CHEMISTRY LETTERS, pp. 1687-1690, 1991.

Doubly-Strapped Porphyrins as Useful Building Blocks for Selectively Metallated Oligoporphyrins

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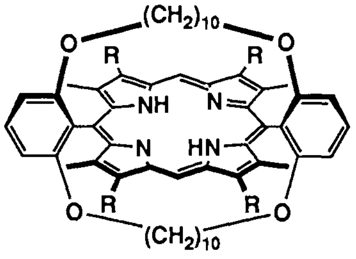
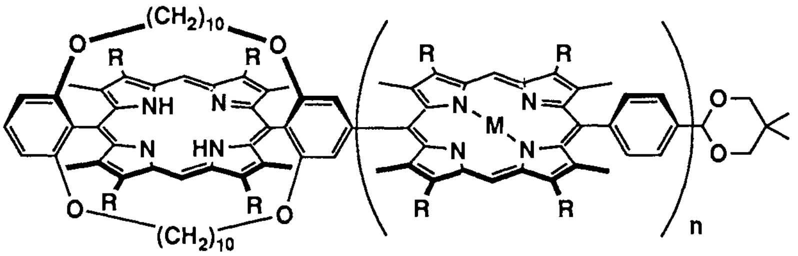
Metallation of a porphyrin ring was completely suppressed by introducing two $(CH_2)_{10}$ "straps" on the both sides of the porphyrin ring. Di- and triporphyrins with one "doubly-strapped" ring were quantitatively converted to the partially metallated product with the metal-free strapped ring. These doubly-strapped porphyrins will be useful for synthesis of selectively metallated oligoporphyrins.

Porphyrin compounds have been widely used as models for photosynthetic pigments.[1] Since the determination of the X-ray structures of photosynthetic bacterial reaction centers,[2] much interest has been focused on model compounds based on functionalized oligomeric porphyrins, which are designed to mimic the arrangement of chromophores in natural systems.[3,4] Such model compounds have been proven to be quite useful in studying dynamics of electron/energy transfers in multicomponent systems.[3,4] The natural bacterial reaction center contains six tetrapyrrolic pigments, two of which are metal-free and the remainder are complexed with magnesium. As the redox and photochemical properties of porphyrins vary significantly with the chelating metals,[5,6] site-selective metallation of oligoporphyrins will be quite promising in controlling properties of photosynthetic model compounds.

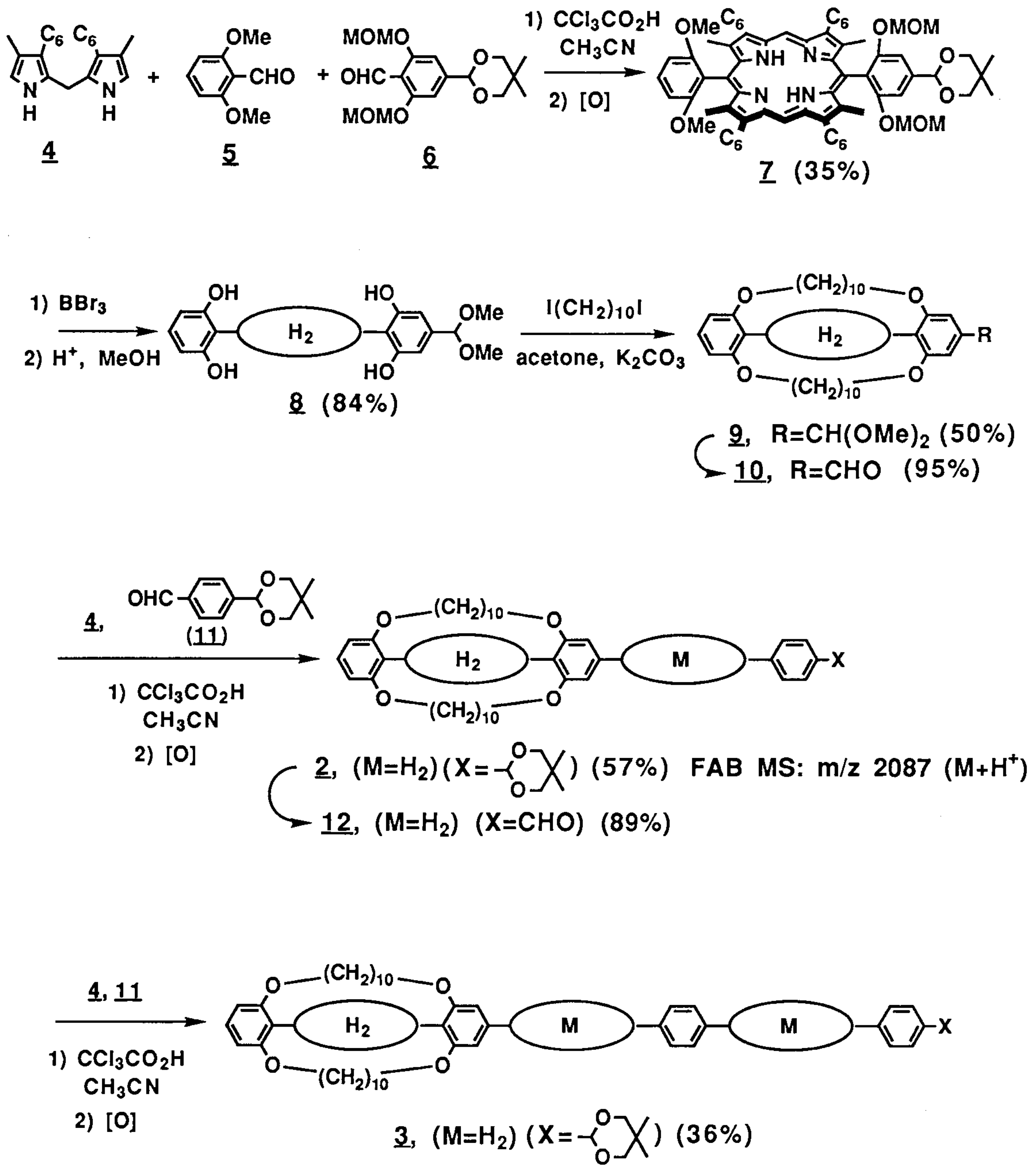
In this report, we wish to present a useful approach toward selectively metallated oligoporphyrins. In the compounds **1**, **2**, and **3**, one porphyrin ring has two $(CH_2)_{10}$ "straps" on both sides, which offer efficient protection of the ring against metallation.[7] One can insert metal to the other porphyrin rings while leaving the "strapped" ring metal-free. Thus partial metallation can be achieved with high site-selectivity.[8]



1 (R = C_6H_{13})



2 (n = 1) , **3** (n = 2)
(M = H_2, Zn)



4

5

6

7 (35%)

8 (84%)

9, R=CH(OMe)$_2$ (50%)

10, R=CHO (95%)

2, (M=H$_2$)(X=) (57%) FAB MS: m/z 2087 (M+H$^+$)

12, (M=H$_2$) (X=CHO) (89%)

3, (M=H$_2$) (X=) (36%)

The "doubly-strapped" porphyrin **1** was synthesized from bis(2,6-dihydroxyphenyl)porphyrin by treatment with 1,10-diiododecane and K_2CO_3 in refluxing acetone. Synthesis of **2** and **3** with one "doubly-strapped" ring was carried out as follows. Acid catalyzed condensation of dipyrrolylmethane **4** and aldehydes **5** and **6** gave the porphyrin **7** after chromatography on silica gel (35%).[9] Treatment of **7** with BBr_3 followed by heating in acidic methanol gave the tetrahydroxyporphyrin **8**. Condensation of **8** with 1,10-diiododecane in the presence of K_2CO_3 in refluxing acetone gave the doubly-strapped porphyrin **9**. The acetal group in **9** was hydrolyzed to give the formylporphyrin **10**, which was allowed to condense with dipyrrolylmethane **4** and aldehyde **11**. After chromatographic separation, the diporphyrin **2** was obtained in 57% yield. Deprotection of **2** (to yield the formyldiporphyrin **12**) followed by condensation with **4** and **11** gave the triporphyrin **3** in 36% yield.

The ^{1}H-NMR spectra of the doubly-strapped porphyrins showed a common characteristic feature, i.e. large up-field shifts of the CH_2 signals of the $(CH_2)_{10}$ "straps" (except for the terminal OCH_2), which appeared in the region from $\delta = 0.8$ to -2.6. This result indicates that the $(CH_2)_{10}$ straps in these compounds are positioned right above (and below) the porphyrin ring.

Metallation experiments were carried out for **1**, **2**, and 5,15-di(*p*-tolyl)-3,7,13,17-tetrahexyl-2,8,12,18-tetramethylporphyrin (a "non-strapped" reference compound) under the following conditions; free-base porphyrin 0.5 mM (1mM = 1mmol dm^{-3}), zinc acetate 50 mM, in CH_2Cl_2/MeOH (v/v = 10/1), at 20°C, 45 min. 5,15-Di(*p*-tolyl)porphyrin was converted to the zinc complex quantitatively, while **1** was recovered without any trace of the metallated product. Apparently, the straps on the both sides of the porphyrin ring in **1** offered efficient protection against metallation. The reaction of **2** resulted in quantitative formation of the monozinc complex of **2**. The FAB-MS spectrum of this complex showed a cluster of peaks at m/z = 2146 to 2155 with the most intense peak at 2150, consistent with the calculated spectrum for $C_{140}H_{195}N_8O_6Zn$ $(M+H^+)$. Considering the results on metallation of the monomeric porphyrins described above, it is reasonable to assume that metallation took place at the ring without straps. The ^{1}H-NMR spectrum of the monozinc-**2** was also consistent with this assignment; the methylene protons of the $(CH_2)_{10}$ straps gave the ^{1}H-NMR signals at exactly the same positions as in the metal-free **2**.

Similarly, metallation of **3** led to the dizinc complex (FAB-MS: m/z = 2983 to 2995), in which the non-strapped two rings were metallated.

In summary, the $(CH_2)_{10}$ straps on the both sides of the porphyrin ring can efficiently prohibit metallation of the ring. These doubly-strapped porphyrins can be utilized for building photosynthetic model compounds in which redox and photophysical properties are controlled by arranging the metal-free and metallated porphyrins in a definite geometry.

The authors thank Professor Ikuo Yamashina of Kyoto Industrial University for his permission to use the JEOL HX-110 mass spectrometer. This work was supported by a Grant-in-Aid for Specially Promoted Research (No. 0201005) from the Ministry of Education, Science and Culture of Japan.

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(Received June 28, 1991)