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Synthesis of Dimeric and Trimeric Porphyrins Based on Intramolecular Macrocyclization Reactions

Atsuhiro OSUKA, Fumikazu KOBAYASHI, and Kazuhiro MARUYAMA*
Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606

An useful method based on acid-catalyzed intramolecular macrocyclization was developed for the synthesis of dimeric and trimeric porphyrins with constrained geometries.

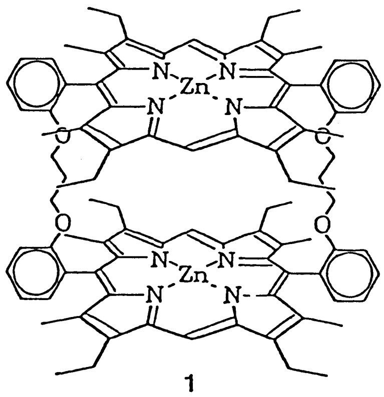
In relation to the important roles of porphyrin aggregates in hemoproteins and photosynthetic pigments, considerable attention has been focused on the synthesis of porphyrin oligomers with restricted geometries.$^{1)}$ A key question concerns the nature and the extent of interactions between the porphyrin pigments in restricted geometries or the geometry-dependence of intramolecular electron transfer reaction. Recently we reported the synthesis of conformationally restricted dimeric porphyrins, in which the two porphyrin rings were bridged by aromatic spacers $^{2)}$ and spiro-biindane spacers.$^{3)}$ Now we wish to report here the synthesis of a different class of dimeric (1 and 3) and trimeric porphyrins (2 and 4) using intramolecular macrocyclization reactions.

Face-to-face dimeric porphyrin 1 was synthesized by the acid-catalyzed cyclization reaction $^{4)}$ of 3,3'-diethyl-4,4'-dimethyl-2,2'-dipyrrylmethane (5) and the porphyrin dialdehyde (6). Isomerically pure porphyrin dialdehyde 6 was prepared in 3 steps in a overall 50% yield from p-xylylene-strapped porphyrin.$^{5,6)}$ The porphyrin dialdehyde 6 was treated with dipyrrylmethane 5 in acetonitrile in the presence of trichloroacetic acid followed by oxidation with p-chloranil to give the porphyrin dimer 1 in 60% yield after purification as a bis-zinc complex (m/z 1530-1535, M^+).$^{7)}$

For the synthesis of the porphyrin trimer 2, 5,15-bis(2,6-dihydroxyphenyl)-etioporphyrin II (7) was prepared in 2 steps (overall 71%) from 2,6-dimethoxybenzaldehyde and 5. Four hydroxyl groups were alkylated with aryloxypropyl iodide 8 $^{8)}$ in refluxing acetone containing K_2CO_3 to give a both-face modified porphyrin 9 (43%). The acetal groups were hydrolyzed under acidic conditions to give porphyrin tetraaldehyde 10a (90%).$^{9)}$ We first tried the reaction of free-base porphyrin 10a with dipyrrylmethane 5, which resulted in the formation of the porphyrin trimer 2a (m/z 2180.5, M^+)

in rather poor yields (< 10%). In contrast, the yield of the trimer (2b) was markedly improved (35%) by the use of the zinc-complex 10b as the starting porphyrin (2b: Found: m/z 2244.120. Calcd for $C_{144}H_{153}N_{12}O_8Zn$: M+H, 2244.126).[7)]

The "T-shaped" porphyrin dimers 3a and 3b were also prepared from porphyrin dialdehydes 11a and 11b in 50% and 33% yield, respectively.[7,11)] The "H-shaped" porphyrin trimer 4 was prepared in a different strategy. The strapped porphyrin 12 was first prepared from the corresponding dialdehyde in 41% yield.[5)] 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.[12)] The strapped porphyrin 13 thus prepared was treated with dipyrrylmethane 5 to give "H-shaped" porphyrin trimer 4 in 59% yield (m/z 2181.6, $M+H^+$).[7,13)]



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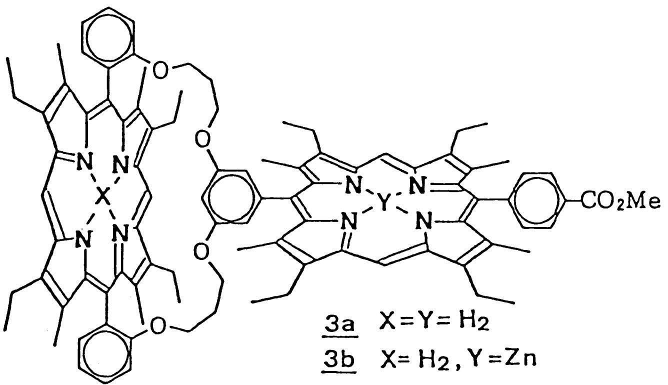
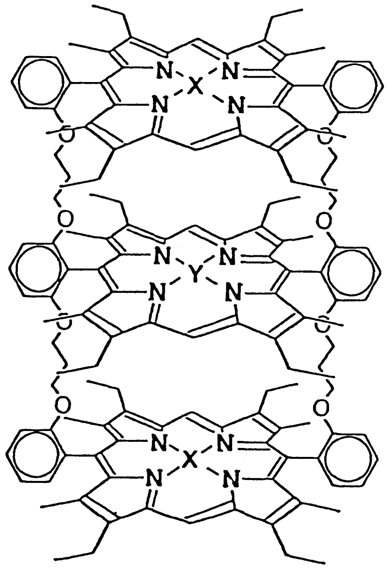
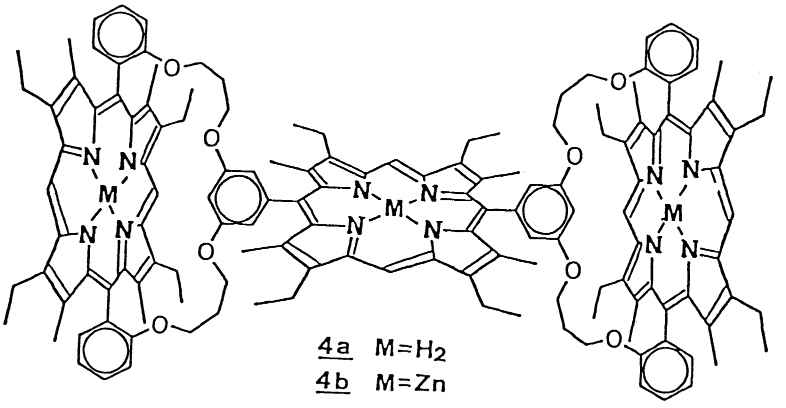


3a X=Y=H₂
3b X=H₂,Y=Zn
3c X=Y=Zn

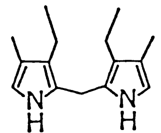


2a X=Y=H₂
2b X=H₂,Y=Zn
2c X=Y=Zn



4a M=H₂
4b M=Zn

The unique geometries of "T-shaped" dimer 3 and "H-shaped" trimer 4 were characterized by their ^{1}H-NMR spectra. The inside aromatic protons (H_a, designated in Table 1) appeared at ca. 3 ppm region due to the strong shielding effect of porphyrin ring current. The center-to-center distances between two porphyrin rings were estimated to be 13 Å from Corey-Pauling-Koltun (CPK) molecular models. The UV-vis spectra of 3 and 4 showed rather small changes with respect to the monomeric porphyrin 14, while the stacked type porphyrins 1 and 2 showed blue-shifted Soret band similar with other face-to-face dimeric porphyrins. (Table 2)



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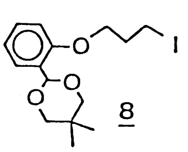

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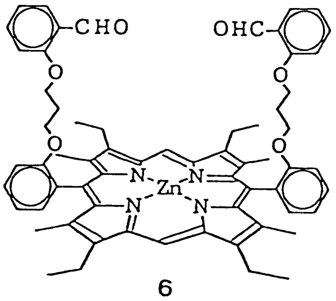

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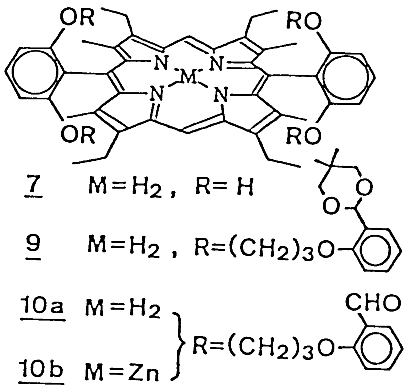


7 M=H_2, R=H

9 M=H_2, R=$(CH_2)_3O$-

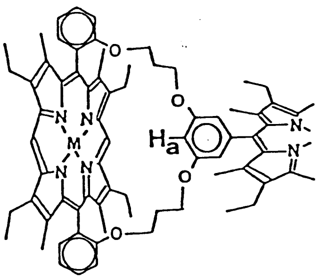
10a M=H_2

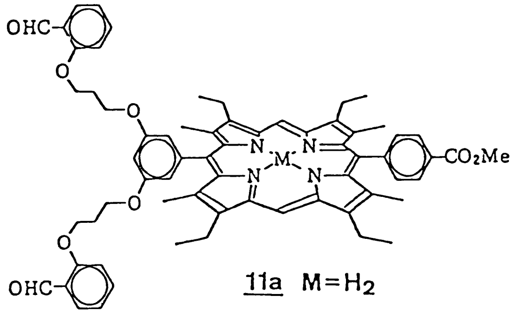
10b M=Zn

R=$(CH_2)_3O$-

Table 1. Chemical Shifts of H_a

Compd.	δ
3a	3.01
3b	3.03
3c	2.93
4a	2.97
4b	2.92





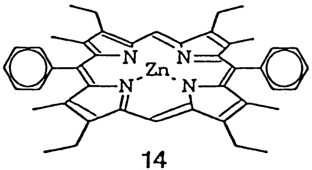
11a M=H_2

11b M=Zn

Table 2. UV-vis Spectra of Zinc-complexes in CH_2Cl_2

Compd.	λ max/nm		
1	405	538	574
2c	404	539	576
3c	411	540	574
4b	411	539	574
14[a)]	409	538	574

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



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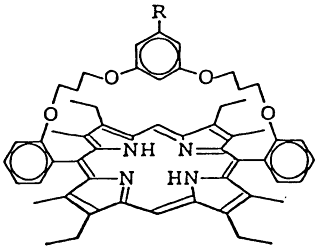

12 R=CO_2Me

13 R=CHO

In summary, the acid-catalyzed intramolecular macrocyclization reaction is particularly useful for the synthesis of dimeric and trimeric porphyrins. The porphyrins synthesized here have restricted geometries between the porphyrin rings due to the steric effects of their strap chains. There exists no direct $\pi-\pi$ conjugation between porphyrin rings, rendering through-bond interactions to be negligibly small. Therefore, these models should be quite useful for studies on through-space electron transfer process, which is now actively in progress.

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6) Synthetic details will be presented elsewhere.
7) All new compounds described in this paper gave satisfactory spectral data consistent with the assigned structure.
8) This compound (8) was prepared in 3 steps from salicylaldehyde in a overall yield 83%.
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10) Fab mass spectra were taken on a JEOL JMS-HX-110 (10 eV) with m-nitrobenzyl alcohol as the matrix.
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