Synthesis of Strapped, Dimeric, and Trimeric Porphyrins Based on Intramolecular Macrocyclization Reactions

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Strapped porphyrins were prepared directly by the acid-catalyzed condensation reaction of 3,3′-diethyl-4,4′-dimethyl-2,2′-dipyrrylmethane and methylenedioxy bridged dialdehydes having a strap linkage longer than 7 atoms. Dimeric and trimeric porphyrins with coplanar and orthogonal (T-shape) geometries were also synthesized in good yields as an application of this method. In the strapped porphyrins, the distortion of porphyrin ring increases systematically on shortening the strap linkage, which is confirmed by their ^{1}H NMR data, red shifted absorption, and fluorescence spectra. In the coplanar dimeric and trimeric porphyrins, the electronic interactions between the porphyrins were distinctly observed, while in the orthogonal "T-shaped" dimers and "H-shaped" trimers, appreciable electronic interactions were not observed.

Important roles of porphyrins and their analogous tetrapyrroles as well as their aggregates in biological proceses such as aspiration, metabolism, and photosynthesis have stimulated the development of a wide range of synthetic porphyrin model compounds in recent years.[1] Among them, 5,15-diaryloctaalkylporphyrin is an useful unit for the model construction because of their easy preparation, high symmetry, and thermal stabillity of atropisomers.[2-4] Synthesis of these porphyrins from 5,5′-unsubstituted dipyrromethane and aromatic aldehydes was first reported by Ogoshi et al.[2] and later modified by Gunter and Mander[3] and Young and Chang.[4] Recently we have found the improved conditions (CCl_3CO_2H/CH_3CN) for the synthesis of these porphyrins[5] and applied them to the synthesis of conformationally restricted oligomeric porphyrins.[6]

Described herein is the direct synthesis of strapped porphyrins from the dialdehydes as well as the synthesis of a novel class of dimeric and trimeric porphyrins based on our improved method.[7,8]

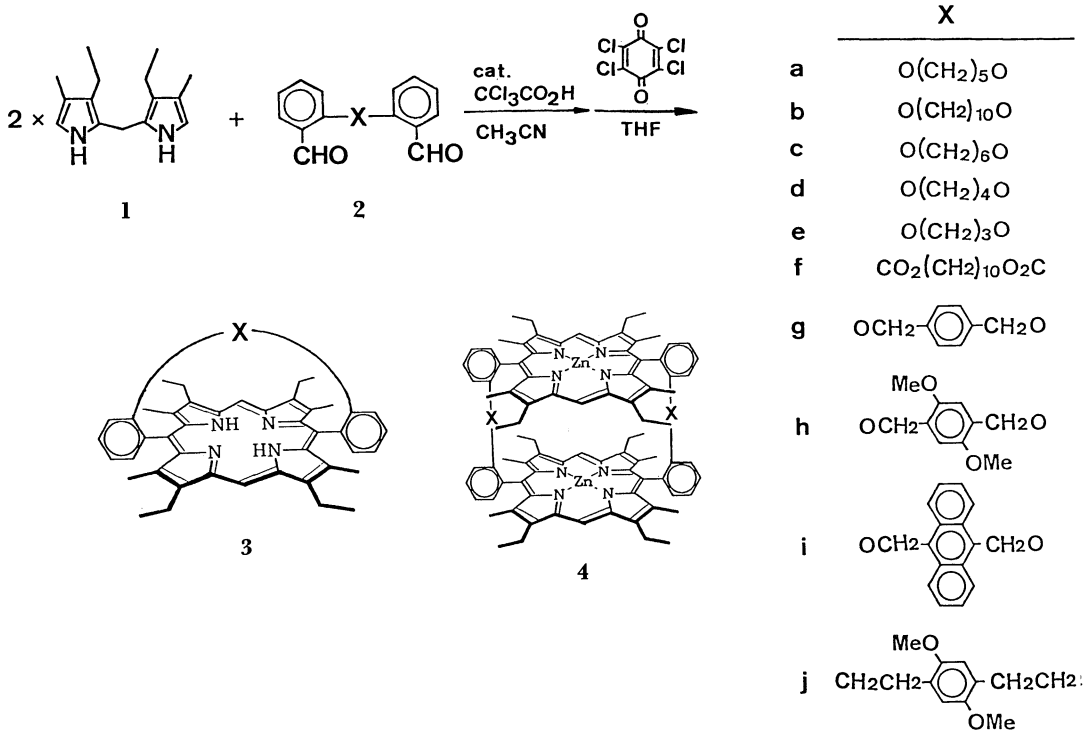
In relation to the importance of porphyrin ring-distortion in biological functions of hemoproteins and photosynthetic pigments, considerable attention has been focused on the synthesis and characterization of permanently distorted porphyrins.[9] One of important issues is the details of how the distortions of the macrocyclic ring influence their electronic and optical properties. Theoretical calculations on the effects of nonplanarity indicate that the highest occupied molecular orbital should be destabilized with respect to the lowest unoccupied molecular orbital, resulting in a red shift of the first visible absorption band.[9] Extremely short-chain-strapped porphyrins are very simple and useful model for this purpose.[10] While the dimeric and trimeric porphyrins synthesized here have rather restricted coplanar and orthogonal geometries and thus are promising models for studies on the geometry dependence of photoinduced excitation energy-transfer and electron-transfer processes.[11]

Results and Discussion

Synthesis of Strapped Porphyrins. Strapped porphyrins synthesized here are 5,15-diphenyl-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphine derivatives in which ortho positions of the *meso*-phenyl groups are bridged by a methylenedioxy chain with chain length longer than 7 atoms.[12] General procedure is as follows: 3,3′-diethyl-4,4′-dimethyl-2,2′-dipyrrylmethane **1**[13] (100 mg, 0.43 mmol) and the dialdehyde **2** (0.22 mmol) were dissolved or suspended in dry acetonitrile under N_2, and to this mixture a catalytic amount of trichloroacetic acid (10 mg) was added.[5] After standing at room temperature for about 5 h, *p*-chloranil (0.3 g, 1.2 mmol) in dry tetrahydrofuran (THF, 10 ml) was added and the mixture was stirred overnight. Porphyrin product was separated on alumima column (activity III) using CH_2Cl_2 as eluent, and recrystallized from CH_2Cl_2-methanol (Table 1). The cyclization yields were found to be dependent on the concentrations of the reactants (Table 1, Runs 1—4). The highest yield (15%) was obtained at [**1**]= 0.02 M (1 M=1 mol dm^{-3}). At high concentrations [**1**]>0.05 M, the formation of the dark blue insoluble

Table 1.

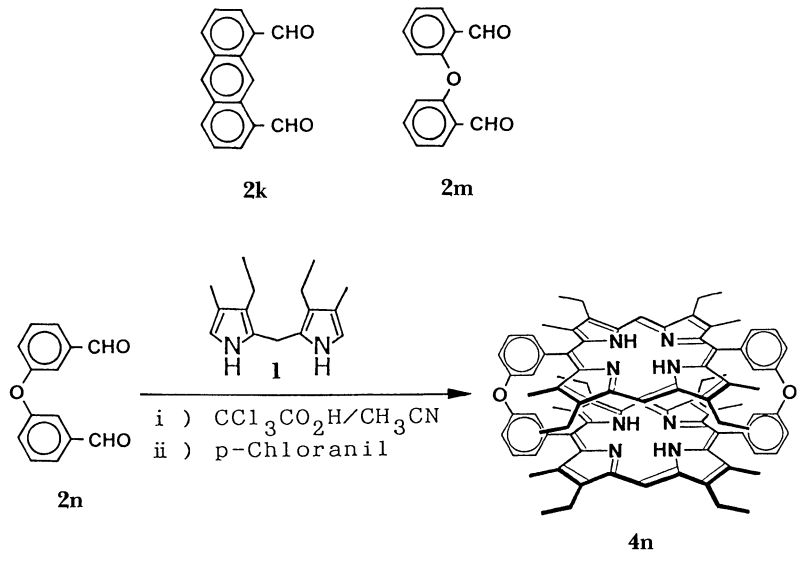
Run	Dialdehyde	Chain length of X	Concn of **1**/M	Product	Yield/%
1	**2a**	7	0.05	**3a**	6
2	**2a**	7	0.03	**3a**	13
3	**2a**	7	0.02	**3a**	15
4	**2a**	7	0.01	**3a**	Trace
5	**2b**	12	0.02	**3b**	21
6	**2c**	8	0.02	**3c**	25
7	**2d**	6	0.02	**4d**	5
8	**2e**	5	0.02	**4e**	2
9	**2f**	14	0.02	**3f**	33
10	**2g**	8	0.02	**3g**	54
11	**2h**	8	0.03	**3h**	61
12	**2i**	8	0.02	**3i**	25
13	**2j**	8	0.02	**4j**	Trace



Scheme 1.

solids took place predominantly, while at low concentrations [**1**]<0.01 M, the yield decreased significantly. In the cases of dialdehydes **2d** and **2e**, the corresponding strapped porphyrins were no longer formed but instead face-to-face porphyrin dimers **4d** and **4e** were obtained in 5% and 2%, respectively (Table 1, Runs 7, 8). Although the yields of **4d** and **4e** are not so high, this reaction will be useful for the preparation of porphyrin dimers of this type in view of its simple manipulation, easy separation, and direct synthesis from easily available starting materials. Of dialdehydes (**2k**, **2m**, and **2n**), only **2n** gave dimeric porphyrin **4n** in 2% yield (Scheme 2). This may be ascribed to more conformational flexibility or less steric hindrance of **2n** compared with **2k** and **2m**.

Strapped porphyrins **3g** and **3h**, in which the strap linkage contains an aromatic ring, were also prepared by this procedure in high yields (Table 1, Runs 10, 11). From the CPK (Corey-Pauling-Koltun) models, it is suggested that the porphyrin ring of **3g** and **3h** is

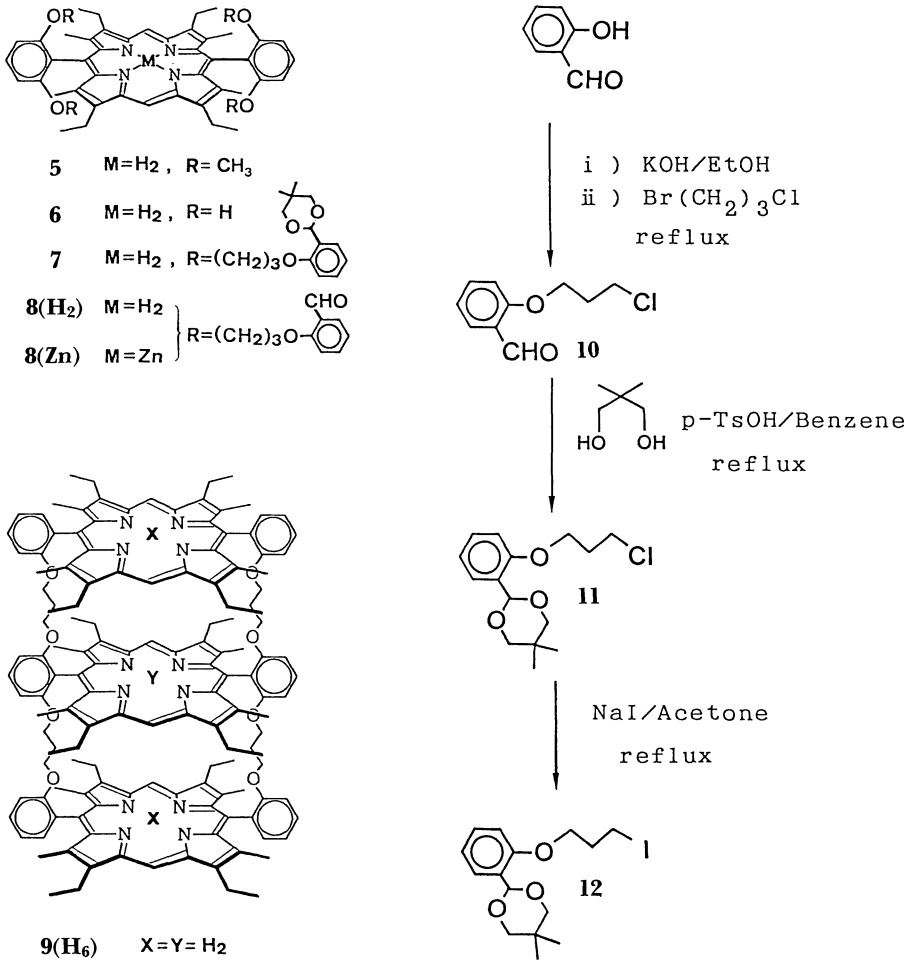


Scheme 2.

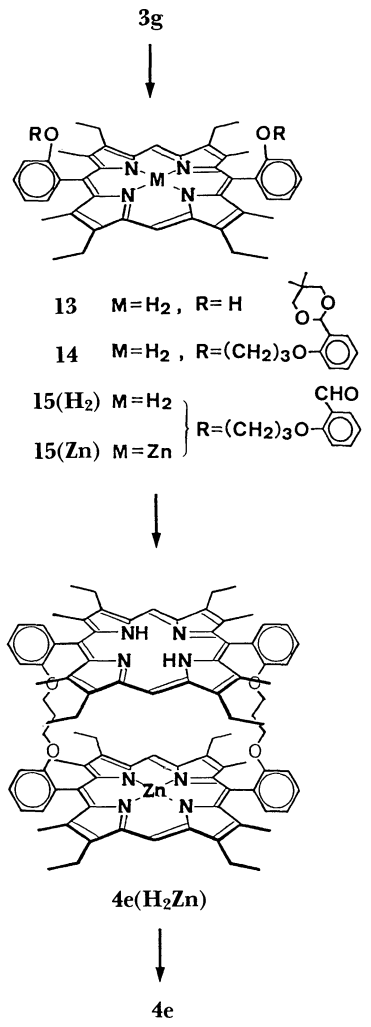
forced to be distorted due to the short *p*-xylylene linkages. However, the *p*-xylylene linkages are best-fitted in length for its porphyrinogen precursor. Probably this situation may account for the high yields of **3g** and **3h**. In the dialdehyde **2i**, *syn-anti* isomers exist due to the steric hindrance around 9,10-positions of the anthracene ring, and only the *syn* isomer seemed to adopt the preferred geometry for the porphyrinogen intermediate. Thus the yield of **3i** was lower than **3g**. The dialdehyde **2j**, which has the same number of chain atoms as **2g** and **2h**, gave no strapped porphyrin (Table 1, Run 13), presumably due to the more crowded steric hindrance around the methylene.

Synthesis of Dimeric and Trimeric Porphyrins. For the synthesis of the porphyrin trimer **9**, 5,15-bis(2,6-dimethoxyphenyl)etioporphyrin II (**5**)[5] was used as a precursor. Demethylation with BBr_3 gave the tetrahydroxy porphyrin **6** and then four hydroxyl groups were alkylated with 3-(aryloxy)propyl iodide **12** in refluxing acetone containing K_2CO_3 to give a both-face modified porphyrin **7** (43%). The iodide **12** was prepared in 3 steps from salicylaldehyde in a overall yield of 78% (Scheme 3). The acetal groups were hydrolyzed under acidic conditions[14] to give porphyrin tetraaldehyde **8**($\mathbf{H_2}$) (92%). We first tried the reaction of free-base porphyrin **8**($\mathbf{H_2}$) with dipyrrylmethane **1**, which resulted in the formation of the porphyrin trimer **9**($\mathbf{H_6}$) (*m/z* 2180.5, M^+) in rather poor yields (<10%). In contrast, the yield of the trimer **9**($\mathbf{H_4Zn}$) was markedly improved (35%) by the use of the zinc complex **8**(**Zn**) as the starting porphyrin (**9**($\mathbf{H_4Zn}$). Found: *m/z* 2244.120. Calcd for $C_{144}H_{153}N_{12}O_8Zn$: M+H, 2244. 126).

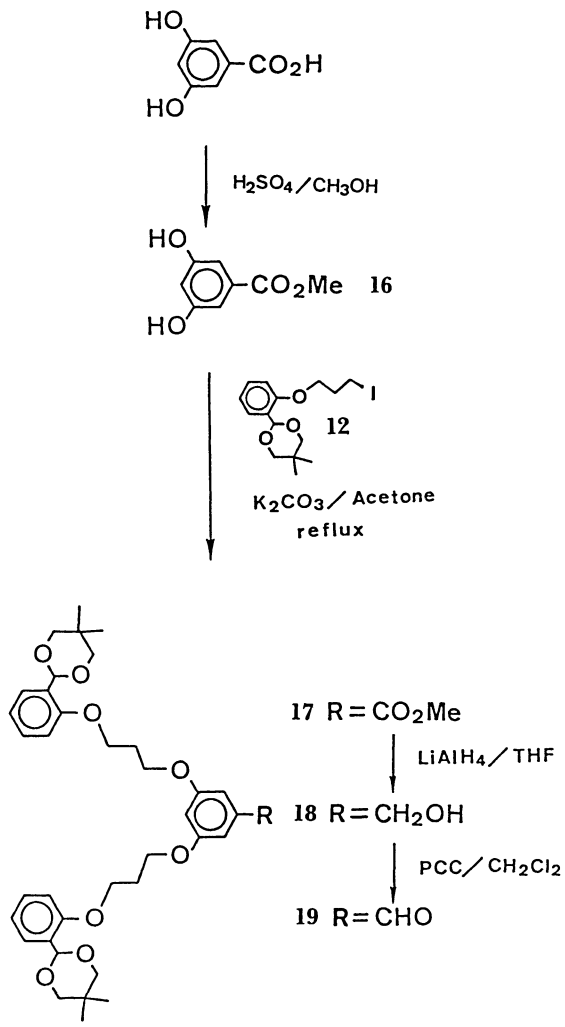
Face-to-face dimeric porphyrin **4e** was alternatively synthesized from the porphyrin dialdehyde (**15**) in a similar manner. Isomerically pure porphyrin dialdehyde **15** was prepared from *p*-xylylene-strapped porphyrin **3g** by the same procedure as **8**. The porphyrin dialdehyde **15**(**Zn**) was treated with dipyrrylmethane **1** in acetonitrile in the presence of trichloroacetic acid followed by oxidation with *p*-chloranil to give the porphyrin dimer **4e**($\mathbf{H_2Zn}$) in 56% yield as a mono-zinc complex. (Scheme 4).



Scheme 3.



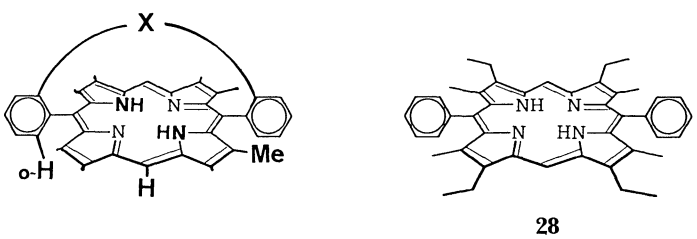
Scheme 4.

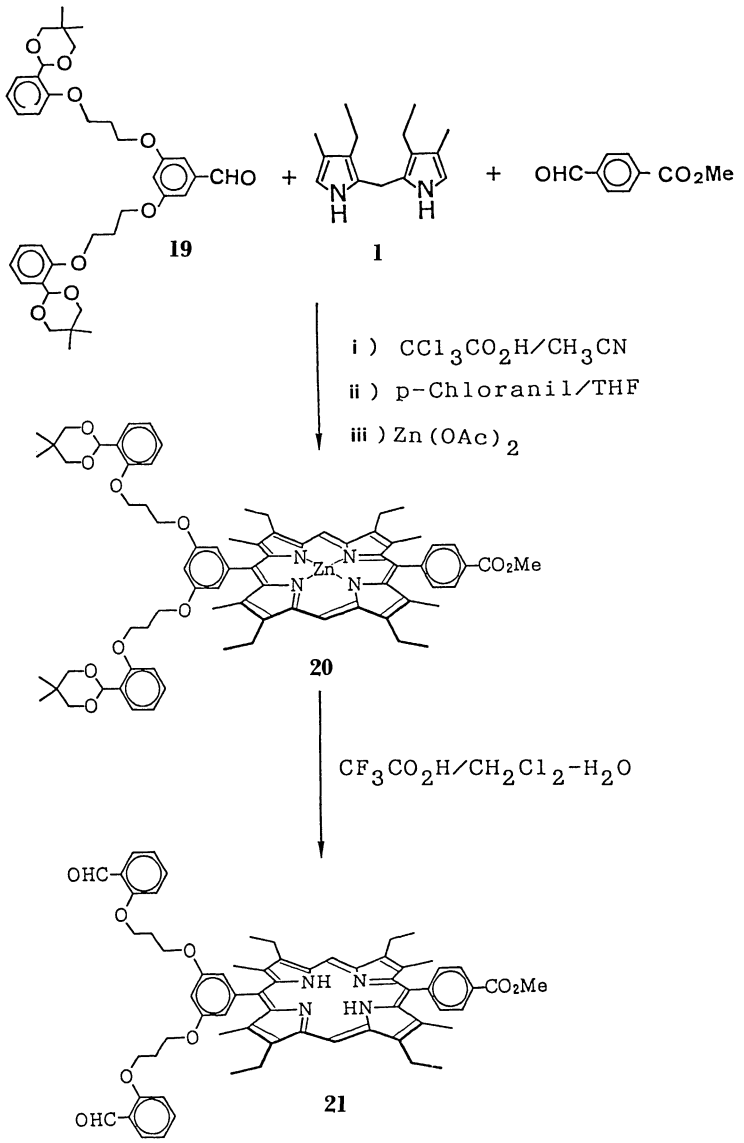


Scheme 5.

Table 2. ^{1}H NMR Chemical Shift of the Strapped Porphyrins in $CDCl_3$

Compound	δ/ppm				
	meso-H	*o*-H	β-CH_3	NH	X
3f	10.16	8.37	2.45	−2.19	3.31, −0.28, −0.83, −1.05, −1.18
3b	10.16	8.25	2.56	−2.33	3.68, 0.55, −0.94, −0.94, −1.69
3c	9.93	8.87	2.60	−1.70	2.29, −1.85, −2.85
3a	9.79	8.94	2.61	−1.27	0.96, −1.70, −3.49
3g	9.74	8.95	2.62	−1.36	2.92 (s, OCH_2), 3.42 (s, Ar-H)
3h	9.76	8.93	2.72, 2.57	−2.52	3.47, 2.44 (d, d, J=13Hz, OCH_2) 3.50 (s, Ar-H), 1.86 (s, OCH_3)
3i	9.39	8.91	2.66	−2.41	4.68 (s, OCH_2) 6.34, 6.11 (m, m, An-H)
28	10.22	8.08	2.48	−2.40	





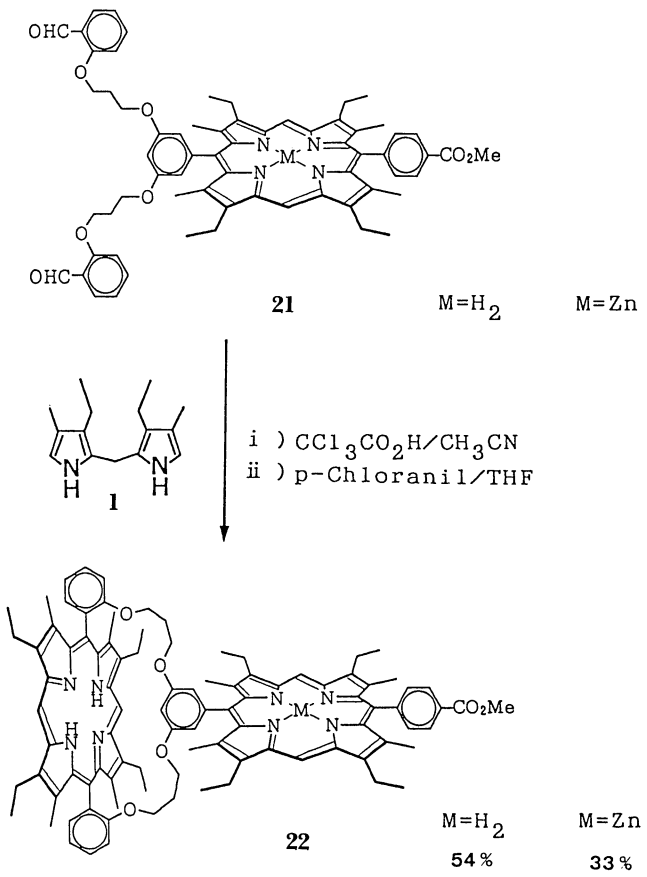
Scheme 6.

The "T-shaped" porphyrin dimers **22**(H_4) and **22**(H_2Zn) were also prepared from porphyrin dialdehydes **21**(H_2) and **21**(**Zn**) in 54% and 33% yield, respectively. (Scheme 5—7).

The "H-shaped" porphyrin trimer **27** was prepared in a different strategy. The strapped porphyrin **24** was first prepared from the corresponding dialdehyde **23** in 41% yield. The ester group on the strap chain was converted into the formyl group by reduction with $LiAlH_4$ followed by oxidation with activated MnO_2 in refluxing chloroform in a overall 82% yield.[15] The strapped porphyrin **26** thus prepared was treated with dipyrrylmethane **1** to give "H-shaped" porphyrin trimer **27**(H_6) in 59% yield (*m/z* 2181.6, $M+H^+$).[6] (Scheme 8).

Ring Distortion of Strapped Porphyrins. ^{1}H NMR and UV-vis Spectra. In their ^{1}H NMR spectra of methylene chain strapped porphyrins (**3a**, **3b**, **3c**, and **3f**), the methylene protons of the strap was significantly upfield shifted in accord with these protons lying above the porphyrin plane (Table 2). On shortening the methylene strap, the ring current effect for the *meso*-H and NH protons decreased systematically presumably due to the ring distortion from planarity. In addition, the ortho protons of the *meso*-phenyl groups were downfield shifted in **3a** and **3c**, suggesting that the phenyl rings are tipped in such a way to place the ortho phenyl protons moving closely into the deshielding field of the porphyrin ring current (Table 2, Fig. 1). Soret and Q-bands of the strapped porphyrins were also red-shifted on shortening the methylene chains, showing the significant perturbations of the π orbitals (Table 3).[9,16]

Similar tendency was observed in the xylene-strapped porpyrins **3g** and **3h**, in which the meso protons were upfield shifted and the ortho phenyl



Scheme 7.

protons were downfield shifted in the ^{1}H NMR spectra (Table 2) and the Soret and Q-bands were 7—17 nm red shifted with respect to the reference porphyrin **28** (Table 3). There exist some conformational differences caused by the methoxyl groups on the xylene moiety between **3g** and **3h**. The aromatic protons of the xylene strap appeared as a singlet at 3.47 ppm for **3g** and 3.50 ppm for **3h**, respectively. But the NH protons of **3g** appeared at −1.36 ppm, while those of **3h** appeared at −2.52 ppm due to the ring current shielding of the xylene cap, indicating that the dimethoxyxylene cap of **3h** was restricted to have a parallel geometry to the porphyrin ring. In accord with this consideration, the benzyl protons of **3h** were observed

Table 3. Absorption Maxima (nm) of the Strapped Porphyrins in CH_2Cl_2

Compound	Free-base		Zinc complex	
	Soret	Q-bands	Soret	Q-bands
3f	411	509 541 580 629	412	540 574
3b	409	507 539 575 629	410	538 574
3c	412	510 543 579 632	413	541 577
3a	417	516 552 587 637	420	550 585
3g	415	514 550 584 637	419	546 579
3h	417	514 550 585 639	419	546 582
3i	422	517 551 588 640	422	550 582
28	407	507 536 574 622	409	537 573

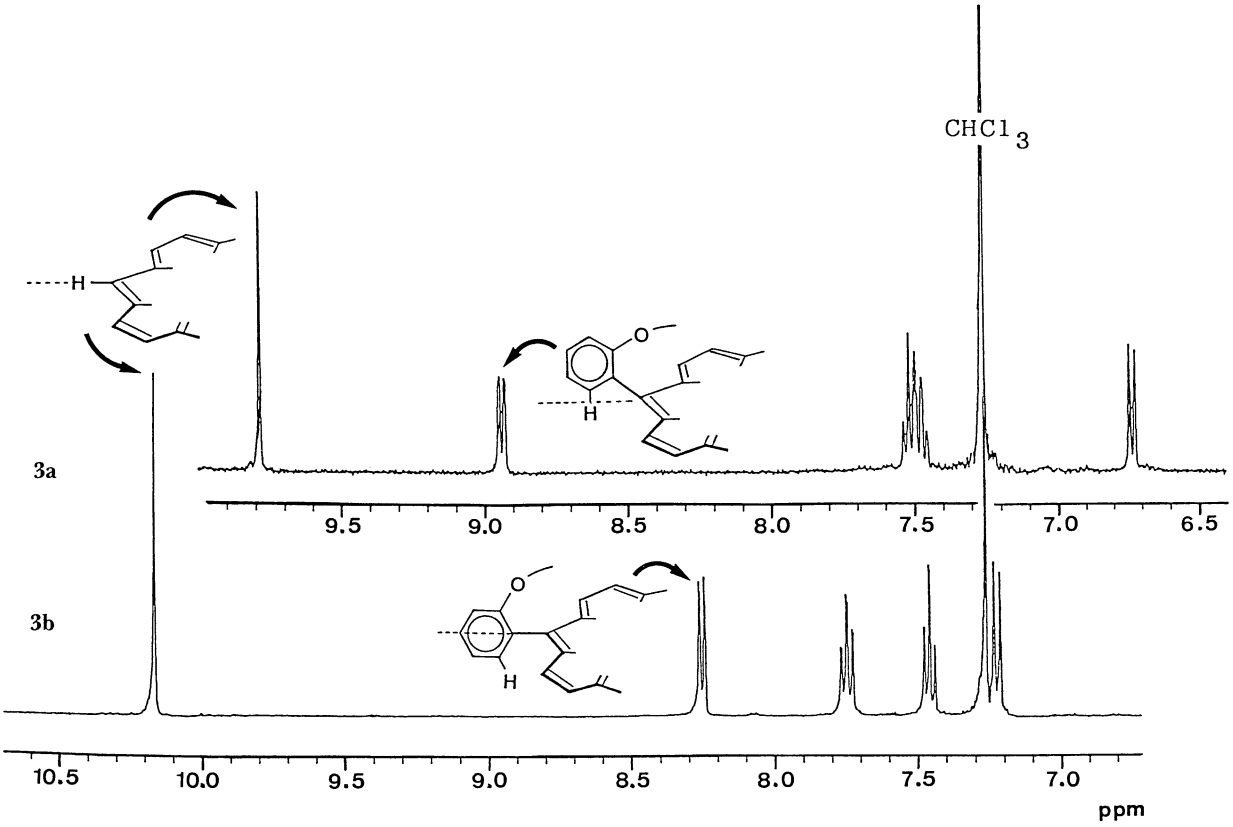
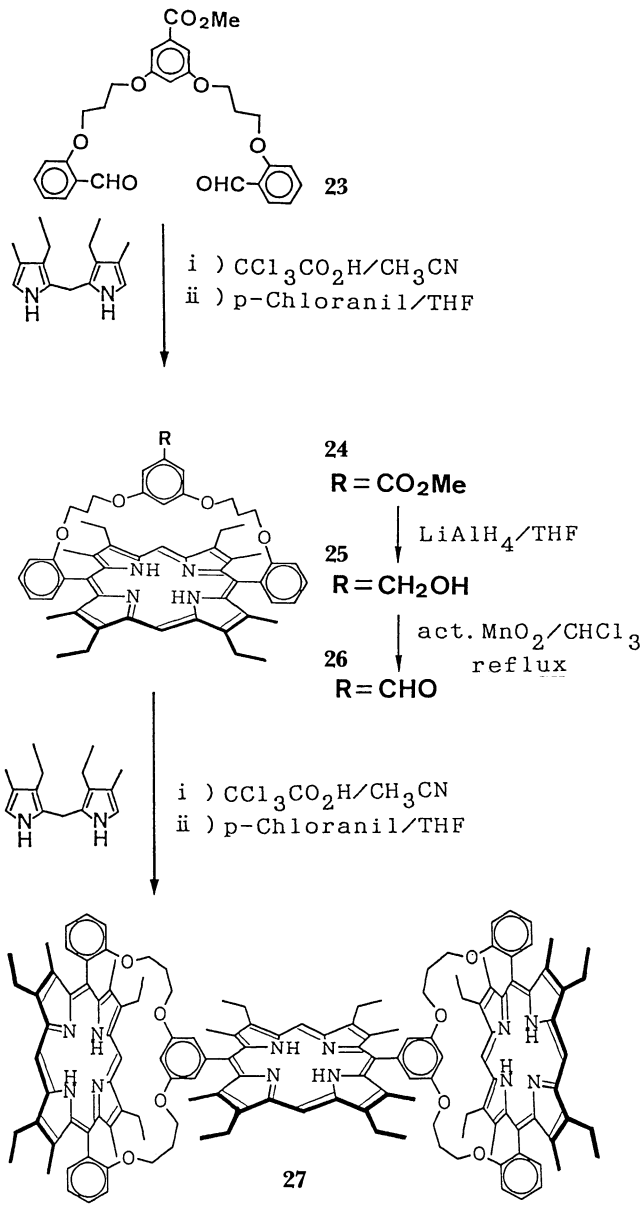


Fig. 1. ^{1}H NMR spectra of strapped porphyrins **3a** and **3b** in $CDCl_3$.



Scheme 8.

as two doublets (3.47 and 2.44 ppm, J=13 Hz). In addition, β-methyl and β-ethyl signals separated to two signals in **3h**, one on the same side with methoxyl groups and the other not. In the case of **3i**, the large anthracene ring was forced to have a parallel geometry to the porphyrin ring, and thus the NH and *meso*-H protons of **3i** appeaed at −2.41 ppm and 9.39 ppm, respectively; both of them were upfield shifted by the ring current shielding of the anthracene cap (Table 2).

Fluorescence Spectra. Fluorescence spectra of the methylene-chain-strapped porphyrins also showed systematic changes. Emission maxima were shifted to the longer wavelength on shortening the strap linkage and the fluorescence quantum yield and fluorescence lifetime were reduced by the ring distortion. The red shift of the emission maxima was in line with those observed in their UV-vis spectra. In addition, a new peak between the two peaks appeared in the free-base porphyrins and this center peak merged with the preceding peak in **3a** and **3c**. (Fig. 2, Table 4). On the other hand, no decrease of the fluorescence intensity and lifetime was observed in the xylylene-strapped porphyrins **3g** and **3h** (Table 4). This difference is presumably due to the difference of the conformational flexibility of the porphyrin ring. The porphyrin ring was distorted in **3g** and **3h** as well as **3a**, but the molecular motion should be restricted in **3g** and **3h** due to the rigid *p*-xylylene linkage.

Table 4. Fluorescence Spectral Data[a)]

Compd	λ em/nm	Φ f, rel[b)]	τ/ns
Free base			
3f	631 658 698	1.0	9.3
3b	630 659 695	1.0	c)
3c	639 654 697	0.9	ca. 8.5
3a	650 711	0.6	5.9
3g	643 707	1.0	9.5
3h	641 706	1.0	c)
Zinc complex			
3f(Zn)	580 637	1.0	1.6
3b(Zn)	578 632	1.0	c)
3c(Zn)	590 636	0.8	c)
3a(Zn)	605 655	0.6	1.2
3g(Zn)	597 654	1.0	1.6
3h(Zn)	595 650	1.0	c)

a) Measured in CH_2Cl_2 solution. b) Relative fluorescence intensities with respect to **3f**; excitation at Soret wavelength. c) Not measured.

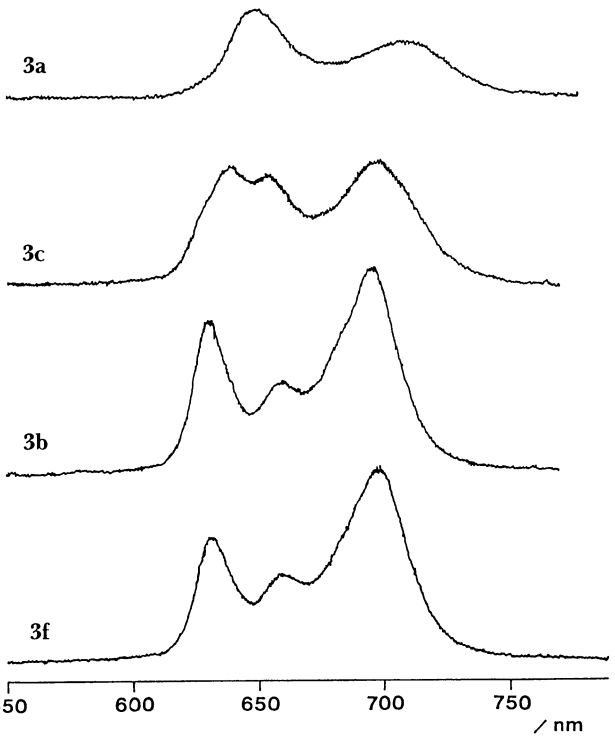


Fig. 2. Fluorescence spectra of strapped porphyrins.

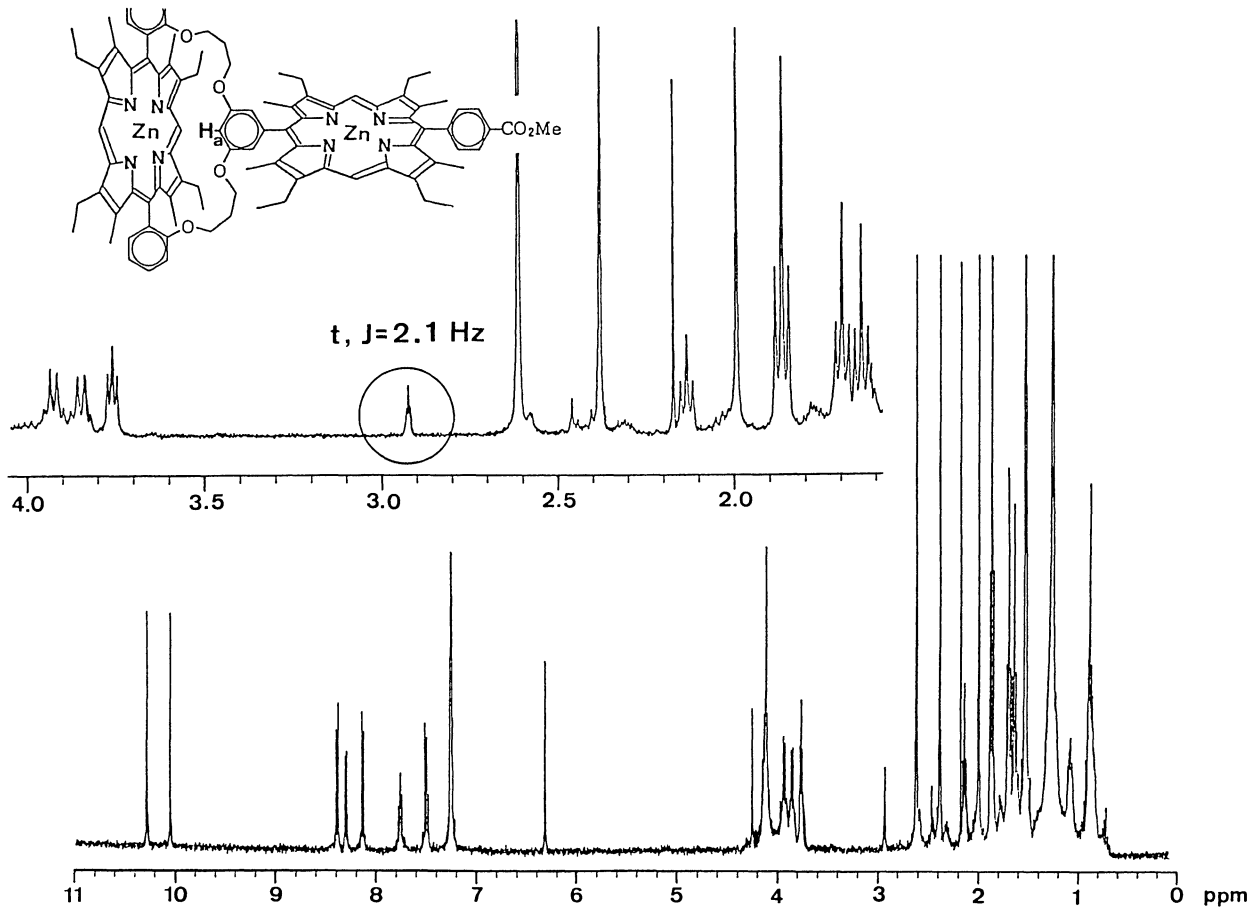


Fig. 3. ^{1}H NMR spectrum of "T-shaped" dimeric porphyrin **22**(Zn_2) in $CDCl_3$.

Table 5. UV-vis Spectra of Dimeric and Trimeric Porphyrins in CH_2Cl_2

Compd	λ_{max}/nm	
	Soret	Q-bands
4d	408	538 574
4e	405	538 574
9(Zn_3)	404	539 576
22(Zn_2)	411	540 574
27(Zn_3)	411	539 574
28(Zn)[a]	409	538 574

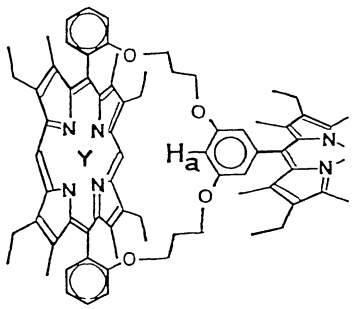
a) Zinc 5,15-diphenyletioporphyrin II was used as a reference porphyrin.

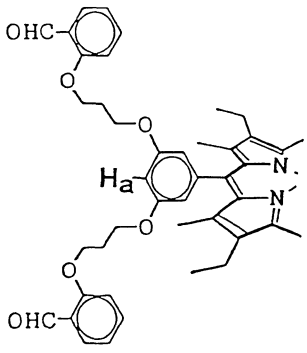
UV-vis and ^{1}H NMR Spectra of Dimeric and Trimeric Porphyrins. The stacked type porphyrins **4e** and **9**(Zn_3) showed blue-shifted Soret band similar to the other face-to-face dimeric porphyrins,[1,6] while the UV-vis spectra of **22**(Zn_2) and **27**(Zn_3) were almost unchanged with respect to the monomeric porphyrin **28** indicating that the ground state interactions between the porphyrins were small in the orthogonal geometries. (Table 5).

The unique geometries of "T-shaped" dimer **22** and "H-shaped" trimer **27** were characterized by their

Table 6. Chemical Shifts of H_a

Compd	δ
22(H_4)	3.01
22(H_2Zn)	3.03
22(Zn_2)	2.93
27(H_6)	2.97
27(Zn_3)	2.92
21	6.94
21(Zn)	6.95





^{1}H NMR spectra. The inside aromatic protons (H_a, designated in Table 6) appeared at ca. 3 ppm region due to the strong shielding effect of porphyrin ring current. The distance between the H_a and the porphyrin plane was estimated to be 4.1 Å in **22** on the basis of the porphyrin ring current model,[17] then the center-to-center distance between two porphyrin rings was estimated to be 12.8 Å, which was in good agreement with those estimated from Corey-Pauling-Koltun (CPK) molecular models (12.5—13 Å for **22** and **27**).

In summary, the acid-catalyzed intramolecular macrocyclization reaction is particularly useful for the synthesis of strapped porphyrins as well as dimeric and trimeric porphyrins. Use of *o*-alkoxybenzaldehydes as the starting material is also useful for model construction because of their easy preparation, high yield of the porphyrin, sufficient stability of the ether linkage, and the possible separation of the porphyrin atropisomers. Strapped porphyrins synthesized here showed systematic increase of ring distortion on shortening the strap linkage, while "T-shaped" dimeric porphyrins and "H-shaped" trimeric porphyrins had unique geometries. In these dimeric and trimeric porphyrins, there exists no direct π-π conjugation between porphyrin rings, rendering through-bond interactions to be negligibly small. Therefore, these models would be quite useful for studies on through-space electron-transfer process.

Experimental

The ^{1}H NMR spectra were recorded at 400 MHz on a JEOL JNM-GX-400 spectrometer, with tetramethylsilane or $CHCl_3$ as internal reference. All ^{1}H NMR spectra were measured in $CDCl_3$ solution. Mass spectra were recorded on a JEOL JMS-DX-300 instrument (EI, 3 kV). Fast atom bombardment mass spectra were recorded on a JEOL JMS-HX-110 (10 kV) or a JEOL JMS-DX-300 (1.5 kV) with *m*-nitrobenzyl alcohol as the matrix. High-resolution mass spectra of porphyrins were obtained on a JEOL JMS-HX-110 (10 kV) with polyethylene glycol as a standard. UV-vis spectra were recorded in dichloromethane on a Shimadzu UV-200 and a Shimadzu UV-3000 spectrophotometer. Steady-state fluorescence spectra were recorded by using a Shimadzu RF-502a spectrofluorometer. Fluorescence lifetimes were measured on a Horiba NAES 1100. Flash column chromatography was carried out using Wakogel FC-40 or Merck Kieselgel 60HF254 Art. 7739.

Anhydrous acetonitrile was distilled from diphosphorus pentaoxide and stored with Molecular Sieves 3A. Anhydrous acetone was distilled and dried over anhydrous calcium sulfate.

Unless otherwise stated all reactions were performed under an atmosphere of dry nitrogen. All organic extracts were dried over anhydrous sodium sulfate.

Preparation of the Dialdehyde Derivatives. Dialdehydes **2a**, **2b**, **2c**, **2d**, **2e**, **2g**, **2h** and **2i** were prepared according to the published procedure.[10a,18]

C3 Dialdehyde 2e. Colorless needles; mp 94—96 °C; ^{1}H NMR ($CDCl_3$) δ=10.50 (2H, s, CHO), 7.83+7.55+7.03 (2H+2H+4H, dd+m+m, Ar-H), 4.33 (4H, t, OCH_2), 2.43 (2H, m, $OCH_2C\underline{H}_2$). MS(EI) Found: *m/z* 284.1060. Calcd for $C_{17}H_{16}O_4$: M, 284.1049.

XY Dialdehyde 2g. Colorless needles; mp 191 °C. Found: C, 76.01; H, 5.08%. Calcd for $C_{22}H_{18}O_4$: C, 76.28; H, 5.24%. ^{1}H NMR ($CDCl_3$) δ=10.56 (2H, s, CHO), 7.87+7.55+7.49+7.07 (2H+2H+4H+4H, dd+m+s+m, Ar-H), 5.22 (4H, s, OCH_2). MS(EI) *m/z* 346 (M^+), 328 ($M-H_2O$).

XY(OMe)$_2$ Dialdehyde 2h. Dialdehyde **2h** was prepared from 2,5-bis(chloromethyl)-1,4-dimethoxybenzene.[19] Colorless needles; mp 193—5 °C. Found: C, 70.68; H, 5.49%. Caicd for $C_{24}H_{22}O_6$: C, 70.92; H, 5.46%. ^{1}H NMR ($CDCl_3$) δ=10.57 (2H, s, CHO), 7.86+7.56+7.12+7.12+7.06 (each 2H, dd+m+s+d+t, Ar-H), 5.24 (4H, s, OCH_2), 3.84 (6H, s, CH_3). MS(EI) *m/z* 406 (M^+).

AN Dialdehyde 2i. Dialdehyde **2i** was prepared from 9,10-bis(chloromethyl)anthracene.[20] Yellow solid; mp> 190 °C. Found: C, 80.74; H, 5.26%. Calcd for $C_{30}H_{22}O_4$: C, 80.70; H, 4.97%. ^{1}H NMR ($CDCl_3$) δ=10.25 (2H, s, CHO), 8.38+7.60 (4H+4H, m+m, An-H), 7.90+7.70+7.47+7.14 (each 2H, dd+m+d+t, Ar-H), 6.15 (4H, s, OCH_2).

C$_{10}$-Diester Dialdehyde 2f. 1,10-dibromodecane (0.43 g, 1.4 mmol) and 2-formylbenzoic acid (0.50 g, 3.3 mmol) was dissolved in dry acetone (10 ml). Anhydrous potassium carbonate (0.32 g, 2.3 mmol) was added and the mixture was refluxed overnight. After cooling, water (10 ml) was added and acetone was evaporated. The precipitated white solid was filtered, washed with water, and dried. (0.50 g, 1.1 mmol, 80%) mp 73—5 °C. Found: C, 69.52; H, 6.82%. Calcd for $C_{26}H_{30}O_6 \cdot 1/2H_2O$: C, 69.78; H, 6.98%. ^{1}H NMR ($CDCl_3$) δ=10.61 (2H, s, CHO), 7.94+7.63 (4H+4H, m+m, Ar-H), 4.37 (4H, t, OCH_2), 1.76+1.40+1.32 (4H+4H+8H, m+br+br, $OCH_2(C\underline{H}_2)_8CH_2O$). MS(FAB) *m/z* 439 ($M+H^+$).

2,5-Bis[2-(2-formylphenyl)ethyl]-1,4-dimethoxybenzene 2j. 2,5-Bis[2-[2-(methoxycarbonyl)phenyl]ethyl]-1,4-dimethoxybenzene was obtained from 2,5-dimethoxy-1,4-benzenedicarbaldehyde[21] according to the published procedure.[22] (2 steps 46%) The dimethyl ester was converted into the dialdehyde **2j** by lithium aluminium hydride reduction (94%) followed by oxidation with activated MnO_2 (61%) according to the usual procedure. **2j**: Pale yellow needles; mp 142—144 °C. ^{1}H NMR ($CDCl_3$) δ=10.29 (2H, s, CHO), 7.85+7.50+7.35+7.25+6.54 (each 2H, d+t+t+d+s, Ar-H), 3.70 (6H, s, CH_3), 3.26+2.88 (4H+4H, m+m, CH_2CH_2). MS (EI) Found: *m/z* 402.1833. Calcd for $C_{26}H_{26}O_4$: M, 402.1831.

2,2′-Oxybis(benzaldehyde) 2m. To the solution of diphenyl ether (1.0 ml) in dry ether (15 ml), butyllithium (1.6 M solution in hexanes, 12 ml) was added dropwise at 0 °C and the mixture was stirred at room temperature for 2 d.[23] *N,N*-dimethylformamide (3.0 ml) was added dropwise at 0 °C and the solution was stirred for 8 h. The mixture poured into the water, acidified with hydrochloric acid, and extracted with ethyl acetate. The organic layer was washed twice with water, dried, and evaporated. The residue was purified by column chromatography (silica gel, benzene) to give colorless crystals. (0.61 g, 43%) mp 74 °C. Found: C, 74.47; H, 4.53%. Calcd for $C_{14}H_{10}O_3$: C, 74.33; H, 4.46%. ^{1}H NMR ($CDCl_3$) δ=10.50 (2H, s, CHO), 7.99+7.58+7.29+6.94 (each 2 H, dd+m+t+d, Ar-H). MS(EI) *m/z* 226 (M^+).

3,3′-Oxybis(benzaldehyde) 2n. 3-Hydroxybenzaldehyde

(5.0 g, 41 mmol), 3-bromobenzaldehyde (5.0 g, 27 mmol), copper (II) oxide (2.9 g) and potassium carbonate (2.8 g) were dissolved in dry pyridine (30 ml) and the solution was refluxed for 20 h.[24] The same work up procedure as described above was carried out to give colorless oil (2.9 g, 47%). Found: C, 74.15; H, 4.32%. Calcd for $C_{14}H_{10}O_3$: C, 74.33; H, 4.46%. ^{1}H NMR ($CDCl_3$) δ=9.98 (2H, s, CHO), 7.67+7.56+7.50+7.32 (each 2H, m+t+m+m, Ar-H). MS (EI) *m/z* 226 (M^+).

General Procedure for the Synthesis of Strapped Porphyrins. 3,3′-Diethyl-4,4′-dimethyl-2,2′-dipyrrylmethane (**1**)[13] (100 mg, 0.43 mmol) and the dialdehyde **2** (0.22 mmol) were dissolved or suspended in dry acetonitrile (20 ml) under N_2, and to this mixture a catalytic amount of trichloroacetic acid (10 mg) was added. After standing at room temperature for about 5 h, *p*-chloranil (0.3 g, 1.2 mmol) in dry tetrahydrofuran (THF, 10 ml) was added and the mixture was stirred overnight. Porphyrin product was separated on alumina column (activity III) eluting with CH_2Cl_2, and recrystallized from CH_2Cl_2-methanol. Yields are listed in Table 1.

C5 Strapped Porphyrin 3a. ^{1}H NMR ($CDCl_3$) δ=9.79 (2H, s, meso-H), 8.94+7.50+6.73 (2H+4H+2H, dd+m+d, ArH), 3.98+3.82 (4H+4H, m+m, Et), 2.60 (12H, s, Me), 1.70 (12H, t, Et), 0.96+−1.73+−3.49 (4H+4H+2H, t+m+m, $O(C\underline{H}_2)_5O$), −1.27 (2H, br, NH). MS(FAB) Found: *m/z* 731.4333. Calcd for $C_{49}H_{55}N_4O_2$: M+H, 731.4325.

C10 Strapped Porphyrin 3b. ^{1}H NMR ($CDCl_3$) δ=10.16 (2H, s, *meso*-H), 8.25+7.75+7.46+7.22 (each 2H, dd+m+m+d, ArH), 4.02 (8H, m, Et), 3.68 (4H, t, OCH_2), 2.56 (12H, s, Me), 1.81 (12H, t, Et), 0.55+−0.94+−1.69 (4H+8H+4H, m+m+m, OCH_2 $(C\underline{H}_2)_8$ CH_2O, −2.33 (2H, br, NH). MS(FAB) *m/z* 918 ($M+H^+$).

C6 Strapped Porphyrin 3c. ^{1}H NMR ($CDCl_3$) δ=9.93 (2H, s, *meso*-H), 8.87+7.56+6.85 (2H+4H+2H, dd+m+dd, ArH), 4.00+3.89 (4H+4H, m+m, Et), 2.60 (12H, s, Me), 2.29 (4H, t, OCH_2), 1.72 (12H, t, Et), −1.70 (2H, br, NH), −1.85+−2.85 (4H+4H, br+br, OCH_2 $(C\underline{H}_2)_4CH_2O$). MS (FAB) Found: *m/z* 745.4481. Calcd for $C_{50}H_{57}N_4O_2$: M+H, 745.4482.

XY Strapped Porphyrin 3g. ^{1}H NMR ($CDCl_3$) δ=9.74 (2H, s, *meso*-H), 8.95+7.54+6.67 (2H+4H+2H, dd+m+d, ArH), 3.89+3.77 (4H+4H, m+m, Et), 3.42 (4H, s, C_6H_4), 2.92 (4H, s, OCH_2), 2.62 (12H, s, Me), 1.63 (12H, t, Et), −1.36 (2H, br, NH). MS (FAB) Found: *m/z* 765.4149. Calcd for $C_{52}H_{53}N_4O_2$: M+H, 765.4169.

XY(OMe)$_2$ Strapped Porphyrin 3h. ^{1}H NMR ($CDCl_3$) δ=9.76 (2H, s, *meso*-H), 8.93+7.64+7.07 (2H+4H+2H, dd+m+d, ArH), 3.91 (8H, m, Et), 3.50 (2H, s, $C_6H_2(OMe)_2$), 3.47+2.44 (2H+2H, d+d, *J*=13 Hz, OCH_2), 2.72+2.57 (6H+6H, s+s, Me), 1.86 (6H, s, OCH_3), 1.82+1.75 (6H+6H, t+t, Et), −2.52 (2H, br, NH). MS (FAB) Found: *m/z* 825.4351. Calcd for $C_{54}H_{57}N_4O_4$: M+H, 825.4380.

AN Strapped Porphyrin 3i. ^{1}H NMR ($CDCl_3$) δ=9.39 (2H, s, *meso*-H), 8.91+7.67+7.53+6.98 (each 2H, dd+m+t+d, ArH), 6.34+6.11 (4H+4H, m+m, An-H), 4.68 (4H, s, OCH_2), 3.87+3.73 (4H+4H, m+m, Et), 2.66 (12H, s, Me), 1.66 (12H, t, Et), −2.41 (2H, br, NH). MS (FAB) *m/z* 865 ($M+H^+$).

C10-Diester Strapped Porphyrin 3f. ^{1}H NMR ($CDCl_3$) δ=10.16 (2H, s, *meso*-H), 8.37+7.8 (8H, m, Ar-H), 3.99 (8H, m, Et), 3.31 (4H, t, OCH_2), 2.45 (12H, s, Me), 1.77 (12H, t, Et), −0.28+−0.83+−1.05+−1.18 (each 4H, m+m+br+br, $OCH_2(C\underline{H}_2)_8CH_2O$), −2.19 (2H, br, NH). MS (FAB) Found: *m/z* 857.5002. Calcd for $C_{56}H_{65}N_4O_4$: M+H, 857.5006.

C4 Dimer 4d. The ^{1}H NMR spectrum of bis-zinc dimer **4d** was broadened and complicated at ambient temperatures. On heating the sample to 100 °C in 1,1,2,2-tetrachloroethane-d_2, the spectrum became sharp and the peak assignment was achieved. **4d**: ^{1}H NMR ($CDCl_2CDCl_2$, at 100 °C) δ=9.67 (s, *meso*-H), 7.64, 7.25—7.14 (each m, Ar-H), 3.73 (m, Et), 3.42 (br, OCH_2), 2.31 (s, Me), 1.56 (t, Et), 0.49 (br, $OCH_2C\underline{H}_2$. MS (FAB) *m/z* 1558—1563 (M^+). UV-vis (CH_2Cl_2) 408, 538, 575 nm.

C3 Dimer 4e. ^{1}H NMR ($CDCl_3$) δ=9.63 (s, *meso*-H), 7.66+7.41+7.17 (m+m+m, ArH), 3.74(m, Et), 2.25 (s, Me), 1.5 (m, Et). MS (FAB) *m/z* 1530—1535 (M^+). UV-vis (CH_2Cl_2) 405, 538, 574 nm.

***m*-Oxy Dimer 4n.** ^{1}H NMR ($CDCl_3$) δ=9.46+8.22 (s+s, *meso*-H), 8.12+7.7+7 50 (dd+m+t, ArH), 3.63 (m, Et), 2.17 (s, Me), 1.45 (t, Et). MS (FAB) *m/z* 1290 ($M+H^+$). UV-vis (CH_2Cl_2) 403, 509, 541, 576, 626 nm.

Preparation of the Iodide 12. 2-(3-Chloropropoxy)-benzaldehyde 10. Salicylaldehyde (4.2 ml, 40 mmol) was added to a solution of potassium hydroxide (85%, 2.6 g, 40 mmol) in ethanol (40 ml) and then 1-bromo-3-chloropropane (4.5 ml, 46 mmol) was added. The mixture was heated under reflux for 10 h and then cooled to 0 °C. The precipitate was filtered off and the filtrate was evaporated. The residue was dissolved in CH_2Cl_2, washed with water, dried and evaporated. Remaining salicylaldehyde and 1-bromo-3-chloropropane were distilled off under reduced pressure to leave colorless oil (7.8 g, 39 mmol, 97%). ^{1}H NMR ($CDCl_3$) δ=10.49 (1H, s, CHO), 7.84+7.55+7.03 (1H+1H+2H, dd+m+m, Ar-H), 4.26+3.38+2.30 (2H+2H+2H, t+t+m, O $(C\underline{H}_2)_3Cl$). MS (FAB) *m/z* 199 ($M+H^+$).

2-(3-Chloropropoxy)-1-(5,5′-dimethyl-1,3-dioxan-2-yl)-benzene 11. The aldehyde **10** (7.8 g, 39 mmol), 2,2-dimethyl-1,3-propanediol (5.0 g, 48 mmol), and *p*-toluenesulfonic acid monohydrate (0.3 g) were dissolved in benzene (80 ml), and the mixture was heated under reflux. Water was removed using a Dien-Stark apparatus. After 7 h, the mixture was cooled and the organic layer was washed with aqueous sodium hydrogencarbonate, with water, and then evaporated. The residue was purified on silica gel (eluting with benzene-ether) to give colorless oil (9.7 g, 34 mmol, 87%). ^{1}H NMR ($CDCl_3$) δ=7.65+7.29+7.01+6.89 (each 1H, dd+m+t+d, Ar-H), 5.74 (1H, s, ArCH), 4.15 (2H, t, $OC\underline{H}_2CH_2$), 3.76 (4H, m, $OC\underline{H}_2$+$CH_2\underline{C}H_2Cl$), 3.66 (2H, d, $OC\underline{H}_2$), 2.26 (2H, m, $C\underline{H}_2CH_2Cl$), 1.32+0.80 (3H+3H, s+s, Me). MS (FAB) *m/z* 285 ($M+H^+$).

2-(3-Iodopropoxy)-1-(5,5′-dimethyl-1,3-dioxan-2-yl)-benzene 12. The chloride **11** (14.2 g, 50 mmol) and sodium iodide (15 g, 0.1 mol) were dissolved in dry acetone (100 ml) and the mixture was refluxed overnight. After cooling, the precipitate was filtered off and the filtrate was evaporated. The residue was dissolved in CH_2Cl_2, washed with aqueous sodium thiosulfate, with water, dried and evaporated to leave pale yellow oil (17.2 g, 46 mmol, 92%). ^{1}H NMR ($CDCl_3$) δ=7.65+7.29+7.01+6.88 (each 1H, dd+m+t+d, Ar-H), 5.73 (1H, s, ArCH), 4.08 (2H, t, $OC\underline{H}_2CH_2$), 3.76+3.66 (2H+2H, d+d, OCH_2), 3.38+2.30 (2H+2H, t+m, $C\underline{H}_2$-$C\underline{H}_2I$), 1.32+0.80 (3H+3H, s+s, Me). MS (EI) Found: *m/z* 376.0538. Calcd for $C_{15}H_{21}IO_3$: M, 376.0534.

Synthesis of Trimeric Porphyrin 9. 5,15-Bis(2,6-dihy-

droxyphenyl)etioporphyrin II (6). 5,15-Bis(2,6-dimethoxyphenyl)etioporphyrin II (**5**)[5] (158 mg, 0.21 mmol) in dry CH_2Cl_2 (30 ml) was treated with BBr_3 (0.3 ml) at −78 °C. The mixture was gradually warmed to room temperature and stirred overnight. The mixture was poured into water and extracted with CH_2Cl_2 and then with ethyl acetate. The extract was washed with aqueous sodium hydrogencarbonate, with water, and then evaporated. Recrystallization from CH_2Cl_2-hexane gave purple microcrystals (145 mg, 0.21 mmol, 99%). ^{1}H NMR ($CDCl_3$) δ=10.31 (2H, s, *meso*-H), 7.64+7.00 (2H+4H, t+d, ArH), 4.66(4H, br, OH), 4.05 (8H, q, Et), 2.78 (12H, s, Me), 1.80 (12H, t, Et). MS (FAB) *m/z* 695 ($M+H^+$).

Porphyrin Tetraacetal 7. 5,15-Bis(2,6-dihydroxyphenyl)-etioporphyrin II (**6**, 135 mg, 0.19 mmol), the iodide **12** (2.85 g, 7.6 mmol), and anhydrous potassium carbonate (1.0 g) were dissolved in dry acetone (90 ml) and refluxed for 2 d. After cooling, acetone was evaporated and the residue was dissolved in CH_2Cl_2, washed with water, dried and evaporated. Porphyrin **7** was separated by flash column chromatography (silica gel, CH_2Cl_2) and then recrystallized from CH_2Cl_2-methanol to give purple crystals (140 mg, 0.083 mmol, 44%). ^{1}H NMR ($CDCl_3$) δ=10.06 (2H, s, *meso*-H), 7.72+7.04 (2H+4H, t+d, C_6H_3), 7.43+6.69+6.48 (4H+4H+8H, dd+t+m, C_6H_4), 5.50 (4H, s, ArCH), 4.08+2.82+1.38 (each 8H, t+t+m, $O(C\underline{H}_2)_3O$), 3.82 (8H, q, Et), 3.65+3.51 (8H+8H, d+d, OCH_2), 2.60 (12H, s, β-Me), 1.65 (12H, t, Et), 1.24+0.72 (12H+12H, s+s, acetal-Me), −2.23 (2H, br, NH). MS (FAB) *m/z* 1688 ($M+H^+$).

Porphyrin Tetraaldehyde 8. To a solution of the porphyrin **7** (100 mg, 0.059 mmol) in CH_2Cl_2 (30 ml), trifluoroacetic acid (5 ml) and water (5 ml) were added and the mixture was stirred for 8 h.[14] The mixture was poured into water and extracted with CH_2Cl_2. The extract was washed with aqueous sodium hydrogen carbonate, with water, dried and evaporated. Porphyrin **8** was purified on silica gel (CH_2Cl_2-1% methanol) and recrystallized from CH_2Cl_2-methanol to give purple crystals (**8**(H_2), 74 mg, 0.055 mmol, 92%). ^{1}H NMR ($CDCl_3$) δ=9.98 (4H, s, CHO), 9.96 (2H, s, *meso*-H), 7.78+7.09 (2H+4H, t+d, C_6H_3), 7.29+6.21+5.35+4.18 (each 4H, dd+t+m+d, C_6H_4), 4.12+2.38+1.44 (each 8H, t+t+m, $O(C\underline{H}_2)_3O$), 3.75 (8H, q, Et), 2.60 (12H, s, Me), 1.59 (12H, t, Et), −2.26 (2H, br, NH). MS (FAB) Found: *m/z* 1343.616. Calcd for $C_{84}H_{87}N_4O_{12}$: M+H, 1343.632.

8(Zn): ^{1}H NMR ($CDCl_3$) δ=9.93(2H, s, *meso*-H), 9.39 (4H, s, CHO), 7.79+7.12 (2H+4H, t+d, C_6H_3), 6.89+6.00+5.29+3.95 (each 4H, dd+t+m+d, C_6H_4), 4.12+2.25+1.46 (each 8H, t+t+m, $O(C\underline{H}_2)_3O$), 3.82 (8H, q, Et), 2.61 (12H, s, Me), 1.65 (12H, t, Et). MS (FAB) *m/z* 1404—1409 (M^+).

Trimeric Porphyrin 9. The porphyrin tetraaldehyde **8(Zn)** (14.8 mg, 0.0105 mmol) and dipyrrylmethane **1** (12. 8 mg, 0.056 mmol) were dissolved in dry acetonitrile (10 ml) containing trichloroacetic acid (3.8 mg, 0.023 mmol) and the mixture was stirred for 12 h. *p*-Chloranil (50 mg) in THF (5 ml) was added and stirring was continued overnight. Solvent was evaporated. Trimeric porphyrin **9(H_4Zn)** was separated on alumina (activity III, eluting with CH_2Cl_2) and then on silica gel (CH_2Cl_2-2% methanol). (8.3 mg, 0.0037 mmol, 35%).

9(H_4Zn): ^{1}H NMR ($CDCl_3$) δ=9.58+9.17 (4H+2H, s+s, *meso*-H), 3.63+3.48 (m, Et), 2.19+2.07 (s+s, Me), 1.41+1.30 (t+t, Et). MS (FAB) Found: *m/z* 2244.120. Calcd for the highest peak of $C_{144}H_{153}N_{12}O_8Zn$: M+H, 2244.126 (CsI was used as a standard).

9(Zn_3): ^{1}H NMR ($CDCl_3$) δ=9.56+9.15 (4H+2H, s+s, *meso*-H), 7.62+7.55+7.43+7.15+7.08+6.72 (m, ArH), 3.63+3.45 (m, Et), 2.17+2.06 (s+s, Me), 1.42+1.30 (t+t, Et). MS (FAB) *m/z* 2364—2375 (M^+).

Stepwise Synthesis of Dimeric Porphyrin 4e. α,α-5,15-Bis(2-hydroxyphenyl)etioporphyrin II (13). Strapped porphyrin **3g** (505 mg, 0.66 mmol) was treated with BBr_3 (1 ml) by the same procedure as **6** to give purple microcrystals (400 mg, 0.60 mmol, 91%). ^{1}H NMR ($CDCl_3$) δ=10.26 (2H, s, *meso*-H), 7.75+7.36+7.28 (2H+4H+2H, t+m+m, ArH), 5.6 (2H, br, OH), 4.04 (8H, m, Et), 2.66 (12H, s, Me), 1.81 (12H, t, Et). MS (FAB) *m/z* 663 ($M+H^+$).

Porphyrin Diacetal 14. Porphyrin diacetal **14** was prepared from the porphyrin **13** (200 mg, 0.30 mmol) and the iodide **12** (1.9 g, 5.0 mmol) by the same procedure as **7**. (187 mg, 0.16 mmol, 54%). ^{1}H NMR ($CDCl_3$) δ=10.15 (2H, s, *meso*-H), 7.77+7.46+7.35+6.75+6.56+5.56 (4H+2H+4H+2H+2H+2H, m+dd+m+t+m+d, ArH), 5.53 (2H, s, ArCH), 4.21+2.97+1.56 (each 4H, t+t+m, $O(C\underline{H}_2)_3O$), 3.96+ 3.85 (4H+4H, m+m, Et), 3.66+3.52 (4H+4H, d+d, OCH_2), 2.53 (12H, s β-Me), 1.72 (12H, t, Et), 1.25+0.72 (6H+6H, s+s, acetal-Me), −2.36 (2H, br, NH). MS (FAB) *m/z* 1160 ($M+H^+$).

Porphyrin Dialdehyde 15. The porphyrin diacetal **14** was hydrolyzed by the same procedure as **8**.

15(H_2): ^{1}H NMR ($CDCl_3$) δ=10.11+10.10 (4H, s+s, CHO+*meso*-H), 7.81+7.39+6.38+5.83+4.71 (4H+6H+2H+2H+2H, m+m+t+m+d, ArH), 4.22+2. 68+1.79 (each 4H, t+t+m, $O(C\underline{H}_2)_3O$), 3.91+3.84 (4H+4H, m+m, Et), 2.52 (12H, s, Me), 1.69 (12H, t, Et), −2.37 (2H, br, NH). MS (FAB) *m/z* 987 ($M+H^+$).

15(Zn): ^{1}H NMR ($CDCl_3$) δ=10.06 (2H, s, *meso*-H), 9.50 (2H, s, CHO), 7.80+7.39+6.95+6.10+5.72+4.55 (4H+4H+2H+2H+2H+2H, m+m+dd+t+m+d, ArH), 4.23+2.61+1.61 (each 4H, t+t+m, $O(C\underline{H}_2)_3O$), 4.1—3.8 (8H, m, Et), 2.52 (12H, s, Me), 1.72 (12H, t, Et). MS (FAB) *m/z* 1048—1052 (M^+).

Face-to-Face Dimeric Porphyrin 4e. The porphyrin dialdehyde **15(Zn)** (30.1 mg, 0.029 mmol) was treated with dipyrrylmethane **1** (16 mg, 0.069 mmol) in acetonitrile (6.8 ml) in the presence of trichloroacetic acid (6 mg) followed by oxidation with *p*-chloranil (75 mg) in a similar manner as **9(H_4Zn)** to give the porphyrin dimer **4e(H_2Zn)** (24 mg, 0.016 mmol, 56%). The bis-zinc complex (**4e**) was identical with that prepared in a one-pot procedure.

4e(H_2Zn): MS (FAB) *m/z* 1468—1472 (M^+).

Synthesis of the Aldehyde 19. Methyl 3,5-Bis[3-[2-(5,5-dimethyl-1,3-dioxan-2-yl)phenoxy]propoxy]benzoate 17. Methyl 3,5-dihydroxybenzoate (**16**, 1.50 g, 8.9 mmol), the iodide **12** (7.61 g, 20 mmol), and anhydrous potassium carbonate (1.4 g) were dissolved in dry acetone (60 ml) and refluxed for 2 d. After cooling, acetone was evaporated and the residue was dissolved in CH_2Cl_2, washed with water, dried and evaporated. The methyl ester **17** was purified on silica gel eluting with CH_2Cl_2. Colorless oil (5.0 g, 7.5 mmol, 83%). ^{1}H NMR ($CDCl_3$) δ=7.64+7.27+7.21+7.00+6.88+6.67 (2H+2H+2H+2H+2H+1H,dd+m+d+m+dd+t, ArH), 5.74 (2H, s, ArCH), 4.2+2.28 (8H+4H, m+m, $O(C\underline{H}_2)_3O$), 3.88 (3H, s, OMe), 3.73+3.61 (4H+4H, d+d, OCH_2), 1.29+0.75 (6H+6H, s+s, acetal-Me) MS (FAB) *m/z* 665 ($M+H^+$).

3,5-Bis[3-[2-(5,5-dimethyl-1,3-dioxan-2-yl)phenoxy]-propoxy]benzyl Alcohol 18. The methyl ester **17** (5.0 g, 7.5

mmol) was treated with $LiAlH_4$ (0.56 g) in dry THF (100 ml) at room temperature. The benzyl alcohol **18** was purified on silica gel eluting with CH_2Cl_2. White Solids (3.7 g, 5.8 mmol, 77%). ^1H NMR ($CDCl_3$) δ=7.65+7.28+6.99+6.87+6.51+6.41 (2H+2H+2H+2H+2H+1H, dd+t+t+d+d+t, ArH), 5.74 (2H, s, ArCH), 4.49 (2H, d, $C\underline{H}_2OH$), 4.17+2.26 (8H+4H, t+m, $O(C\underline{H}_2)_3O$), 3.72+3.62 (4H+4H, d+d, OCH_2), 1.88 (1H, t, OH), 1.30+0.76 (6H+6H, s+s, Me). MS (FAB) m/z 637 ($M+H^+$).

3,5-Bis[3-[2-(5,5′-dimethyl-1,3-dioxan-2-yl)phenoxy]-propoxy]benzaldehyde 19. To a suspension of pyridinium chlorochromate (PCC, 0.33 g, 1.5 mmol) and anhydrous sodium acetate (35 mg, 0.42 mmol) in dry CH_2Cl_2, a solution of the benzyl alcohol **18** (0.54 g, 0.85 mmol) in CH_2Cl_2 (25 ml) was added in one portion. After stirring for 2 h, ether (50 ml) was added and the liquid phase was separated by decantation. The residual gummy solids were washed with ether, and the combined liquid phase was passed through a Florisil short column. Evaporation of solvent gave viscous oil (0.47 g, 0.74 mmol, 87%). ^1H NMR ($CDCl_3$) δ=9.87 (1H, s, CHO), 7.65+7.28+7.03+7.00+6.89+6.73 (2H+2H+2H+2H+2H+1H, dd+m+d+m+dd+t, ArH), 5.74 (2H, s, ArCH), 4.20+2.29 (8H+4H, m+m, $O(C\underline{H}_2)_3O$), 3.72+3.61 (4H+4H, d+d, OCH_2), 1.29+0.75 (6H+6H, s+s, Me). MS (FAB) m/z 635 ($M+H^+$).

Synthesis of the "T-Shaped" Dimeric Porphyrin 22. Porphyrin 20. The aldehyde **19** (250 mg, 0.39 mmol), methyl 4-formylbenzoate (128 mg, 0.78 mmol), and dipyrrylmethane **1** (271 mg, 1.18 mmol) were dissolved in dry acetonitrile (22 ml) containing trichloroacetic acid (32 mg, 0.2 mmol) and the mixture was stirred for 15 h. *p*-Chloranil (0.8 g) dissolved in THF (30 ml) was added and stirring was continued overnight. Solvent was evaporated and the residue was purified on alumina (activity III, CH_2Cl_2). The resulting porphyrins were converted to the zinc complexes ($Zn(OAc)_2$ in CH_2Cl_2–methanol) and separated by flash column chromatography (silica gel, CH_2Cl_2).

20: Red crystals (220 mg, 0.17 mmol, 44% based on **19**). ^1H NMR ($CDCl_3$) δ=10.20 (2H, s, *meso*-H), 8.84+8.21 (2H+2H, d+d, $C_6\underline{H}_4CO_2Me$), 7.59+7.30+7.25+6.96+6.91 (2H+2H+2H+3H+2H, dd+d+m+m+d, ArH), 5.71 (2H, s, ArCH), 4.34+4.24+2.35 (each 4H, t+t+m, $O(C\underline{H}_2)_3O$), 4.13 (3H, s, OMe), 4.01 (8H, m, Et), 3.59+3.51 (4H+4H, d+d, OCH_2), 2.67+2.44 (6H+6H, s+s, β-Me), 1.77 (12H, t, Et), 1.17+0.48 (6H+6H, s+s, acetal-Me). MS (FAB) m/z 1278—1284 (M^+).

Porphyrin Dialdehyde 21. The acetal groups were hydrolyzed under acidic conditions[14] as described for **8** to give porphyrin dialdehyde **21(H)** (99%).

21(H_2): Purple crystals; mp 105—107 °C. ^1H NMR ($CDCl_3$) δ=10.52 (2H, s, CHO), 10.24 (2H, s, *meso*-H), 8.44+8.19 (2H+2H, d+d, $C_6\underline{H}_4CO_2Me$), 7.80+7.51+7.04+6.99 (each 2H, dd+m+d+t, $C_6\underline{H}_4CHO$), 7.28+6.94 (2H+1H, d+t, C_6H_3), 4.36+2.41 (8H+4H, t+t+m, $O(C\underline{H}_2)_3O$), 4.13 (3H, s, OMe), 4.02 (8H, m, Et), 2.60+2.47 (6H+6H, s+s, β-Me), 1.77 (12H, m, Et), −2.44 (2H, br, NH). MS (FAB) m/z 1045 ($M+H^+$).

21(Zn): Red crystals. ^1H NMR ($CDCl_3$) δ=10.34 (2H, s, CHO), 10.20 (2H, s, *meso*-H), 8.44+8.21 (2H+2H, d+d, $C_6\underline{H}_4CO_2Me$), 7.72+7.49+7.01+6.96 (each 2H, dd+m+d+t, $C_6\underline{H}_4CHO$), 7.31+6.95 (2H+1H, d+t, C_6H_3), 4.34+2.40 (8H+4H, t+t+m, $O(C\underline{H}_2)_3O$), 4.13 (3H, s, OMe), 4.01 (8H, m, Et), 2.63+2.44 (6H+6H, s+s, β-Me), 1.77 (12H, m, Et). MS(FAB) m/z 1106—1110 (M^+).

"T-Shaped" Dimeric Porphyrin 22. The porphyrin dialdehyde **21(H_2)** (110 mg, 0.105 mmol) and dipyrrylmethane **1** (58.5 mg, 0.25 mmol) were dissolved in dry acetonitrile (40 ml). Trichloroacetic acid (41 mg, 0.25 mmol) dissolved in dry acetonitrile (1.4 ml) was added and the mixture was stirred for 10 h. *p*-Chloranil (0.18 g) in THF (7 ml) was added and stirring was continued overnight. Solvent was evaporated and the residue was purified on alumina (activity III, CH_2Cl_2), then on silica gel (CH_2Cl_2–2% methanol) and recrystallized from CH_2Cl_2–methanol to give purple microcrystals (82.5 mg, 0.056 mmol, 54%).

22(H_4): Mp >270 °C (decomp). ^1H NMR ($CDCl_3$) δ=10.30+10.10 (2H+2H, s+s, *meso*-H), 8.40+8.13 (2H+2H, d+d, $C_6\underline{H}_4CO_2Me$), 8.32+7.76+7.50+7.2 (each 2H, dd+m+t+d, $C_6\underline{H}_4O$), 6.36+3.01 (2H+1H, d+t, J=2.4 Hz, C_6H_3), 4.12+3.94+3.87 (8H+4H+4H, m+m+m, Et), 4.11 (3H, s, OMe), 3.77+1.98+1.09 (each 4H, t+t+m, $O(C\underline{H}_2)_3O$), 2.63+2.41+2.06 (12H+6H+6H, s+s+s, β-Me), 1.87+1.70+1.65 (12H+6H+6H, t+t+t, Et); −2.10+−2.59+ −2.71 (2H+1H+1H, br, NH). MS (FAB) Found: m/z 1463.802. Calcd for $C_{90}H_{103}N_8O_6$: M+H, 1463.800.

The porphyrin dialdehyde **21(Zn)** (14. 4 mg, 0.013 mmol) was treated with dipyrrylmethane **1** (6.7 mg, 0.029 mmol) in the presence of trichloroacetic acid (2 mg, 0.012 mmol) in dry acetonitrile (3.5 ml) as described above to give a monozinc complex **22(H_2Zn)** (6.6 mg, 0.0043 mmol, 33%).

22(H_2Zn): Red crystals. ^1H NMR ($CDCl_3$) δ=10.31+10.06 (2H+2H, s+s, *meso*-H), 8.40+8.14 (2H+2H, d+d, $C_4\underline{H}_6CO_2Me$), 8.32+7.76+7.50+7.2 (each 2H, dd+m+t+d, $C_6\underline{H}_4O$), 6.37+3.03 (2H+1H, d+t, J=2.4 Hz, C_6H_3), 4.11 (3H, s, OMe), 4.11+3.92+3.85 (8H+4H+4H, m+m+m, Et), 3.77+1.77+1.08 (each 4H, t+t+m, $O(C\underline{H}_2)_3O$), 2.63+2.38+2.02 (12H+6H+6H, s+s+s, β-Me), 1.87+1.70+1.65 (12H+6H+6H, t+t+t, Et), −2.10 (2H, br, NH.) MS (FAB) m/z 1525—1530 (M^+).

Synthesis of the "H-Shaped" Porphyrin Trimer 27. Dialdehyde 23. The diacetal **17** was hydrolyzed by the same procedure as **8** to give dialdehyde **23**.

White crystals; mp 127 °C. Found: C, 67.81; H, 5.85%. Calcd for $C_{28}H_{26}O_8$: C, 68.28; H, 5.73%. ^1H NMR ($CDCl_3$) δ=10.51 (2H, s, CHO), 7.82+7.53+7.19+7.02+6.66 (2H+2H+2H+4H+1H, dd+m+d+m+t, ArH), 4.29+4.21+2.34 (each 4H, t+t+m, $O(C\underline{H}_2)_3O$), 3.89 (3H, s, Me). IR (KBr) 1705 and 1680 cm^{-1} (C=O). MS(FAB) m/z 493 ($M+H^+$).

Strapped Porphyrin 24. The strapped porphyrin **24** was prepared from the dialdehyde **23** in 41% yield. ^1H NMR ($CDCl_3$) δ=9.88 (2H, s, *meso*-H), 8.21+7.78+7.48+7.34 (each 2H, dd+m+t+d, $C_6\underline{H}_4O$), 6.54+2.99 (2H+1H, d+t, J=2 Hz, $C_6\underline{H}_3CO_2Me$), 4.06 (3H, s, OMe), 4.01—3.82 (12H, m, Et+$OC\underline{H}_2$), 2.57 (12H, s, β-Me), 1.75 (12H, t, Et), 1.56+1.22 (4H+4H, t+m, $OC\underline{H}_2C\underline{H}_2$), −2.51 (2H, br, NH). IR (KBr) 1718 cm^{-1} (C=O). MS (FAB) m/z 911 ($M+H^+$).

Strapped Porphyrin 25. The strapped porphyrin **24** (204 mg, 0.22 mmol) was treated with $LiAlH_4$ (120 mg, 3.2 mmol) in dry THF (80 ml) at room temperature for 4 h. The strapped porphyrin **25** was purified by flash column chromatography (silica gel, CH_2Cl_2) and recrystallized from CH_2Cl_2–methanol (196 mg, 0.22 mmol, 99%). ^1H NMR ($CDCl_3$) δ=9.95 (2H, s, *meso*-H), 8.24+7.78+7.48+7.33 (each 2H, dd+m+t+d, $C_6\underline{H}_4O$), 5.43+2.99 (2H+1H, d+t, J=2 Hz, $C_6\underline{H}_3$), 4.00—3.86 (12H, m, Et+$OC\underline{H}_2$), 3.79 (2H, br, $C\underline{H}_2OH$), 2.56 (12H, s, Me), 1.76 (12H, t, Et), 1.58+1.24

(4H+4H, t+m, $OC\underline{H}_2C\underline{H}_2$), −2.49 (2H, br, NH). MS (FAB) m/z 883 ($M+H^+$).

Strapped Porphyrin 26. To a suspension of activated MnO_2 (1.2 g) in $CHCl_3$ (methanol free, 15 ml), a solution of the strapped porphyrin **25** (196 mg, 0.22 mmol) in $CHCl_3$ (methanol free, 70 ml) was added dropwise and the mixture was refluxed for 2 d.[15] Solid material was filtered off, washed with $CHCl_3$ and the filtrate was evaporated. The residue was recrystallized from CH_2Cl_2-methanol to give purple microcrystals (162 mg, 0.18 mmol, 83%). ^1H NMR ($CDCl_3$) δ=9.88 (2H, s, *meso*-H), 9.61 (1H, s, CHO), 8.17+7.78+7.47+7.35 (each 2H, dd+m+t+d, $C_6\underline{H}_4O$), 6.02+3.22 (2H+1H,d+t, J=2 Hz, C_6H_3CHO, 4.0—3.8 (12H, m, Et+$OC\underline{H}_2$), 2.56 (12H, s, β-Me), 1.75 (12H, t, Et), 1.71+1.26 (4H+4H, t+m, $OC\underline{H}_2C\underline{H}_2$), −2.57 (2H, br, NH). IR (KBr) 1700 cm^{-1} (C=O). MS (FAB) m/z 881 ($M+H^+$).

"H-Shaped" Trimeric Porphyrin 27. The strapped porphyrin **26** was treated with dipyrrylmethane **1** to give "H-shaped" trimeric porphyrin **27(H$_6$)** in 59% yield.[6] Purple crystals; mp >300 °C. ^1H NMR ($CDCl_3$) δ=10.28+9.95 (4H+2H, s+s, *meso*-H), 8.31+7.75+7.49+7.25 (each 2H, dd+m+t+d, $C_6\underline{H}_4O$), 6.30+2.97 (4H+2H, d+t, J=2. 4 Hz, C_6H_3), 4.09+3.79 (8H+8H, m+m, Et), 3.74+1.95+1.06 (each 4H, t+t+m, $O(C\underline{H}_2)_3O$), 2.61+2.00 (12H+12H, s+s, Me), 1.84+1.57 (12H+12H, t+t, Et), −2.14+−2.91 (4H+2H, br+br, NH). MS (FAB) m/z 2181.6 ($M+H^+$).

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