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 (CH₂)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.³⁴ Such model compounds have been proven to be quite useful in studying dynamics of electron/energy transfers in multicomponent systems.³⁴ 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,⁵⁶ 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 (CH₂)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
The "doubly-strapped" porphyrin 1 was synthesized from bis(2,6-dihydroxyphenyl)porphyrin by treatment with 1,10-diiododecane and K$_2$CO$_3$ 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%). 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 K₂CO₃ 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 ¹H-NMR spectra of the doubly-strapped porphyrins showed a common characteristic feature, i.e. large up-field shifts of the CH₂ signals of the (CH₂)₁₀ "straps" (except for the terminal OCH₂), which appeared in the region from δ = 0.8 to -2.6. This result indicates that the (CH₂)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 CH₂Cl₂/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 C₁₄₀H₁₉₅N₈O₆Zn (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 ¹H-NMR spectrum of the monozinc-2 was also consistent with this assignment; the methylene protons of the (CH₂)₁₀ straps gave the ¹H-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 (CH₂)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.

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References


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