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Synthesis of Conformationally Restricted Dimeric Porphyrins Unsymmetrically Linked with Quinone

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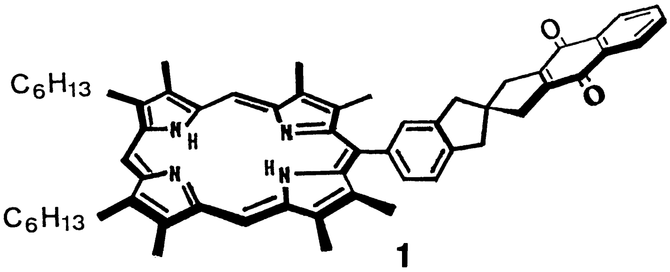
Unsymmetrically quinone-substituted porphyrin dimers were synthesized. The fluorescence of the both porphyrins in these models was effectively quenched by the attached quinone.

The recent X-ray analysis of the photosynthetic reaction center from photosynthetic bacteria provides the first unambiguous characterization of the photosynthetic active site and a structural basis for understanding biological electron transfer.[1)] Covalently-linked porphyrin-quinone molecules have been studied extensively as models for the light-initiated charge separation in photosynthesis.[2)] A key question concerns the dependence of the electron transfer reactions on free energy, distance, and orientation. Synthetic model compounds with well-defined geometries are particularly useful in probing this problem. Recently we reported the synthesis of a porphyrin-quinone model compound **1** linked by a rigid spiro-indane spacer, so as to ensure the relative geometry of the porphyrin and quinone to be held in a twisted orientation with center-to-center distance of 14-15 Å.[3)]

Reported herein is the synthesis of conformationally restricted dimeric porphyrins unsymmetrically linked with a quinone **2a-d** (Scheme 1).[4)] These compounds will be useful for studies on energy transfer and electron transfer coupled reaction as well as long-distance electron transfer reaction via superexchange mechanism.[4)] Typically, the synthesis of 4,4'-biphenyl-linked diporphyrin **2a** was outlined in Scheme 2. Acid-catalyzed condensation of 1,19-



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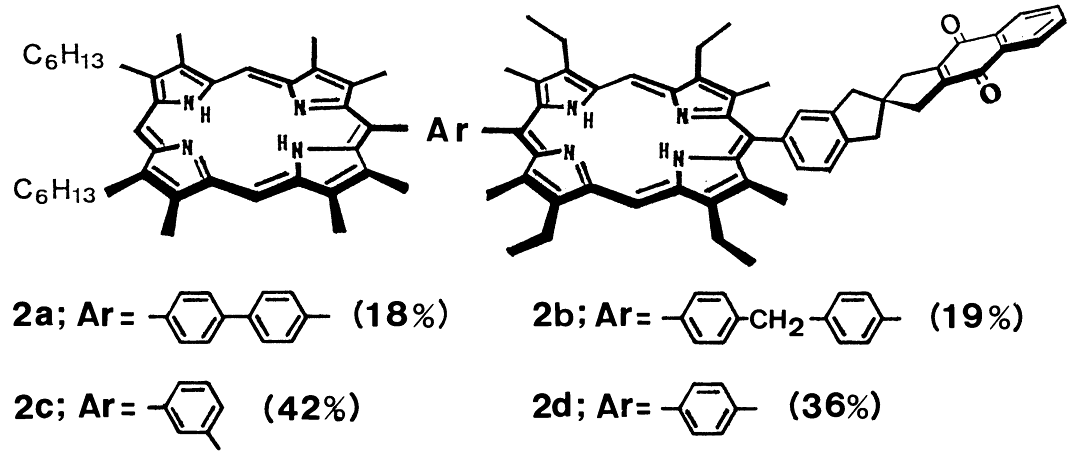


Scheme 1. Unsymmetrically quinone-substituted porphyrin dimers. Numbers in the parentheses are the isolated yields of the cross condensation reaction described in the text.

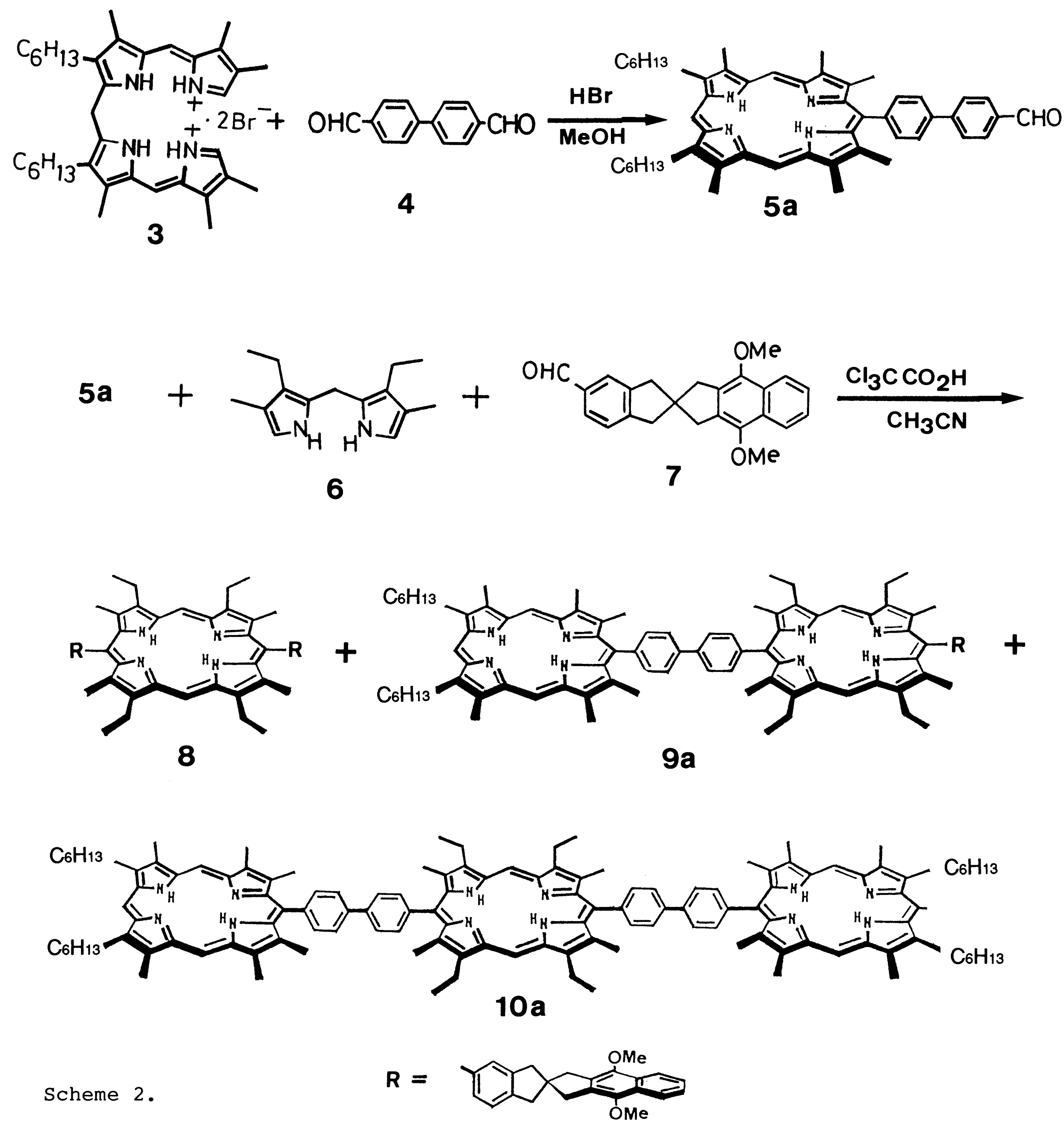
dideoxybiladiene-ac dihydrobromide **3** with 4,4'-diformylbiphenyl**4** gave the key formyl-substituted porphyrinic intermediate **5a** in 34% yield.[5] Cross condensation of **5a**, 5,5'-unsubstituted dipyrrylmethane **6**, and aldehyde **7**[3] in a ratio of 1:2:1 with trichloroacetic acid as acid-catalyst[6] followed by chromatographic separation gave monomeric porphyrin **8**, dimeric porphyrin **9a**, and trimeric porphyrin **10a** in 11%, 18%, and 10% yields, respectively.[7] Demethylation of **9a** with an excess of BBr_3 followed by oxidation with PbO_2 in CH_2Cl_2 gave **2a** in 80% yield (FAB mass spectrum, m-nitrobenzyl alcohol matrix, 10 keV; 1489.867, $C_{103}H_{108}N_8O_2$ requires 1489.863). In a similar manner, unsymmetrically quinone-substituted porphyrins **2b**, **2c**, and **2d** were synthesized. It is worthy to note that the center-to-center distance of the porphyrins is fixed in **2a** and **2b** and the whole geometries of the two porphyrins and quinone are conformationally restricted in **2c** and **2d**.

As was observed in the dimeric porphyrins held in similar geometries,[8] the bis-zinc complexes **2c(Zn_2)** and **2d(Zn_2)** displayed split Soret bands; 406 and

Table 1. Fluorescence properties of unsymmetrically quinone-substituted dimeric porphyrins

Model	ϕ_f[a]	τ_f[b]/ns	Model	ϕ_f[a]	τ_f[b]/ns
2a	0.33	2.9	**2a(Zn_2)**	0.19	0.19
2b	0.40	2.9	**2b(Zn_2)**	0.19	0.15
2c	0.38	2.8	**2c(Zn_2)**	0.16	0.15
2d	0.28	3.1	**2d(Zn_2)**	0.17	0.15
1	0.19	1.8	**1(Zn)**	0.06	0.09

a) Relative fluorescence quantum yields of the quinone-linked porphyrins **2a-d** to **9a-d** and those of **2a-d(Zn_2)** to **9a-d(Zn_2)** measured in air-saturated CH_2Cl_2 at 25 °C. b) Fluorescence lifetimes determined by pico-second time resolved fluorescence spectroscopy in air-saturated CH_2Cl_2.



Scheme 2.

421 nm for **2c(Zn$_2$)** and 407.5 and 420 nm for **2d(Zn$_2$)**, respectively, providing clear evidence for the dimeric structures. On the other hand, the bis-zinc complexes **2a(Zn$_2$)** and **2b(Zn$_2$)** did not exhibit such strong excitonic interactions but showed slight broadening of the Soret bands. The absorption and fluorescence spectra of **2a-d** and their bis-zinc complexes **2a-d(Zn$_2$)** were not perturbed by the linked quinone. However, the fluorescence quantum yields of **2a-d** and **2a-d(Zn$_2$)** decreased significantly (Table 1). An important observation here is that even the fluorescence of the "distal (distal to the quinone)" porphyrin in the dimers **2a-d** and **2a-d(Zn$_2$)** was effectively quenched by the

attached quinone. This was confirmed by the pico-second time resolved fluorescence spectroscopy,$^{9)}$ which revealed the fluorescence decays of **2a-d** and **2a-d(Zn_2)** to be analyzed roughly as a single exponential with the lifetime summarized in Table 1. These results can be interpreted in terms of efficient intramolecular singlet energy transfer between the porphyrins followed by electron transfer from the "proximal" porphyrin to the quinone.

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