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

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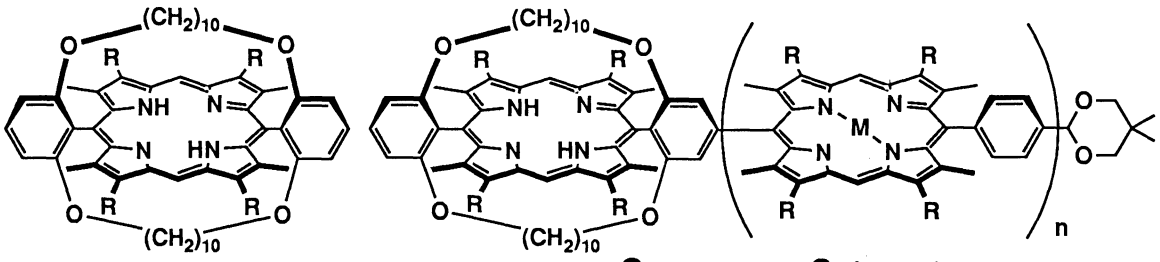
Metallation of a porphyrin ring was completely suppressed by introducing two $(CH_2)_{10}$ "straps" on the both sides of the porphyrin ring. Di- and triporphyrins with one "doubly-strapped" ring were quantitatively converted to the partially metallated product with the metal-free strapped ring. These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

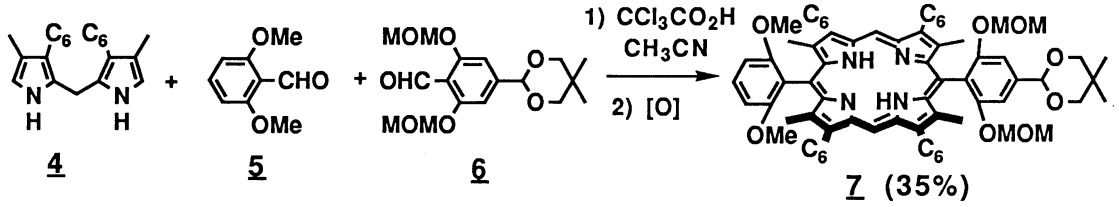
Porphyrin compounds have been widely used as models for photosynthetic pigments.[1] Since the determination of the X-ray structures of photosynthetic bacterial reaction centers,[2] much interest has been focused on model compounds based on functionalized oligomeric porphyrins, which are designed to mimic 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.

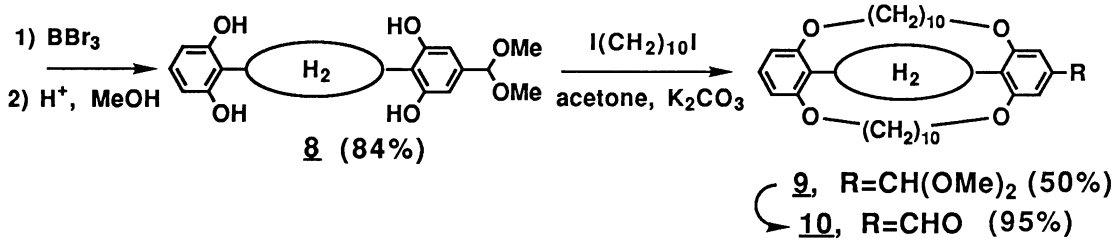
In this report, we wish to present a useful approach toward selectively metallated oligoporphyrins. In the compounds **1**, **2**, and **3**, one porphyrin ring has two $(CH_2)_{10}$ "straps" on both sides, which offer efficient protection of the ring against metallation.[7] One can insert metal to the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

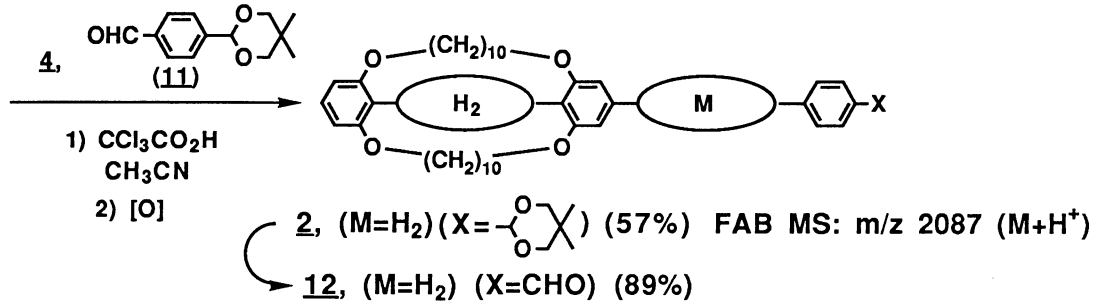


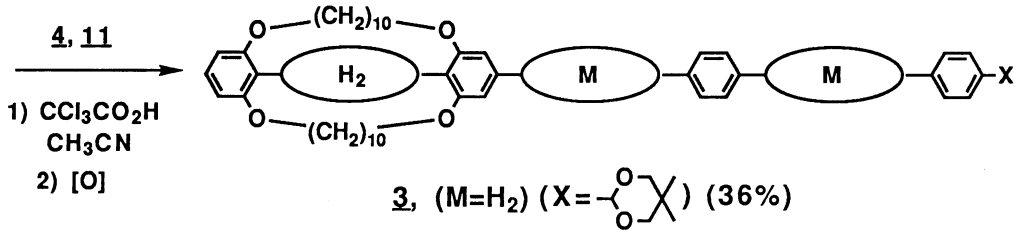
1 (R = C_6H_{13})

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









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 δ = 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.

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References

1) Reviews: M. R. Wasielewski, *Photochem. Photobiol.*,**48**, 923 (1988); S. G. Boxer, *Biochim. Biophys. Acta*, **726**, 265 (1983).
2) J. Deisenhofer, O. Epp, K. Miki, R. Huber,and H. Michel, *J. Mol. Biol.*,**180**, 385 (1984); C.-H. Chang, D. M. Tiede, J. Tang, J. Norris,and M. Schiffer, *FEBS Lett.*,**205**, 82 (1986).
3) J. Rodriguez, C. Kirmaier, M. R. Johnson, R. A. Friesner, D. Holten, and J. L. Sessler, *J. Am. Chem. Soc.*, **113**, 1652 (1991); J. L. Sessler, M. R. Johnson, S. E. Creager, J. C. Fettinger, and J. A. Ibers,

ibid., **112**, 9310 (1990); J. L. Sessler, M. R. Johnson, and T.-Y. Lin, *Tetrahedron*, **45**, 4767 (1989); S. Chardron-Noblat, J.-P. Sauvage, and P. Mathis, *Angew. Chem., Int. Ed. Engl.*, **28**, 593 (1989); M. R. Wasielewski, D. G. Johnson, M. P. Niemczyk, G. L. Gaines, III, M. P. O'Neil, and W. A. Svec, *J. Am. Chem. Soc.*, **112**, 6482 (1990).

4) A. Osuka, S. Nakajima, K. Maruyama, N. Mataga, and T. Asahi, *Chem. Lett.*, **1991**, 1003; A. Osuka, K. Maruyama, N. Mataga, T. Asahi, I. Yamazaki, and Y. Nishimura, *J. Am. Chem. Soc.*, **112**, 4958 (1990); K. Maruyama and A. Osuka, *Pure Appl. Chem.*, **62**, 1511 (1990); A. Osuka, K. Maruyama, I. Yamazaki, and N. Tamai, *Chem. Phys. Lett.*, **165**, 392 (1990);

5) M. Gouterman, "The Porphyrins," ed by D. Dolphin, Academic Press, London (1978), p. 1.

6) K. M. Kadish, *Prog. Inorg. Chem.*, **34**, 435 (1986).

7) Several "doubly-strapped" porphyrins have been reported; U. Simonis, F. A. Walker, P. L. Lee, B. J. Hanquet, D. J. Meyerhoff, and W. R. Scheidt, *J. Am. Chem. Soc.*, **109**, 2659 (1987); K. Maruyama, S. Morikawa, and A. Osuka, *Bull. Chem. Soc. Jpn.*, **60**, 1015 (1987); M. Momenteau, J. Mispelter, B. Loock, and E. Bisagni, *J. Chem. Soc., Perkin Trans. 1*, **1983**, 189.

8) Previous studies on partially metallated oligoporphyrins: O. Ohno, Y. Ogasawara, M. Asano, Y. Kajii, Y. Kaizu, K. Obi, and H. Kobayashi, *J. Phys. Chem.*, **91**, 4269 (1987); R. L. Brookfield, H. Ellul, A. Harriman, and G. Porter, *J. Chem. Soc., Faraday Trans. 2*, **1986**, 219; J. P. Collman, C. S. Bencosme, R. R. Durand, Jr., R. P. Kreh, and F. C. Anson, *J. Am. Chem. Soc.*, **105**, 2699 (1983); J. A. Anton and P. A. Loach, *Photochem. Photobiol.*, **28**, 235 (1978); F. P. Schwarz, M. Gouterman, Z. Muljrani, and D. Dolphin, *Bioinorg. Chem.*, **2**, 1 (1972). See also Refs. 3 and 4.

9) A. Osuka, T. Nagata, F. Kobayashi, and K. Maruyama, *J. Heterocyclic Chem.*, **27**, 1657 (1990).

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