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A Twisted and Partially Overlapping Porphyrin Dimer as a New Model of Special Pair in Photosynthetic Reaction Center†

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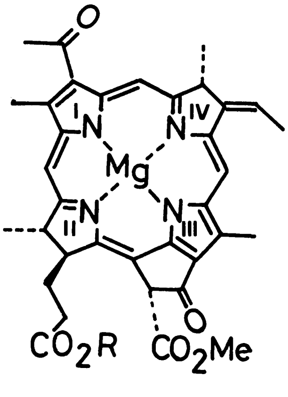
A twisted and partially overlapping porphyrin dimer bridged by a 1,1'-spirobiindane spacer was synthesized. Its biszinc complex and bismagnesium complex showed a split Soret band, indicating the exciton interaction of the two porphyrin ring. Bismagnesium complex underwent reversible one-electron oxidation 40 mV more easily than the corresponding monomeric porphyrin.

The recent X-ray analysis of a bacterial photosynthetic reaction center from Rhodopseudomonas viridis dramatically shows the critical arrangement of six interacting tetrapyrroles at the active site.1) Among the many important structural features disclosed, the arrangement of bacteriochlorophyll b (BChl b) in the special pair was precisely determined. The two BChl-b molecules interact most closely with their pyrrole ring I, which is overlapping each other with a



BChl b

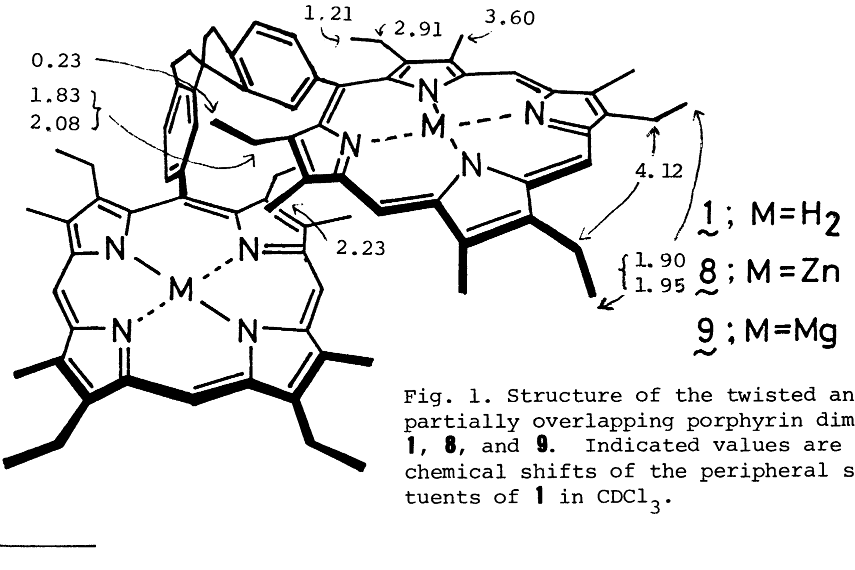


Fig. 1. Structure of the twisted and partially overlapping porphyrin dimers, **1**, **8**, and **9**. Indicated values are the chemical shifts of the peripheral substituents of **1** in $CDCl_3$.

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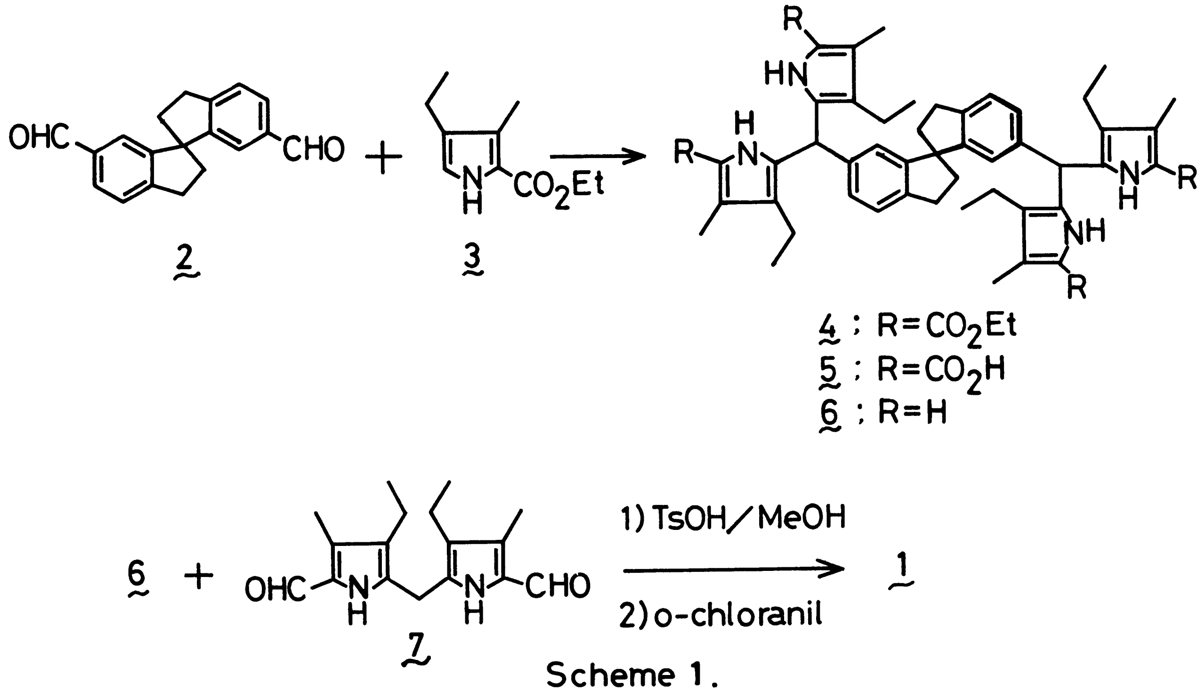
†This paper is dedicated to the late Professor Ryozo Goto, Kyoto University.

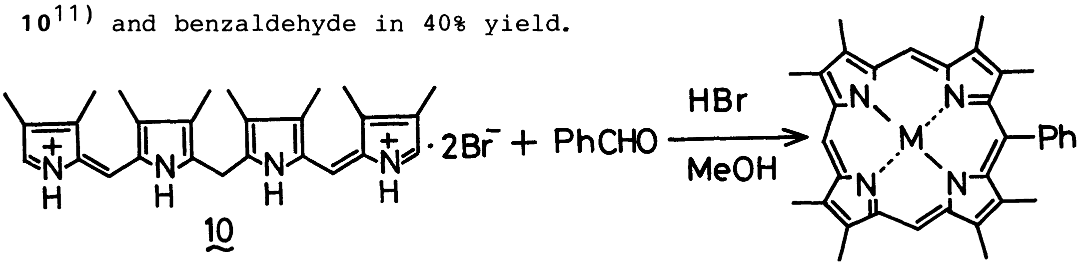
vertical separation of ca. 3 Å. Characteristically, the special pairs in vivo are responsible for 870 nm absorption band in the reaction center and are more easily oxidized than bulk BChl b in the organism.[2] A considerable amount of effort has been done for the purpose of building model dimers which duplicate some of the characteristic properties of the special pair.[3,4] However, no model could realize the partially overlapping relative orientation. As a part of our research program aimed at the construction of controlled aggregates of multiple porphyrins capable of being highly active as photosensitizer for charge separation, we have synthesized a novel porphyrin dimer **1**, in which two porphyrin rings are bridged by a 1,1'-spirobiindane spacer. The configuration of two porphyrin rings in **1** is rigidly fixed by the combined steric restrictions of the spiro spacer and the flanking ethyl groups, as shown in Fig. 1. The unique structural feature of this dimeric porphyrin **1** is that the two porphyrin rings are partially overlapping each other onto one pyrrole ring with a dihedral angle of about 10-35°. Space-filling molecular model analysis showed that the vertical separation of the two porphyrin rings was within 4 Å and the center-to-center separation was ca. 10 Å.

The synthesis of **1** is outlined in Scheme 1. Condensation of ethyl 4-ethyl-3-methylpyrrole-2-carboxylate **3**[5] with 6,6'-diformyl-1,1'-spirobiindane[3] **2**[6] in ethanol-HCl gave bis(dipyrryl)methane **4** in 85% yield. Hydrolysis and



Scheme 1.

decarboxylation by Chang's procedure[7)] gave the α-unsubstituted bis(dipyrryl)methane **6** in 75% yield. The final cyclization was carried out by treating **6** and 2 equiv. of **7** with p-toluenesulfonic acid in methanol for 48 h, furnishing **1**[8)] in 20% yield. Biszinc complex **8** was prepared quantitatively by treating **1** with zinc acetate in $CHCl_3$, and magnesium insertion into both porphyrin ring of **1** was effected with iodomagnesium 2,6-di-tert-butyl-4-methylphenolate [9)] in CH_2Cl_2 at room temperature, giving **9** in 75% yield. As a monomeric reference porphyrin, 5-phenyl substituted octamethylporphyrin **11** was synthesized by the condensation reaction[10)] of the corresponding ac-biladiene **10**[11)] and benzaldehyde in 40% yield.



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11; M = H_2
12; M = Zn
13; M = Mg

The ^{1}H-NMR spectrum of **1** was consistent with the twisted and partially overlapping structure. Peripheral substituents of four methyl groups and four ethyl groups of **1** were unequivalent and thus appeared at the different chemical shifts in the ^{1}H-NMR spectrum (Fig. 1). Among these, the peaks due to the ethyl and methyl groups attached to the overlapping pyrrole ring were most shielded by the porphyrin ring current and appeared at δ 1.83 and 2.08 ppm ($\text{-C}\underline{\text{H}}_2\text{CH}_3$) and 0.23 ppm ($\text{-CH}_2\text{C}\underline{\text{H}}_3$) and at δ 2.23 ppm, respectively. Secondary high field-shifted ethyl signals at δ 2.91 (q) and 1.21 (t) were assigned to the other ethyl group flanking the spacer moiety, which experienced the diamagnetic ring current of the aromatic ring of the spacer moiety.

Evidence for the electronic interaction between the porphyrin macrocycles in **1**, **8**, and **9** was obtained from their UV/vis spectroscopy. The dimeric porphyrin **1** showed a rather broadened Soret band centered at 403 nm, which was slightly red shifted compared to the 5-phenyl substituted octamethylporphyrin **10** (λ_{max} 401.5 nm). The biszinc complex **8** and the bismagnesium complex **9** presented a split Soret band (402 and 410 nm in **8**, and 409 and 417 nm in **9**), indicating the exciton interaction of the two porphyrin rings. On the other hand, the fluorescence spectra of **1**, **8**, and **9** were unchanged relative to the monomeric porphyrins **11**, **12**, and **13** with maxima at 628 and 693 nm, 575 and 627 nm, and 587 and 643 nm, respectively, in CH_2Cl_2. Interestingly, the fluorescence intensities of **1**, **8**, and **9** were not reduced appreciably compared to the corresponding monomeric porphyrins in spite of the close proximity of the two porphyrin rings. This finding may be important to understand the unique properties of antenna chlorophyll, which transfer excitation energy without loss of self-quenching.

First reversible one-electron oxidation potentials of **9** and **13** were measured in butyronitrile to be 0.12 V and 0.16 V vs. (ferrocene/ferrocene$^+$), respectively.$^{12)}$ This result indicates that the cation radical of **9** may be stabilized by the delocalization of unpaired electron density over both macrocycles, as such in the special pair in vivo.

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6) The bisaldehyde **2** was prepared in 5 steps from 1,1'-spirobiindane$^{13)}$ in overall yield 12%; mp 104-105 °C; IR (KBr) 1700 cm^{-1}; MS, m/e 276 (M$^+$); ^{1}H-NMR (CDCl$_3$) δ 9.88(s, 2H), 7.72(d, J=8.6 Hz, 2H), 7.44(d, J=8.6 Hz, 2H), 7.40(s, 2H), 3.10(m, 4H), 2.35(m, 2H), and 2.25(m, 2H).
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8) Diporphyrin **1**; mp > 300 °C; UV-vis, λ_{max}, 403, 501, 535, 570, and 624 nm; ^{1}H-NMR (CDCl$_3$) δ 10.21(s, 2H, meso), 10.12(s, 2H, meso), 9.97(s, 2H, meso), 7.98(s, 2H), 7.89(d, J=8 Hz, 2H), 7.40(d, J=8 Hz, 2H), 3.45(m, 2H), 3.30(m, 2H), 2.84(m, 2H), and -3.10(2H, NH).
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