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Synthesis of 1,2-Phenylene-Bridged Diporphyrin Linked with Porphyrin Monomer and Its Intramolecular Singlet-Singlet Excitation Energy Transfer

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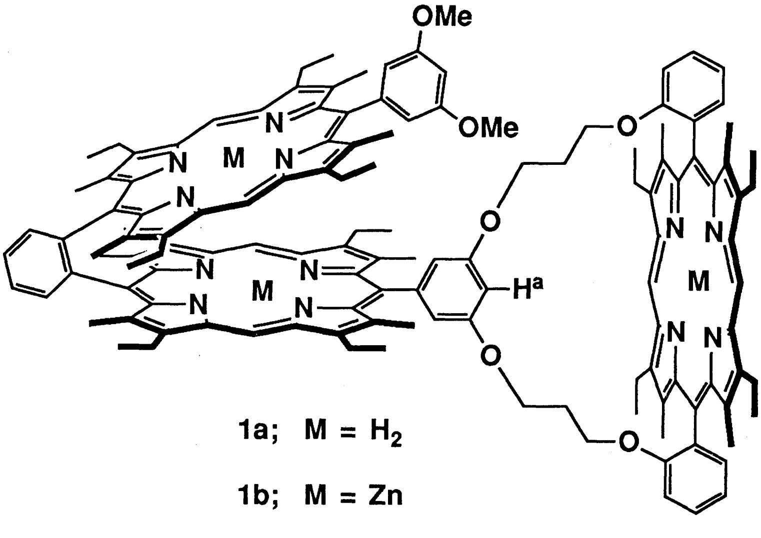
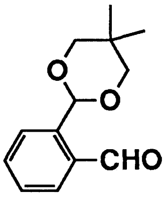
A new photosynthetic model, in which 1,2-phenylene-bridged diporphyrin is connected with monomeric porphyrin through strapped chain, was synthesized by acid-catalyzed intramolecular cyclization reaction. Picosecond time-resolved fluorescence spectroscopy has revealed the efficient unidirectional singlet-singlet energy transfer from the monomeric porphyrin to the diporphyrin.

In the natural photosynthetic reaction center (RC), the excitation energy absorbed by photosynthetic pigments is efficiently transferred to the special pair (SP) to yield its singlet excited state, from which a stable ion pair state $(SP)^{+}$—(bacteriopheophytin, BPh)$^{-}$ is formed within 3 ps.¹⁾ As characterized by the X-ray structure determinations, two of the bacteriochlorophyll (BChl) molecules are closely associated spatially and electronically to form SP.²⁾ Two BChl molecules that comprise SP have the same structure with other BChl molecules mostly working as antenna pigments. Extended electronic interactions between the two BChl molecules lead to the unusual chemical and spectroscopic properties of SP, thus enabling SP to act as the final singlet-energy sink of energy relay system as well as the initial electron donor in the RC. In fact, either irradiation of BChl or BPh in the RC leads to the instantaneous population of $^{1}(SP)^{*}$ in less than several 100 femtosecond.³⁾ In order better to understand electron and/or energy transfer processes in the RC, a number of models have been studied so far.⁴⁾



1a; M = H_2

1b; M = Zn



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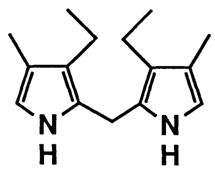

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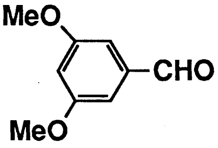

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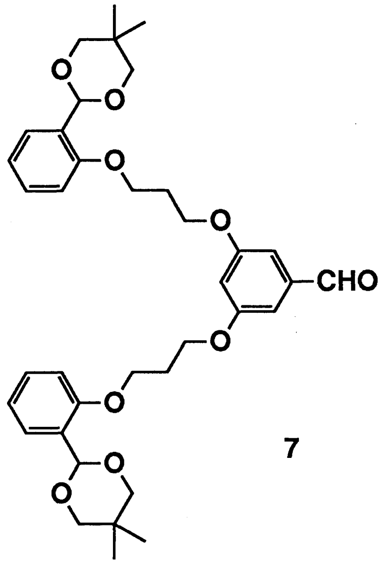

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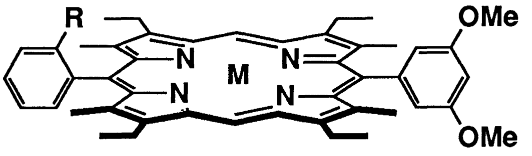
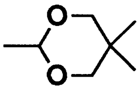
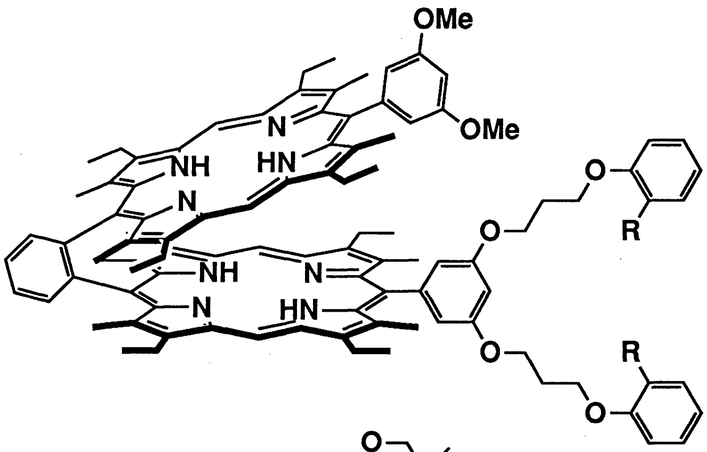


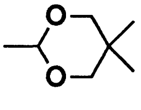
5; M = Zn, R =



6; M = H_2, R = CHO



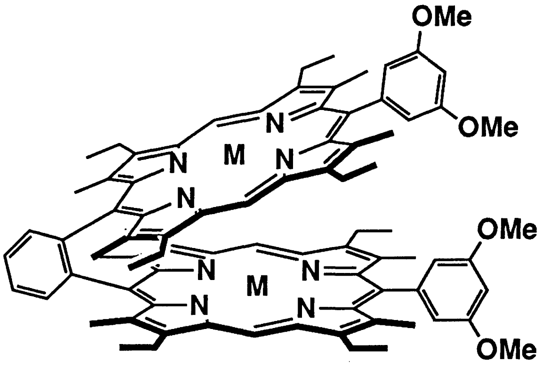
8; R =



9; R = CHO

Here, we describe the synthesis and picosecond fluorescence behavior of model compound **1b**, in which 1,2-phenylene-bridged bis-zinc-diporphyrin (D) is connected with monomeric zinc-porphyrin (M) via strapped linkage. Recently, we have synthesized 1,2-phenylene-bridged bis-zinc-porphyrin, in which both the one electron oxidation potentials and the singlet excitation energy are substantially lowered in comparison to M.5) These findings led us to consider that D unit could act as a singlet energy acceptor toward M.

Acid-catalyzed cross condensation7) (trichloroacetic acid/acetonitrile) of **2**, **3**, and **4** in a ratio of 1:2.2:1.2 followed by separation by column chromatography gave porphyrin **5**8) in 34% yield based on the amount of **4** used. Deprotection of the acetal group under acidic conditions (trifluoroacetic acid/H_2O/CH_2Cl_2) quantitatively provided a formyl-substituted porphyrin **6**, which was again cyclized with **3** and aldehyde **7**$^{8)}$ in a ratio of 1:5:4, giving 1,2-phenylene-bridged diporphyrin **8** in 54% yield based on the amount of **6** used. Finally, bis-formyl substituted diporphyrin **9**, which was obtained from **8** in quantitative yield by acidic hydrolysis, was condensed with **3** under the intramolecular cyclization conditions,$^{7)}$ to give the model **1a** in 57% yield (FAB mass, m-nitrobenzyl alcohol matrix, 10 keV, 2020; $C_{134}H_{144}N_{12}O_6$ requires 2019). The corresponding tris-zinc complex **1b** was readily prepared by the reaction with $Zn(OAc)_2$ in methanol. As the reference dimer, the diporphyrin **10b** (FAB mass, 1430; Calcd for $C_{86}H_{90}N_8O_4Zn_2$ = 1430.5) was similarly prepared in 54 % yield from the reaction of **6**, **3**, and **4**. In the ^{1}H-NMR spectrum of **1b** ($CDCl_3$), the meso protons in D appear at 8.15 and 8.19 ppm as slightly broad singlets, while those in M appear at 10.31 ppm, and the H^a (designated in the structure of **1**) appears rather high field at 3.02 ppm, being characteristic of the strapped linkage.$^{5)}$ The meso protons of **10b** appear at 8.39 ppm as a sharp singlet at room temperature.



10a; M = H_2

10b; M = Zn

The absorption spectra of **1b** in THF is a simple sum of D and M, suggesting the electronic interaction between the two subunits in the ground state is negligible. In contrast, the steady state fluorescence spectrum of **1b** differs from the fluorescence spectrum of a 1:1 mixture of D and M, in that the fluorescence due to M is significantly quenched while the fluorescence due to D is enhanced, indicating the occurrence of intramolecular singlet-singlet energy transfer in the model **1b**. This has been confirmed by fluorescence decay and rise time measurement on **1b** in THF at 585 and 700 nm. The fluorescence decay of **10b** in THF could not be satisfactorily reproduced by a single exponential function, while a biexponential fit gave a reasonably good agreement with τ_1 = 830 ps (91%) and τ_2 = 270 ps (9%) (χ^2 = 1.11). This complex fluorescence decay behavior of **10b** remains to be explored, but may be explained in terms of change of the relative geometry of the porphyrin in the relaxation of ^{1}(**10b**)*. In the fluorescence spectrum of **1b**, the main emitting species at 585 nm is M and the decay time of the main component has been obtained as τ(M) = 29 ps. At 700 nm, where the emitting species is solely D, we have observed fluorescence rise with τ = 36 ps and slow decay with τ_1 = 360 (19%) and τ_2 = 980 (81%). By using τ(M) value, we have evaluated the rate of the energy transfer to be 3.4×10^{10} s^{-1}.$^{9)}$

This singlet-singlet energy transfer process, although its rate is still smaller than those observed in RC, is quite similar to the observed mode of singlet-singlet EN in the natural RC with the special pair as the final energy sink. While intramolecular singlet-singlet EN has been reported in a number of zinc-porphyrin free base porphyrin hybrid models,$^{8)}$ examples of an unidirectional EN from monomer to dimer comprising the same porphyrin chromophore are quite rare. In a related model in which the D and M moieties are connected by 4,4'-biphenylnylene spacer, we have observed a similar unidirectional EN with $k_{EN} = 1.4 \times 10^{10}$ s^{-1}.[10] In these models, $^1(D)^*$ lies at 1.93-1.97 eV energy level, which is distinctly lower than that (2.13 eV) of $^1(M)^*$, thus enabling the unidirectional EN energetically favorable. In addition, significant spectral overlap of the emission spectra of the donor $^1(M)^*$ and the absorption spectra of the acceptor (D) permits this efficient EN. Faster energy transfer in **1b** in comparison with that in the model bridged by 4,4'-biphenylnylene indicates that this singlet-singlet EN proceeds mainly via dipole-dipole interaction mechanism (through space), since through-bond electronic exchange interaction between the D and M is expected to be smaller in **1b**.

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7) All new compounds described in this paper gave satisfactory spectral data consistent with the assigned structures.
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9) The rate of energy transfer (k_{EN}) was calculated by the following equation; $k_{EN} = 1/\tau(M) - 1/\tau_0$, where τ_0 is the fluorescence lifetime of the reference monomeric zinc porphyrin in THF (1.37 ns).
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