CHEMISTRY LETTERS, pp. 1905-1908, 1990.

Synthesis of Conformationally Restricted Carotenoid-linked Porphyrins

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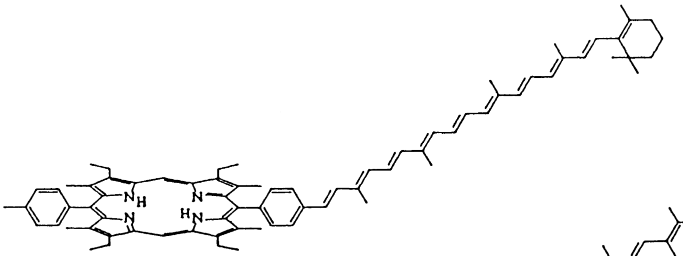
Carotenoid-linked porphyrin compounds were synthesized in acceptable to good yields (15 - 94%) by the acid-catalyzed condensation of dipyrrylmethane and carotenoid-linked aryl aldehyde. Comparison of the absorption spectra with fluorescence excitation spectra indicated the efficient intramolecular singlet energy transfer from the carotenoid to the porphyrin.

Carotenoids perform two major functions in the photosynthesis of green plants and photosynthetic bacteria. They act as photoprotective agents, preventing the formation of harmful singlet oxygen, and as accessory antenna pigments, absorbing light in regions of the spectrum where chlorophylls are not able to efficiently absorb, and thus transferring excitation energy to the chlorophyll singlet manifold. Recently it has been revealed by the X-ray diffraction technique that the carotenoid, spheroidene, is present in the photosynthetic reaction center (RC) of *Rhodobacter sphaeroides* 2.4.1. in the neighborhood of monomeric bacteriochlorophyll (BC_M) in the M-chain.$^{1)}$ Evidence has been accumulated to suggest the involvement of the carotenoid and BC_M in quenching the triplet of the special pair (P) in the RC.$^{2-7)}$ Apparently, it may be conceivable that the spatial arrangement of the carotenoid to P and BC_M is quite essential for its presumed biological function.

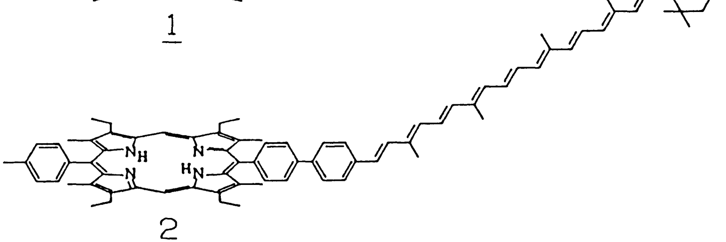
In order to mimic biological functions of carotenoids in the natural photosynthetic systems, a large number of covalently-linked carotenoid-porphyrin molecules have been studied by Gust and Moore.$^{8)}$ In these compounds, however, the carotenoid was linked to the porphyrin by ester, amide, or ether linkage, allowing the geometry of carotenoid to be rather flexible. Here we report the synthesis and optical properties of conformationally restricted carotenoid-linked porphyrins (1, 2, 3, and 4), in which the carotenoid is linked to the porphyrin via a rigid aromatic spacer, such as phenyl or biphenyl group. The synthesis of these model compounds is based on the modified procedure of the acid-catalyzed condensation of dipyrrylmethane and aromatic aldehyde.$^{9)}$

Typically, the synthetic procedure of 1 was described. 3,3'-Diethyl-4,4'-dimethyl-2,2'-dipyrrylmethane 5 (0.25 mmol), 4-methylbenzaldehyde 6 (0.16 mmol), and 7'-*apo*-7'-(4-formylphenyl)-β-carotene 7 (0.04 mmol), were dissolved in a benzene-acetonitrile (3/7) mixture (25 ml), and a catalytic amount of trichloroacetic acid (0.08 mmol) was added to this mixture. After standing at room temperature for 12 h, *p*-chloranil (0.6 mmol) in dry THF (25 ml) was added, and the mixture was stirred for 5 h. Separation by flash column chromatography gave the desired porphyrin 1 (FAB mass spectrum, m-nitro-benzylalcohol matrix, 10 KeV, 1057.6950 for $M^{+}+1$; $C_{76}H_{89}N_4$ requires 1057.7090) in 95% yield,[10] based on the used amount of 7. The 400 MHz ^{1}H-NMR spectrum of 1 revealed that the stereochemistry of the newly formed carbon-carbon double bond was exclusively trans; the chemical shifts of H^a and H^b (designated in Scheme 1) were 7.22 (d, J= 15.6 Hz) and 6.96 (d, J= 15.6 Hz) ppm, respectively. In a similar manner, carotenoid-linked porphyrins 2 and 3 were synthesized in 50 and 15% yields, respectively. Bis-carotenoid-linked porphyrin 4 was synthesized by the condensation of 5 and 7 in 63 % yield.[11]

The absorption spectra and the fluorescence excitation spectra of 1 and 4 are shown in Fig. 1. The absorption spectra are approximately identical to the sum of those of the individual chromophores, while the fluorescence spectra are that of the unperturbed porphyrin alone. When the concentration of 1 was more than 10^{-6} mM, the concentration quenching of the fluorescence was observed, presumably due to the aggregation of 1 through the long carotenoid chain. From the comparison of the absorption spectra with the fluorescence excitation spectra, it is obvious that a part of the singlet excitation energy of the carotenoid moiety is transferred to the porphyrin moiety. Applying Gust and Moore's method,[8] we estimated the singlet energy transfer efficiency to be 40% for 1, 13% for 2, 35% for 3, and 20% for 4. Since the singlet life time of carotenoid is very short (< 20 ps),[12] the estimated efficiency of the singlet energy transfer corresponds to very fast intramolecular singlet



1



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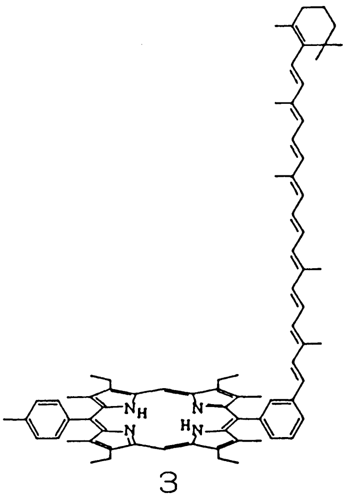

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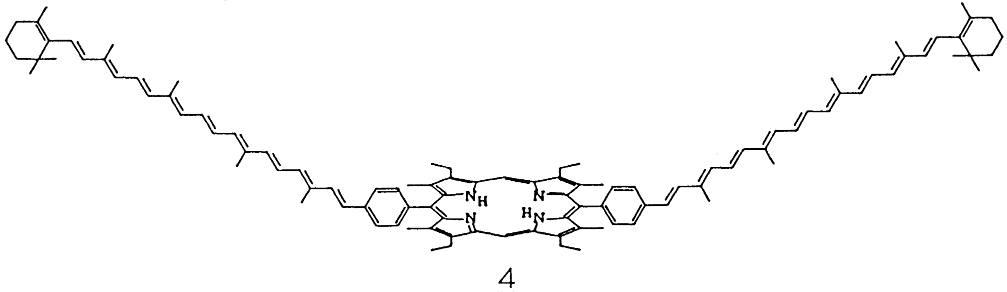

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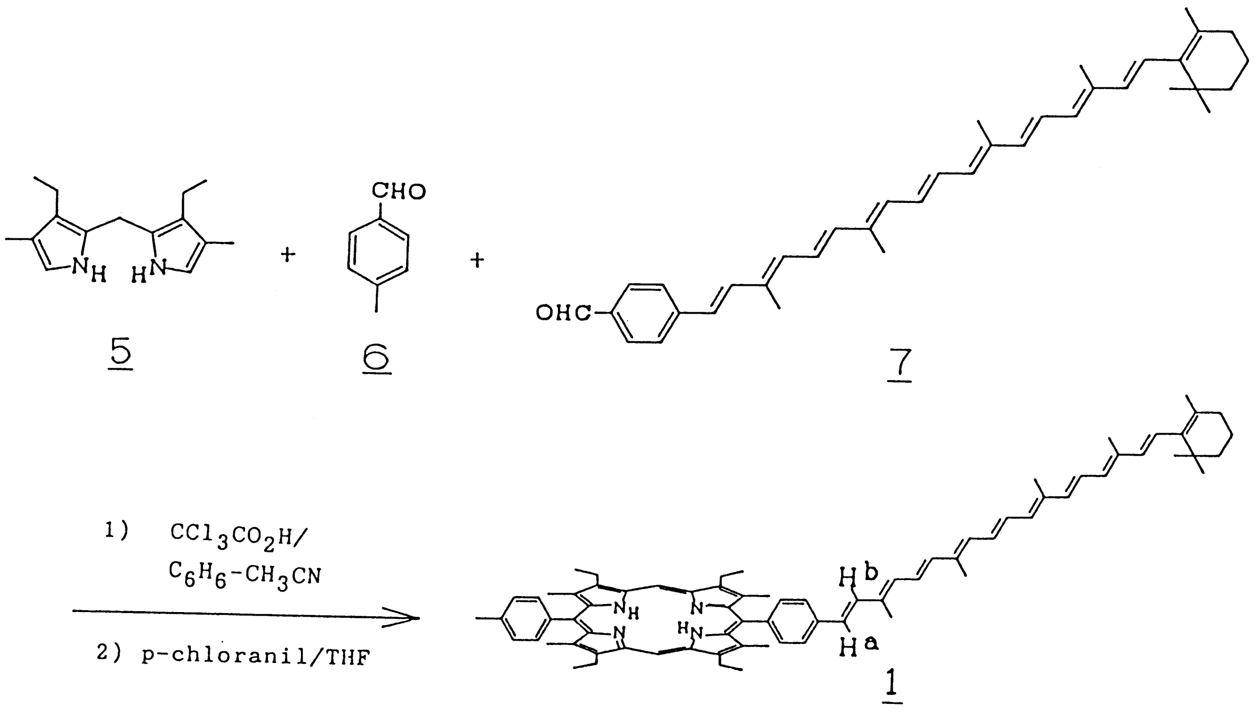

Scheme 1.

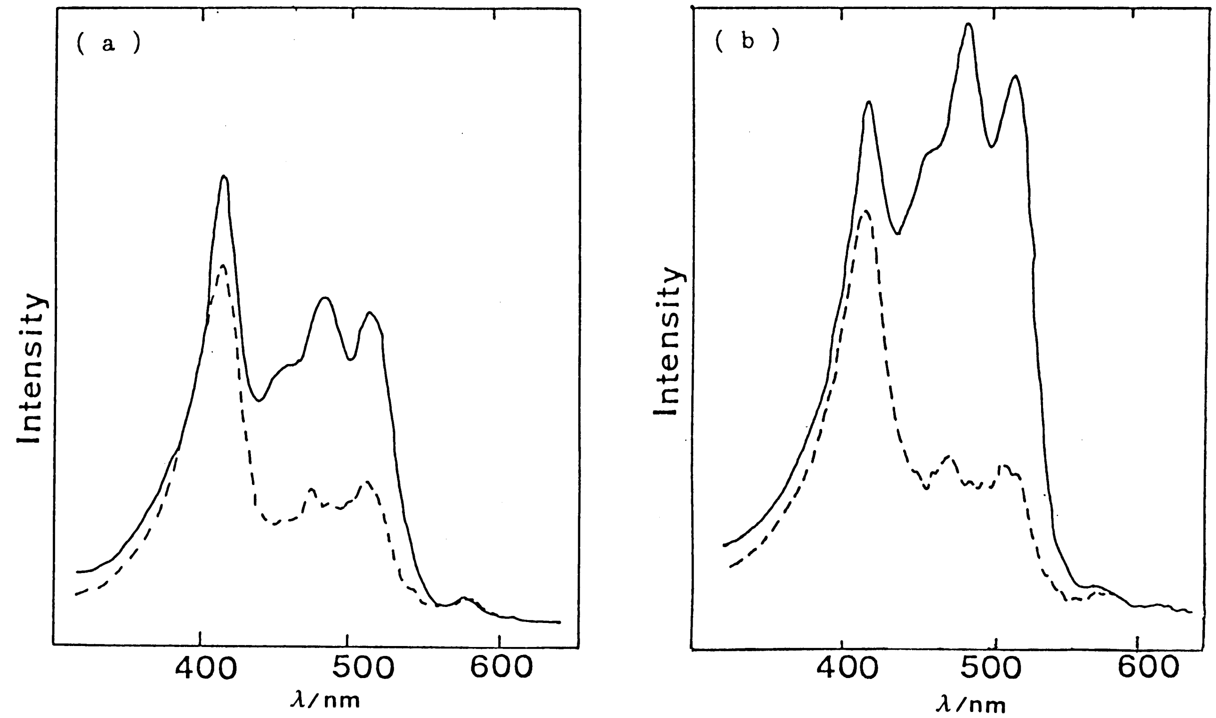

Fig.1. The UV-vis absorption spectra (———) and the fluorescence excitation spectra (- - -) of 1 (a) and 4 (b) in dichloromethane. The fluorescence excitation spectra were detected at 693 nm and normalized to the absorption spectra over the region 625-700 nm.

energy transfer; the rates of the energy transfer (k_e) were calculated as 4×10^{10} s^{-1} for 1, 9×10^{9} s^{-1} for 2, and 3×10^{10} s^{-1} for 3.13)

This work was partially supported by the Grand-in Aid for Scientic Research NO. 1649508 and Nissan Science Foundation.

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9) This reaction was first utilized by Ogoshi et al.a) and later modified by Gunter et al.b) An improved procedure of this reaction was recently applied to the synthesis of conformationally restricted trimeric and pentameric porphyrins.c) a) H. Ogoshi, H. Sugimoto, T. Nishiguchi, T. Watanabe, Y. Matsuda,and Z. Yoshida, *Chem. Lett.*, 1978, 29; b) M. J. Gunter and L. M. Mander, *J. Org. Chem.*, 46, 4792 (1981); c) T. Nagata, A. Osuka, and K. Maruyama *J. Am. Chem. Soc.*, 112, 3054 (1990).
10) All new compounds described in this paper gave satisfactory spectral data consistent with the assigned structures.
11) The compounds 1 - 3 were relatively unstable and were stored for several weeks at 77 K, and the compound 4 was unstable even at 77 K.
12) The singlet lifetime of 7'-*apo*-7'-(4-N-acetylaminophenyl)-β-carotene was recently determined to be 16 ps. M. R. Wasielewski, P. A. Liddell, D. Barrett, T. A. Moore, and D. Gust, *Nature*, 322, 570 (1986).
13) We calculated k_e by the following equation;

$$k_e = x/((1-x)\tau_0) \qquad (1)$$

where x is the efficiency of singlet energy transfer and τ_0 is the singlet lifetime of carotenoid (16 ps).

(Received July 2, 1990)