603 and 658 nm; IR (KBr) 2954, 2908, 2870 ($C(CH_3)_3$), and 1643 cm^{-1} (C=O); MS (FAB) m/z 2377 ($[M-Cl]^+$, for ^{56}Fe and ^{64}Zn).

FeP–CO–Pro_4–NH–ZnP (F-4-Z). 80%; Fluorescence (EtOH) 603 and 657 nm; IR (KBr) 2962, 2870 ($C(CH_3)_3$), and 1650 cm^{-1} (C=O); MS (FAB) m/z 2474 ($[M-Cl]^+$, for ^{56}Fe and ^{64}Zn).

FeP–CO–Pro_5–NH–ZnP (F-5-Z). 83%; Fluorescence (EtOH) 602 and 656 nm; IR (KBr) 2954, 2870 ($C(CH_3)_3$), and 1643 cm^{-1} (C=O); MS (FAB) m/z 2571 ($[M-Cl]^+$, for ^{56}Fe and ^{64}Zn).

FeP–CO–Pro_6–NH–ZnP (F-6-Z). 85%; Fluorescence (EtOH) 603 and 657 nm; IR (KBr) 2954, 2870 ($C(CH_3)_3$), and 1643 cm^{-1} (C=O); MS (FAB) m/z 2668 ($[M-Cl]^+$, for ^{56}Fe and ^{64}Zn).

FeP–CO–Pro_7–NH–ZnP (F-7-Z). 80%; Fluorescence (EtOH) 604 and 657 nm; IR (KBr) 2960, 2870 ($C(CH_3)_3$), and 1649 cm^{-1} (C=O); MS (FAB) m/z 2766 ($[M-Cl]^+ +1$, for ^{56}Fe and ^{64}Zn).

FeP–CO–Pro_8–NH–ZnP (F-8-Z). 85%; Fluorescence (EtOH) 604 and 657 nm; IR (KBr) 2954, 2870 ($C(CH_3)_3$), and 1643 cm^{-1} (C=O); MS (FAB) m/z 2862 ($[M-Cl]^+$, for ^{56}Fe and ^{64}Zn).

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10) The following abbreviations are used in this paper; Boc– =*t*-butoxycarbonyl, EDC=1-ethyl-3-(3-dimethylaminopropyl)carbodiimide, HOBt=1-hydroxybenzotriazole, P– =4-[10,15,20-tris(3,5-di-*t*-butylphenyl)porphyrin-5-yl]phenylmethyl, TDBPP=5,10,15,20-tetrakis(3,5-di-*t*-butylphenyl)porphyrin.

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