September, 1993] *Bull. Chem. Soc. Jpn.*, ***66***, *2633—2637(1993)*

Intramolecular Interaction of Porphyrin Moieties in 2,5-Piperazinedione-Bridged Porphyrin Dimers

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(Received February 15, 1993)

Diastereomerically pure 2,5-piperazinedione-bridged *meso*-tetraarylporphyrin dimers were synthesized with easy procedures. ^{1}H NMR, UV-vis, and CD spectra showed that porphyrin moieties in the L,L-molecule interacted more strongly than those in the D,L-isomer and this interaction decreased with substitution by 3,5-di-*t*-butyl groups on the *meso*-phenyl substituents.

In photosynthetic antennae and reaction centers, interaction of chlorophyll or bacteriochlorophyll molecules in proteins affects their physical properties (absorption bands, redox potentials, and so on) compared with the corresponding monomeric molecules.[1] Synthetic oligomers of porphyrins or chlorins with hydrocarbons as the spacer were already available[2] but peptide-bridged porphyrin dimers and oligomers have never been reported to our knowledge. As the synthetic model for the natural systems, we here report the preparation of novel porphyrin dimers covalently-linked with cyclic dipeptides (2,5-piperazinediones) and the intramolecular interaction of the porphyrin moieties (Fig. 1).

Results and Discussion

Synthesis of 2,5-Piperazinedione-Bridged Porphyrins. Porphyrins covalently-linked (through an ether bond) with tyrosine of 2,5-piperazinediones **1**—**3** (see Fig. 1) were synthesized according to Schemes 1 and 2; the suffix **a** of the compound number indicates 10,15,20-tri-*p*-tolyl substituents and the suffix **b** does 3,5-di-*t*-butylphenyl. During the coupling of 2,5-piperazinedione and zinc porphyrin (**6Z**), no racemization could be observed and diastereomerically pure 2,5-piperazinedione-bridged zinc-porphyrins (**1-3Z**) were afforded. The reaction of 2,5-piperazinedione and free base porphyrin (**6H**) gave complex mixtures as the products and isolation of 2,5-piperazinedione-bridged porphyrin (**1-3H**) was very difficult. Demetallation of **1-3Z** gave diastereomerically pure **1-3H** easily and quantitatively.

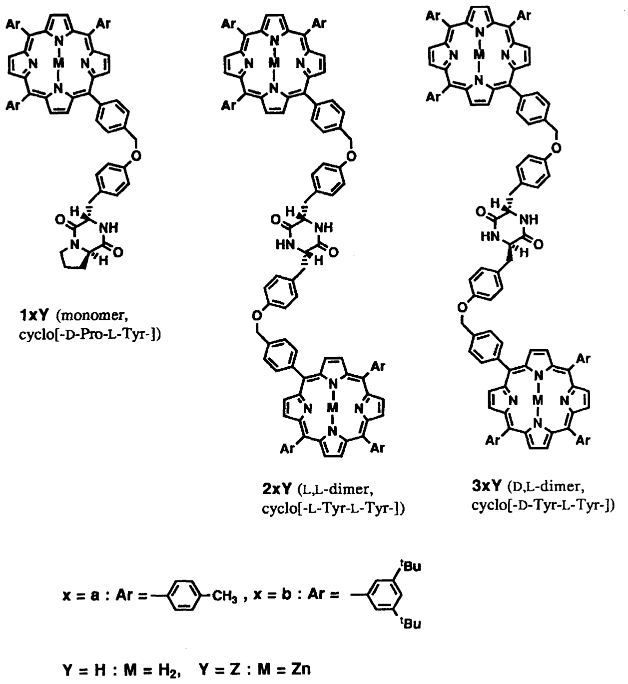
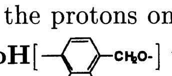
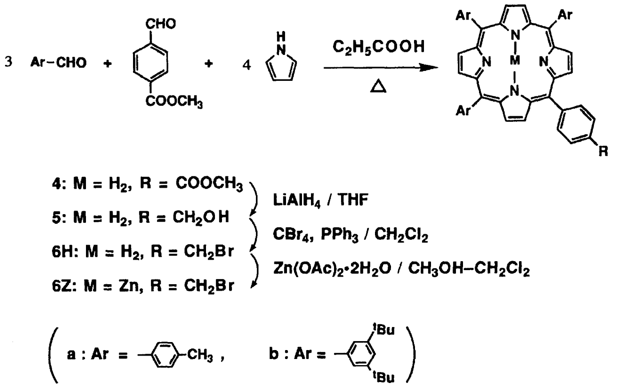


Fig. 1. Synthetic 2,5-piperazinedione-bridged porphyrins **1**—**3**.

Intramolecular Interaction in Porphyrin Dimers. The chemical shifts (δ) characteristic of porphyrin moiety in ^{1}H NMR spectrum of monomer **1aH** (>7.3 ppm) were similar to those of D,L-dimer **3aH** within 0.01—0.04 ppm difference (see Experimental part). Figure 2 shows all the δ of L,L-dimer **2aH** were high-field shifted compared with those of the diastereomeric D,L-dimer **3aH**. On the other hand, the δ of D,L-dimer **3bH** were almost similar to those of the monomer **1bH** (0—−0.02 ppm-shift) and small difference with those of L,L-dimer **2bH** (+0.02—−0.01 ppm-shift except the protons on the 5-phenyl groups: $\delta_{\mathrm{H_a}}$ and $\delta_{\mathrm{H_b}}$ of **2bH**[] were 0.08 and 0.11 ppm higher-field



Scheme 1. Synthesis of monosubstituted *meso*-tetraarylporphyrins.

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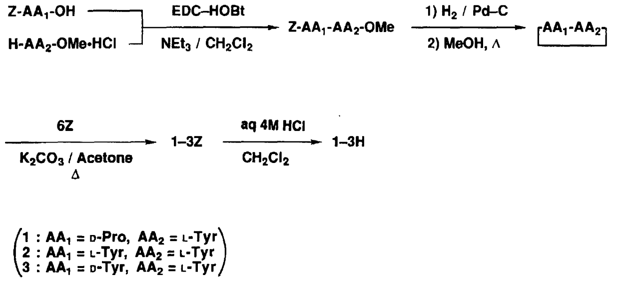

Scheme 2. Synthesis of 2,5-piperazinediones and **1**—**3** (see Ref. 6 for abbreviations).

shifted than those of **3bH**, respectively.).

These results indicated 1) the porphyrin moieties of L,L-dimer **2H** in $CDCl_3$ interacted in the molecules, the chemical shifts of which were high-field shifted by porphyrin ring current effect and the similar intramolecular interaction in D,L-dimer **3H** was small; 2) in L,L-dimer **2aH** with *p*-tolyl substituents, larger interaction was observed than in L,L-dimer **2bH** with 3,5-di-*t*-butylphenyl substituents. In L,L-dimer **2H**, both the phenylene groups of tyrosine were on the same side based on the 2,5-piperazinedione plane and those in D,L-dimer **3H** were on the opposite side. Then, the porphyrin moieties of L,L-dimer **2H** should be closer-situated each other than those of D,L-**3H**. 3,5-Di-*t*-butyl groups were sterically bulkier than *p*-methyl group[3] and disturbed the interaction of porphyrin rings.

The absorption maxima of each 4 series (**1-3aH**, **aZ**, **bH**, and **bZ**) in THF (ca. 10^{-6} mol dm^{-3}) are the same within 1 nm-difference (see Table 1). However, the half-height band-widths (Δ) of the Soret band are different in each series as shown in Fig. 3A and broadened in the following order; **2aH**>**3aH**>**1aH** (see also Table 1). The broadening of Soret bands in the dimer must be due to the exciton coupling of the porphyrin moieties in the molecule.[4] In CD spectra of the region of Soret band under the same conditions as in UV-vis spectra (Fig. 3B), monomer-**1aH** gave no peak but Cotton effect[5] was appeared in dimers **2aH** (−/+ peaks); achiral D,L-dimers **3** gave no CD peaks. These CD spectra supported the intramolecular exciton coupling in the dimer. UV-vis spectra showed that the interaction of porphyrin moieties in L,L-**2aH** was larger than in D,L-**3aH** as mentioned in the above ^{1}H NMR study. Similarly, in zinc complexes, the porphyrin–porphyrin interaction of L,L-**2aZ** was larger than that in D,L-**3aZ** from their UV-vis spectra.

On the other hand, the Δ values of the molecules with 3,5-di-*t*-butyl groups decreased in the order, **2b**>**3b**≈**1b**. Moreover, relative Δ values and relative intensities of CD peaks in the Soret region of L,L-dimer **2** decreased in the order, **2a**>**2b** (both in M=H_2 and Zn). These results showed that the porphyrin moieties of D,L-**3b** in THF hardly interacted in the molecules and those of L,L-**2b** interacted more weakly than those of L,L-**2a**. The studies on UV-vis and CD spectra indicated that 3,5-di-*t*-butyl groups suppressed the intramolecular interaction, as mentioned in the study on ^{1}H NMR spectra.

In one isomer of the diastereomeric 2,5-piperazinedione-bridged *meso*-tetraarylporphyrin dimers L,L-**2**, the porphyrin moieties interacted strongly in the molecule and substitution by 3,5-di-*t*-butyl groups on the *meso*-phenyl group (**a**→**b**) decreased the intramolecular interaction. Disturbance of π–π interaction in the porphyrin-molecules with 3,5-di-*t*-butyl groups makes such molecules highly soluble in variety of solvents, including the low-polar solvent (for example, hydrocarbons: hexane, cyclohexane, etc) in which normal porphyrins are hardly soluble because of their large aggregation. Therefore, such porphyrins with 3,5-di-*t*-butylphenyl groups might be available for the measurement of their monomeric physical properties even in high concentration and in low-polar solvents. Moreover, porphyrin-linked oligopeptides as reported here might be available for the conformational analysis of oligopeptides.

Experimental

Apparatus. All melting points were measured with a Yanagimoto micro melting point apparatus and were uncorrected. Ultraviolet and visible spectra were measured with a Shimadzu UV-3000 spectrometer. Circular dichroism spectra were measured with a JASCO J-600 spectropolarimeter. ^{1}H NMR spectra were recorded on a JEOL JMN-FX 400 instrument; chemical shift (δ) are expressed in parts per million relative to Me_4Si. FAB mass spectra were measured with a JEOL JMS-DX-300 spectrometer; samples were dissolved in $CHCl_3$ and *m*-nitrobenzyl alcohol was used as the matrix.

Materials. Dry CH_2Cl_2 and THF were prepared from fresh distillation over P_2O_5 and Na, respectively, under N_2. Dipeptides were synthesized according to the usual methods (see Scheme 2).[7] 2,5-Piperazinediones were prepared by half-day reflux of MeOH solution of dipeptides methyl ester (see Scheme 2). Porphyrins **4a**,[8] **5a**,[9] **6aH**[9] and 3,5-di-*t*-butylbenzaldehyde[10] were synthesized according to the procedures in the literature. Zinc-metallation of porphyrins (**6H**→**6Z**) was done by standard methods.[11] All porphyrins reported below were given as purple solids (mp>300°C). Other reagents and solvents were commercially available and used without purification.

5-(4-Methoxycarbonylphenyl)-10,15,20-tri-*p*-tolylporphyrin (4a): ^{1}H NMR ($CDCl_3$) δ=−2.78 (2H, s), 2.71 (9H, s), 4.11 (3H, s), 7.56 (6H, d, J=8 Hz), 8.09 (6H, d, J=8 Hz), 8.30 (2H, d, J=8 Hz), 8.43 (2H, d, J=8 Hz), 8.76 (2H, d, J=5 Hz), 8.86 (4H, s), and 8.87 (2H, d, J=5 Hz).

5-(4-Hydroxymethylphenyl)-10,15,20-tri-*p*-tolylporphyrin (5a): ^{1}H NMR ($CDCl_3$) δ=−2.78 (2H, s), 2.71 (9H, s), 5.07 (2H, d, J=4 Hz), 7.55 (6H, d, J=8 Hz), 7.76 (2H, d, J=8 Hz), 8.09 (6H, d, J=8 Hz), 8.21 (2H, d, J=8 Hz), 8.83 (2H, d, J=3 Hz), 8.85 (4H, s), and 8.86 (2H, d, J=3 Hz).

5-(4-Bromomethylphenyl)-10,15,20-tri-*p*-tolylporphyrin (6aH): ^{1}H NMR ($CDCl_3$) δ=−2.78 (2H, s), 2.71 (9H, s), 4.86 (2H, s), 7.56 (6H, d, J=8 Hz), 7.78 (2H,

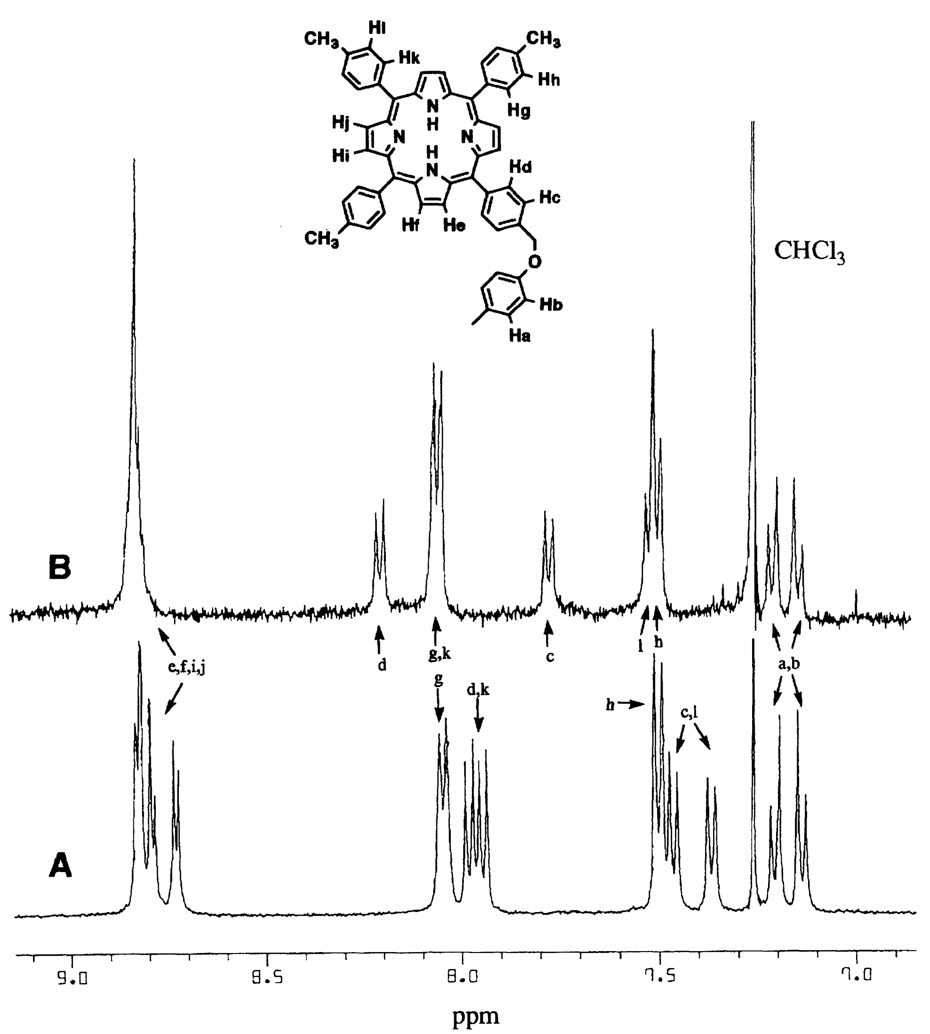

Fig. 2. ^{1}H NMR spectra of L,L-dimer **2aH** (A) and D,L-dimer **3aH** (B) in $CDCl_3$ at 298 K.

d, J=8 Hz), 8.09 (6H, d, J=8 Hz), 8.19 (2H, d, J=8 Hz), 8.81 (2H, d, J=4 Hz), 8.85 (4H, s), and 8.86 (2H, d, J=4 Hz).

5-(4-Bromomethylphenyl)-10,15,20-tri-*p*-tolylporphyrin Zinc Complex (6aZ): 92%; ^{1}H NMR ($CDCl_3$) δ=2.71 (9H, s), 4.87 (2H, s), 7.55 (6H, d, J=8 Hz), 7.78 (2H, d, J=8 Hz), 8.10 (6H, d, J=8 Hz), 8.20 (2H, d, J=8 Hz), 8.92 (2H, d, J=5 Hz), 8.96 (4H, s), and 8.97 (2H, d, J=5 Hz).

5-(4-Methoxycarbonylphenyl)-10,15,20-tris(3,5-di-*t*-butylphenyl)porphyrin (4b). Methyl 4-formylbenzoate (6.77 g, 40 mmol) and 3,5-di-*t*-butylbenzaldehyde (26.2 g, 120 mmol) were heated to reflux in 700 ml propionic acid. Pyrrole (11.1 ml, 160 mmol) was added dropwise with vigorous stirring. The reaction mixture was refluxed for 30 min and concentrated in vacuo. The residue was flash-chromatographed on silica gel (Wakogel FC-40) with CH_2Cl_2–hexane as eluants. The first purple fraction contained 5,10,15,20-tetrakis(3,5-di-*t*-butylphenyl)porphyrin. The second fraction was evaporated in vacuo and the residue was triturated in MeOH and filtered. The crystals obtained were purified by recrystallization from CH_2Cl_2–MeOH to give **4b** (6.7%); ^{1}H NMR ($CDCl_3$) δ=−2.67 (2H, s), 1.54 (54H, s), 4.12 (3H, s), 7.82 (3H, t, J=2 Hz), 8.097 (2H, d, J=2 Hz), 8.104 (4H, d, J=2 Hz), 8.35 (2H, d, J=8 Hz), 8.45

Table 1. UV-vis Spectral Data of 2,5-Piperazinedione-Bridged Porphyrins **1-3H**[a)]

	Soret	Δ		Q			
1aH	417	12.4	(1.00)	513	548.5	591.5	647.5
2aH	417.5	15.4	(1.24)	514	549	592	647.5
3aH	417	13.6	(1.10)	514	549	591	648
1aZ	424	9.6	(1.00)		556	596	
2aZ	424	12.4	(1.29)		556	596	
3aZ	424.5	10.6	(1.10)		556.5	596	
1bH	418.5	11.2	(1.00)	512	547.5	590	647
2bH	418.5	12.2	(1.09)	512.5	547.5	590	647
3bH	418.5	11.3	(1.01)	512.5	547.5	590	647
1bZ	425	8.4	(1.00)		556	595	
2bZ	425	9.7	(1.15)		556	595	
3bZ	425	8.6	(1.02)		556	595	

a) In THF, ca. 10^{-6} mol dm^{-3} at 298 K. These values show the wavelength of absorption maxima (Soret and Q bands) and the half-height band-width (Δ) of Soret band in nm. The errors of Δ were within ±0.1 nm. Parenthesis indicates relative value to the Δ in **1**.

(2H, d, J=8 Hz), 8.80 (2H, d, J=5 Hz), 8.92 (2H, d, J=5 Hz) and 8.93 (4H, s); MS m/z 1009 (MH$^+$, 100%) and 953 (M$-{}^t$Bu+2H, 66).

5-(4-Hydroxymethylphenyl)-10,15,20-tris(3,5-di-*t*-butylphenyl)porphyrin (5b). LiAlH$_4$ (120 mg, 3.16 mmol) was slowly added to ice-cooled dry THF solution (200 ml) of **4b** (1.082 g, 1.092 mmol). The solution was stirred at room temperature under N$_2$ overnight in the dark. The reaction mixture was quenched by addition of 5 ml of AcOEt followed by addition of 60 ml of aq 3 mol dm^{-3} HCl. The organic layer was separated and washed with aq 10% Na$_2$CO$_3$, dried over Na$_2$SO$_4$ and concentrated in vacuo. Purification by flash column chromatography on silica gel with CH$_2$Cl$_2$ as an eluant and recrystallization from CH$_2$Cl$_2$–MeOH gave **5b** (87%); ^{1}H NMR (CDCl$_3$) δ=-2.64 (2H, s), 1.57 (54H, s), 5.02 (2H, s), 7.74 (2H, d, J=8 Hz), 7.84 (3H, t, J=2 Hz), 8.13 (2H, d, J=2 Hz), 8.14 (4H, d, J=2 Hz), 8.26 (2H, d, J=8 Hz), 8.88 (2H, d, J=5 Hz), 8.94 (2H, d, J=5 Hz), and 8.96 (4H, s); MS m/z 981 (MH$^+$).

5-(4-Bromomethylphenyl)-10,15,20-tris(3,5-di-*t*-butylphenyl)porphyrin (6bH). After 3 h stirring of **5b** (815 mg, 0.831 mmol) and PPh$_3$ (654 mg, 2.49 mmol) under N$_2$ in the dark were added CBr$_4$ (995 mg, 2.49 mmol) and CH$_2$Cl$_2$ (180 ml) at room temperature. After stirring overnight, the reaction mixture was washed with aq 2 mol dm^{-3} HCl and aq 10% Na$_2$CO$_3$, dried over Na$_2$SO$_4$ and concentrated in vacuo. Purification by flash column chromatography on silica gel with CH$_2$Cl$_2$–hexane as eluants and recrystallization from CH$_2$Cl$_2$–MeOH gave **6bH** (97%); ^{1}H NMR (CDCl$_3$) δ=-2.69 (2H, s), 1.53 (18H, s), 1.54 (36H, s), 4.86 (2H, s), 7.79 (2H, d, J=8 Hz), 7.81 (3H, t, J=2 Hz), 8.09 (2H, d, J=2 Hz), 8.10 (4H, d, J=2 Hz), 8.23 (2H, d, J=8 Hz), 8.84 (2H, d, J=5 Hz), 8.91 (2H, d, J=5 Hz), and 8.92 (4H, s); MS m/z 1043, 1045 (MH$^+$, 83% (^{79}Br), 100 (^{81}Br)), 987, 989 (M$-{}^t$Bu+2H, 54, 69), and 964 (M$-$Br+1, 75).

5-(4-Bromomethylphenyl)-10,15,20-tris(3,5-di-*t*-butylphenyl)porphyrin Zinc Complex (6bZ). 94%; ^{1}H NMR (CDCl$_3$) δ=1.67 (54H, s), 5.01 (2H, s), 7.85 (2H, d, J=8 Hz), 7.95 (3H, br-s), 8.27 (6H, br-s), 8.36 (2H, d, J=8 Hz), 9.09 (2H, d, J=5 Hz), 9.17 (2H, d, J=5 Hz), and 9.19 (4H, s); MS m/z 1104, 1106, 1108, 1110 (M$^+$, 7% (^{64}Zn·^{79}Br), 14 (^{64}Zn·^{81}Br, ^{66}Zn·^{79}Br), 11 (^{66}Zn·^{81}Br, ^{68}Zn·^{79}Br), 6 (^{68}Zn·^{81}Br)), 1060, 1062, 1064, and 1066 (M$-$C$_3$H$_8$, 82, 100, 76, 36).

General Procedure for the Coupling of 2,5-Piperazinediones and Zinc Porphyrins. An acetone (40 ml) suspension of 2,5-piperazinedione (0.18 mmol), K$_2$CO$_3$ (0.3 mmol) and zinc porphyrin (**6Z**, 0.83 equiv) was refluxed under N$_2$ in the dark overnight. After concentrated in vacuo, the residue was purified by flash column chromatography on silica gel with CH$_2$Cl$_2$–Et$_2$O as eluants to give 2,5-piperazinedione-linked zinc porphyrin (**1-3Z**). **1-3Z** were quantitatively converted to **1-3H** by standard demetallation.[12]

1aZ: 79%; ^{1}H NMR (CDCl$_3$) δ=1.53 (2H, m), 1.81 (1H, m), 2.03 (1H, m), 2.43 (1H, m), 2.71 (9H, s), 2.90 (2H, m), 3.22 (1H, m), 3.36 (1H, m), 3.80 (1H, m), 5.35 (1H, br-d, J=2 Hz), 5.38 (2H, s), 7.03 (2H, d, J=9 Hz), 7.08 (2H, d, J=9 Hz), 7.56 (6H, d, J=8 Hz), 7.81 (2H, d, J=8 Hz), 8.10 (6H, d, J=8 Hz), 8.22 (2H, d, J=8 Hz), 8.93 (2H, d, J=5 Hz), 8.96 (4H, s), and 8.97 (2H, d, J=5 Hz); MS m/z 990, 992, 994 (M$^+$, 69% (^{64}Zn), 82 (^{66}Zn), 65 (^{68}Zn)), 731, 733, and 735 (ZnTTPCH$_2^+$, 100, 98, 64).

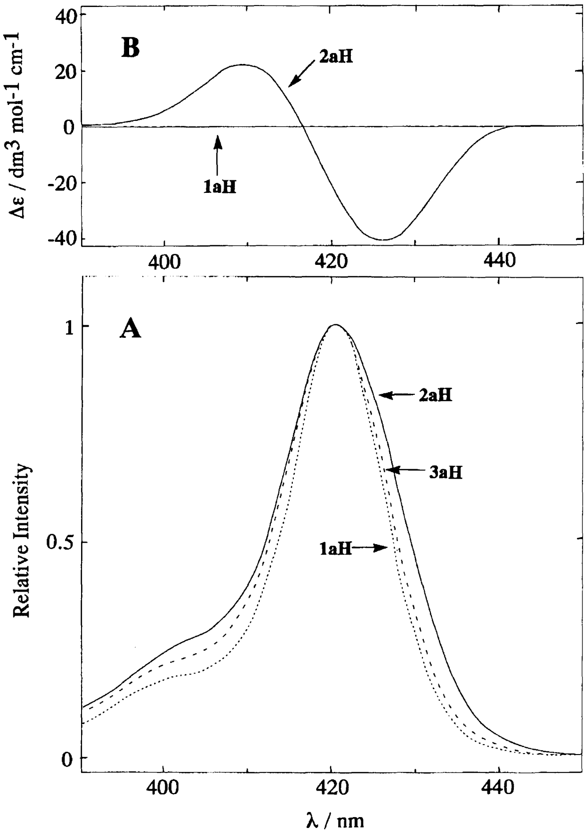

Fig. 3. UV-vis (A) and CD (B) spectra of **1-3aH** in THF. In UV-vis spectra, intensities in absorption maximum of Soret band were normalized. CD spectra of **1aH** indicated $2\times\Delta\varepsilon$ for normalization of porphyrin chromophore unit. ·····: **1aH**, ——: **2aH**, - - -: **3aH**.

1aH: ^{1}H NMR (CDCl$_3$) δ=-2.77 (2H, s), 1.77 (1H, m), 1.82 (1H, m), 1.95 (1H, m), 2.26 (1H, m), 2.70 (9H, s), 3.08 (1H, m), 3.10—3.20 (2H, m), 3.45 (1H, m), 3.66 (1H, m), 4.22 (1H, m), 5.20 (2H, s), 5.89 (1H, br), 7.14 (2H, d, J=9 Hz, Tyr-phenylene), 7.24 (2H, d, J=9 Hz, Tyr-phenylene), 7.55 (6H, d, J=8 Hz, 10,15,20-*m*-H), 7.81 (2H, d, J=8 Hz, 5-*m*-H), 8.10 (6H, d, J=8 Hz, 10,15,20-*o*-H), 8.24 (2H, d, J=8 Hz, 5-*o*-H), 8.83 (2H, d, J=5 Hz, 2,8- or 3,7-H), 8.86 (4H, s, 12,13,17,18-H), and 8.87 (2H, d, J=5 Hz, 2,8- or 3,7-H); MS m/z 929 (MH$^+$, 100%) and 669 (H$_2$TTPCH$_2^+$, 55).

2aZ: 45%; MS m/z 1787, 1789, 1791, 1793, 1795 (MH$^+$, 21% (^{64}Zn·^{64}Zn), 15 (^{64}Zn·^{66}Zn), 21 (^{64}Zn·^{68}Zn, ^{66}Zn·^{66}Zn), 15 (^{66}Zn·^{68}Zn), 8 (^{68}Zn·^{68}Zn)), 731, 733, and 735 (ZnTTPCH$_2^+$, 100, 90, 62).

2aH: ^{1}H NMR (CDCl$_3$) δ=-2.77 (4H, s), 2.46 (2H, dd, J=9 and 14 Hz), 2.61 (6H, s), 2.66 (12H, s), 3.17 (2H, dd, J=3 and 14 Hz), 4.19 (2H, dt, J=8 and 2 Hz), 5.11 (2H, d, J=12 Hz), 5.19 (2H, d, J=12 Hz), 5.86 (2H, d, J=1 Hz), 7.14 (4H, d, J=9 Hz, Tyr-phenylene), 7.20 (4H, d, J=9 Hz, Tyr-phenylene), 7.37 (4H, d, J=8 Hz, 5- or 15-*m*-H), 7.47 (4H, d, J=8 Hz, 5- or 15-*m*-H), 7.50 (8H, d, J=8 Hz, 10, 20-*m*-H), 7.93 (4H, d, J=8 Hz, 5- or 15-*o*-H), 7.98 (4H, d, J=8 Hz, 5- or 15-*o*-H), 8.06 (8H, d, J=8 Hz, 10,20-*o*-H), 8.73 (4H, d, J=5 Hz, 2,8-, 3,7-, 12,18- or 13,17-H), 8.79 (4H, d, J=5 Hz, 2,8-, 3,7-, 12,18- or 13,17-H), and 8.83 (8H, d,

$J=5$ Hz, 2,8-, 3,7-, 12,18- and/or 13,17-H); MS m/z 1664 (MH$^+$+1).

3aZ: 31%; MS m/z 1787, 1789, 1791, 1793, 1795 (MH$^+$, 20% (^{64}Zn·^{64}Zn), 27 (^{64}Zn·^{66}Zn), 29 (^{64}Zn·^{68}Zn, ^{66}Zn·^{66}Zn), 17 (^{66}Zn·^{68}Zn), 9 (^{68}Zn·^{68}Zn)), 731, 733, and 735 (ZnTTPCH$_2^+$, 100, 94, 55).

3aH: ^{1}H NMR (CDCl$_3$) $\delta=-2.77$ (4H, s), 2.66 (12H, s), 2.69 (6H, s), 2.96 (2H, dd, $J=8$ and 14 Hz), 3.26 (2H, dd, $J=4$ and 14 Hz), 3.83 (2H, br-d, $J=7$ Hz), 5.37 (4H, s), 5.75 (2H, s), 7.15 (4H, d, $J=9$ Hz, Tyr-phenylene), 7.21 (4H, d, $J=9$ Hz, Tyr-phenylene), 7.51 (8H, d, $J=8$ Hz, 10, 20-*m*-H), 7.52 (4H, d, $J=8$ Hz, 15-*m*-H), 7.78 (4H, d, $J=8$ Hz, 5-*m*-H), 8.06 (12H, d, $J=8$ Hz, 10,15,20-*o*-H), 8.21 (4H, d, $J=8$ Hz, 5-*o*-H), 8.82 (4H, d, $J=4$ Hz, 2,8 or 3,7-H), 8.84 (8H, s, 12,13,17,18-H), and 8.85 (4H, d, $J=4$ Hz, 2,8- or 3, 7-H); MS m/z 1663 (MH$^+$).

1bZ: 66%; ^{1}H NMR (CDCl$_3$) $\delta=1.30$—1.55 (2H, m), 1.53 (18H, s), 1.54 (36H, s), 1.76 (1H, m), 1.93 (1H, m), 2.73—2.86 (3H, m), 3.06—3.09 (2H, m), 3.49 (1H, br), 5.19 (1H, br-d, $J=2$ Hz), 5.37 (2H, s), 6.94 (2H, d, $J=8$ Hz), 7.07 (2H, d, $J=9$ Hz), 7.80 (3H, d, $J=2$ Hz), 7.81 (2H, d, $J=9$ Hz), 8.10 (6H, m), 8.21 (2H, d, $J=8$ Hz), 8.95 (2H, d, $J=4$ Hz), 9.01 (4H, s), and 9.01 (2H, d, $J=4$ Hz); MS m/z 1285, 1287, 1289 (MH$^+$, 100% (^{64}Zn), 83 (^{66}Zn), 48 (^{68}Zn)), 1025, 1027, and 1029 (ZnTDBPCH$_2^+$, 68, 66, 44).

1bH: ^{1}H NMR (CDCl$_3$) $\delta=-2.69$ (2H, s), 1.526 (18H, s), 1.531 (36H, s), 1.77 (1H, m), 1.85 (1H, m), 1.95 (1H, m), 2.27 (1H, m), 3.08 (1H, dd, $J=4$ and 14 Hz), 3.13 (1H, dd, $J=6$ and 10 Hz), 3.17 (1H, dd, $J=6$ and 14 Hz), 3.46 (1H, tt, $J=2$ and 3 Hz), 3.67 (1H, dt, $J=12$ and 8 Hz), 4.23 (1H, dt, $J=6$ and 4 Hz), 5.41 (2H, s), 5.91 (1H, d, $J=4$ Hz), 7.14 (2H, d, $J=9$ Hz, Tyr-phenylene), 7.24 (2H, d, $J=9$ Hz, Tyr-phenylene), 7.79 (3H, t, $J=2$ Hz, 10,15,20-*p*-H), 7.82 (2H, d, $J=8$ Hz, 5-*m*-H), 8.08 (2H, d, $J=2$ Hz, 15-*o*-H), 8.09 (4H, d, $J=2$ Hz, 10,20-*o*-H), 8.27 (2H, d, $J=8$ Hz, 5-*o*-H), 8.86 (2H, d, $J=5$ Hz, 2,8- or 3,7-H), 8.90 (2H, d, $J=5$ Hz, 2, 8- or 3,7-H), and 8.91 (4H, s, 12,13,17,18-H); MS m/z 1223 (MH$^+$, 87%) and 964 (H$_2$TDBPCH$_2^+$+1, 100).

2bZ: 44%; MS m/z 2376, 2378, 2380, 2382, 2384 (MH$^+$, 4% (^{64}Zn·^{64}Zn), 4 (^{64}Zn·^{66}Zn), 6 (^{64}Zn·^{68}Zn, ^{66}Zn·^{66}Zn), 4 (^{66}Zn·^{68}Zn), 2 (^{68}Zn·^{68}Zn)), 1025, 1027, and 1029 (ZnTDBPCH$_2^+$, 100, 92, 64).

2bH: ^{1}H NMR (CDCl$_3$) $\delta=-2.69$ (4H, s), 1.49 (36H, s), 1.52 (72H, s), 2.50 (2H, dd, $J=9$ and 14 Hz), 3.23 (2H, dd, $J=3$ and 14 Hz), 4.21 (2H, br-d, $J=8$ Hz), 5.29 (2H, d, $J=12$ Hz), 5.33 (2H, d, $J=12$ Hz), 5.86 (2H, s), 7.19 (4H, d, $J=9$ Hz, Tyr-phenylene), 7.24 (4H, d, $J=9$ Hz, Tyr-phenylene), 7.70 (4H, d, $J=8$ Hz, 5-*m*-H), 7.77 (2H, t, $J=2$ Hz, 15-*p*-H), 7.79 (4H, t, $J=2$ Hz, 10,20-*p*-H), 8.06 (4H, d, $J=2$ Hz, 15-*o*-H), 8.09 (8H, d, $J=2$ Hz, 10,20-*p*-H), 8.19 (4H, d, $J=8$ Hz, 5-*o*-H), 8.84 (4H, d, $J=4$ Hz, 2,8- or 3,7-H), and 8.88—8.91 (12H, m, 2,8- or 3,7- and 12,13,17,18-H); MS m/z 2252 (MH$^+$, 7%) and 964 (H$_2$TDBPCH$_2^+$+1, 100).

3bZ: 58%; MS m/z 2376, 2378, 2380, 2382 (MH$^+$, 4% (^{64}Zn·^{64}Zn), 1 (^{64}Zn·^{66}Zn), 4 (^{64}Zn·^{68}Zn, ^{66}Zn·^{66}Zn), 2 (^{66}Zn·^{68}Zn), 1025, 1027, and 1029 (ZnTDBPCH$_2^+$, 100, 89, 63).

3bH: ^{1}H NMR (CDCl$_3$) $\delta=-2.70$ (4H, s), 1.507 (72H, s), 1.510 (36H, s), 2.96 (2H, dd, $J=9$ and 14 Hz), 3.28 (2H, dd, $J=3$ and 14 Hz), 3.86 (2H, br(dt)), 5.40 (4H, s), 5.76 (2H, s), 7.15 (4H, d, $J=9$ Hz, Tyr-phenylene), 7.22 (4H, d, $J=9$ Hz, Tyr-phenylene), 7.78 (6H, t, $J=2$ Hz, 10,15,20-*p*-H), 7.81 (4H, d, $J=8$ Hz, 5-*m*-H), 8.07 (4H, d, $J=2$ Hz, 15-*o*-H), 8.08 (8H, d, $J=2$ Hz, 10,20-*o*-H), 8.27 (4H, d, $J=8$ Hz, 5-*o*-H), 8.85 (4H, d, $J=4$ Hz, 2,8- or 3,7-H), 8.88 (4H, d, $J=4$ Hz, 2,8- or 3,7-H), and 8.89 (8H, s, 12,13,17,18-H); MS m/z 2252 (MH$^+$, 2%) and 964 (H$_2$TDBPCH$_2^+$+1, 100).

We thank Professor Muneo Sasaki and Dr. Naoki Sugimoto, Konan University, for the measurement of CD spectra.

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6) The following abbreviations are used in this paper; Z = benzyloxycarbonyl, EDC = 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide, HOBt = 1-hydroxybenzotriazole, TTPCH$_2$= 5-[10,15,20-tri-*p*-tolylporphyrinyl]methyl, and TDBPCH$_2$ = 5-[10,15,20-tris(3,5-di-*t*-butylphenyl)porphyrinyl]methyl.

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