CHEMISTRY LETTERS, pp. 949-952, 1993.


# An Efficient One-Pot Synthetic Procedure of Multiple Porphyrin-Cyclization

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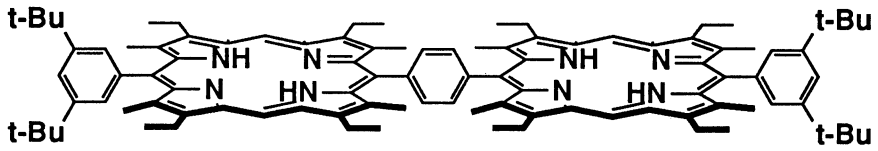
Trichloroacetic acid catalyzed condensation of an aldehyde carrying more than two formyl groups and 3,5-di-tert-butylbenzaldehyde with bis(3-ethyl-4-methyl-2-pyrrolyl)-methane in acetonitrile followed by p-chloranil oxidation gave oligomeric porphyrins in good yield via multiple porphyrin-cyclization.

Considerable efforts have been devoted to the synthesis of covalently linked porphyrin oligomers in relation to their relevance as models for photosynthetic reaction centers and cytochromes. In recent years, increasing attention has been focused on conformationally restricted molecules.[1] Among these, 5-aryl or 5,15-diaryl-octaalkylporphyrins are proved to be a quite useful unit,[2] since steric hindrance between the flanking alkyl groups and the aromatic bridge tends to force the porphyrin plane to be nearly perpendicular to the bridge and thus the relative geometry of porphyrins is held with a reasonable rigidity. Although many examples of such diporphyrin system were known,[3-8] there are only a limited number of successful synthesis of triporphyrins or higher homologues.[9-11] Most of the synthetic methods so far developed for such triporphyrins and higher homologues were based on the acid-catalyzed condensation of a formyl-substituted porphyrin with dipyrrylmethane, which provided trimer with final formation of the central porphyrin.

We now disclose an efficient method for the synthesis of porphyrin oligomers via multiple porphyrin-cyclization in a one-pot procedure. General procedure is as follows; to an acetonitrile solution (15 ml) of dialdehyde or trialdehyde (0.1 mmol), 3,5-di-tert-butylbenzaldehyde (4 equivalent to each formyl group), and bis(3-ethyl-4-methyl-2-pyrrolyl)methane[12] (5 equivalent to each formyl group), trichloroacetic acid (0.6 equivalent to the dipyrrylmethane used) was added under nitrogen atmosphere in the dark. After stirring for 16 h, p-chloranil (1.2 equivalent to the dipyrrylmethane used) in THF was added and the resulting mixture was stirred for 3-4 h. Porphyrin product was isolated by usual work-up and subsequent flash column chromatography on silica gel. 1,4-Phenylene- and 1,3-phenylene-bridged diporphyrins **1** and **2** were prepared from terephthalaldehyde and isophthalaldehyde in 55 and 60% yields, respectively.

3,5-Di-tert-butylbenzaldehyde has been often employed as a building block in porphyrin models,[13] presumably because bulky 3,5-di-tert-butylphenyl substituents at meso-position enhance the solubility of porphyrins in most of organic solvents by retarding porphyrin aggregation. This property seems to be important for the high yields of **1** and **2**. When p-tolualdehyde was used instead of 3,5-di-tert-butylbenzaldehyde under identical conditions, the diporphyrin yields dropped to ca. 20-30%.

1,4-Phenylene-bridged triporphyrin **3** (m/z(FAB)=1961; Calcd for $C_{136}H_{158}N_{12}$=1960.8) was prepared from 5,15-bis(4-formylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphine in 40% yield. A 1,3,5-pheneylene-bridged triporphyrin **4** (m/z(FAB)=2074; Calcd for $C_{144}H_{174}N_{12}$=2073.0) having a propeller-like geometry was also prepared from 1,3,5-triformylbenzene in 65% yield, indicating that even triple formation of porphyrin was also effective by this method.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HN
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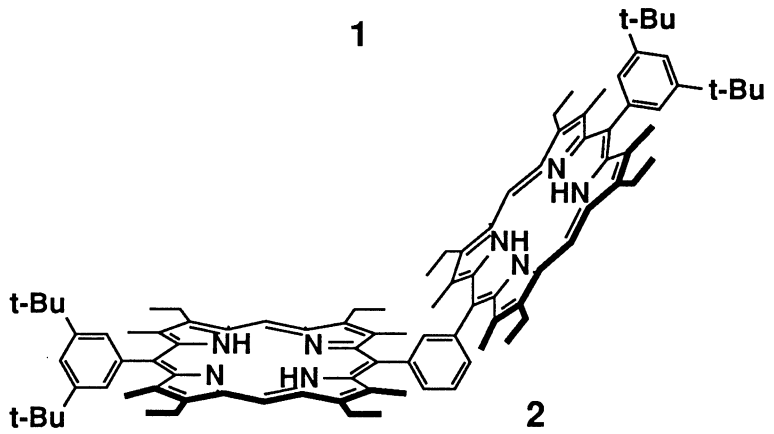
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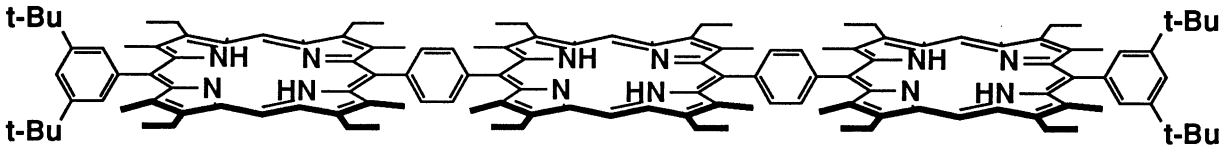
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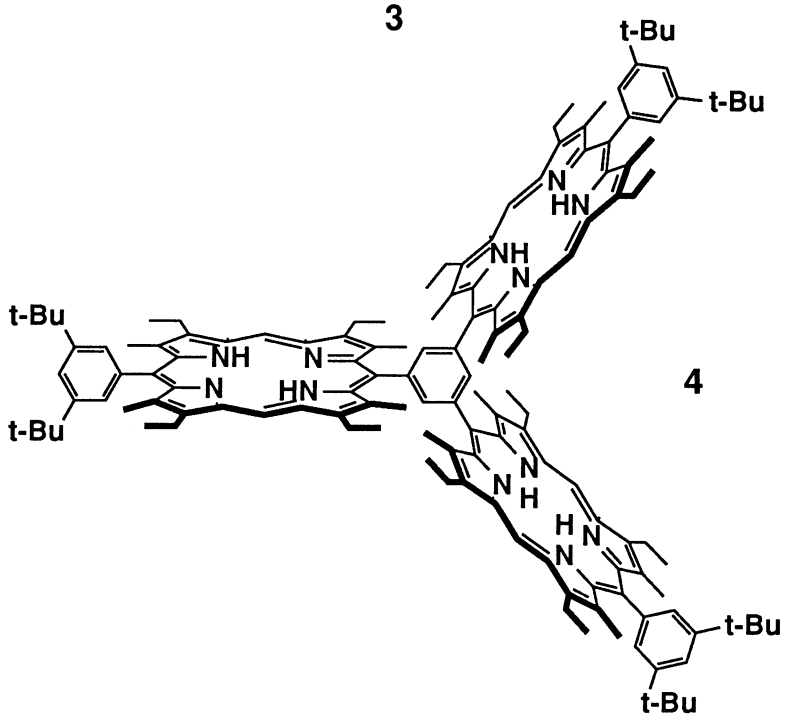
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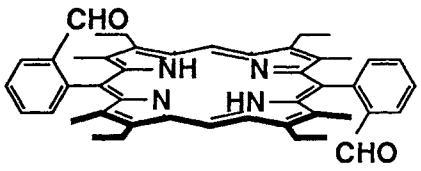
t-Bu

4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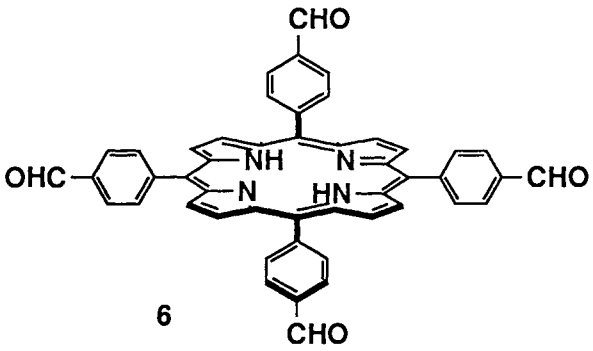
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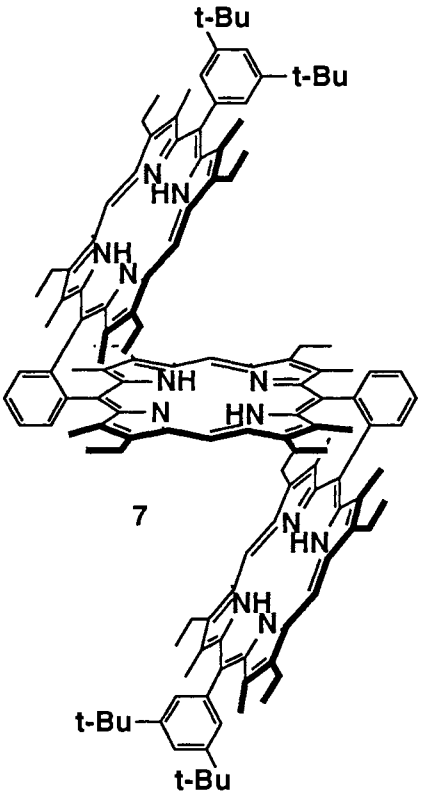
6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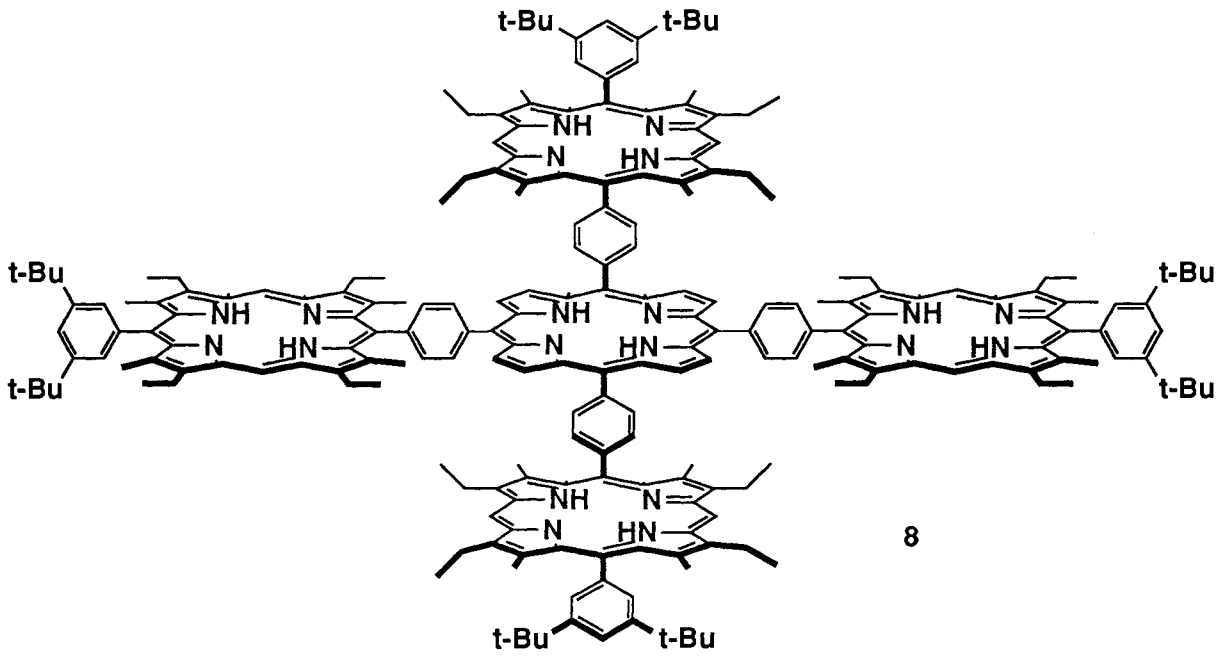
7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t-Bu
NH
N
N
HN
t-Bu
t-Bu

8

This synthetic procedure was further extended to the synthesis of 1,2-pheneylene-bridged triporphyrin **7** (30%, m/z(FAB)=1962; Calcd for $C_{136}H_{158}N_{12}$=1960.8) from porphyrin monomer **5**.[14] Finally, even porphyrin pentamer **8** (m/z=3276; Calcd for $C_{228}H_{254}N_{20}$=3274.6) was prepared from 5,10,15,20-tetrakis(4-formylphenyl)porphine **6**[15] in 15% yield.[16]

The synthetic procedure presented here is quite simple, easy, and straightforward to conformationally-restricted porphyrin oligomers.

This work was supported by a Grant-in-Aid for Specially Promoted Research (No. 02101005) from the Ministry of Education, Science and Culture of Japan. B-l. L. thanks for JSPS Foundation for a postdoctoral fellowship.

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(Received March 9, 1993)