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Synthesis of Quinone-linked Porphyrin Dimer, Trimer, and Tetramer As Models for Photosynthetic Reaction Center

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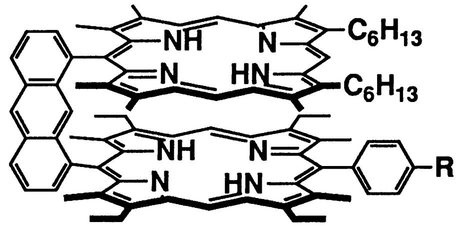
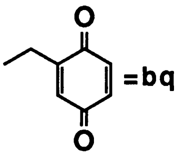
As models for the photosynthetic reaction center, conformationally restricted quinone-linked porphyrin dimer, trimer, and tetramer were synthesized. The Soret bands of these zinc complexes are blue-shifted or split due to the exciton coupling depending on the geometries and compositions. The fluorescence intensities of these models are significantly reduced by the attached quinone, indicating the efficient electron transfer to the quinone.

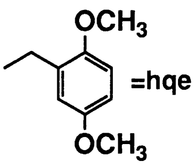
In the purple bacterial photosynthetic reaction centers, the chromophores are positioned at precise distances and orientations to attain the high efficiency of charge separation which proceeds from dimeric bacteriochlorophylls (special pair), via monomeric bacteriopheophytin, to quinone.[1] On the basis of the X-ray structure of these photosynthetic pigments, several mechanisms have been proposed to explain the primary electron transfer events with as yet no consensus.[2] Synthetic model compounds with well-defined geometries

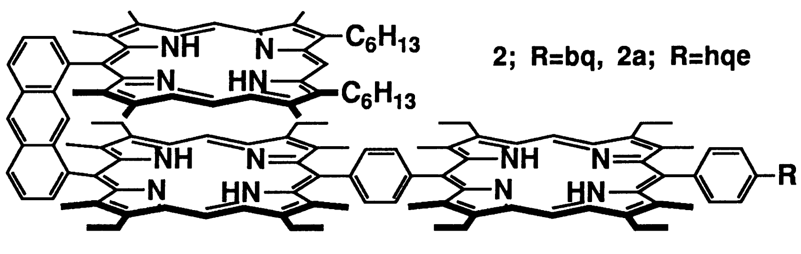


1; R=bq

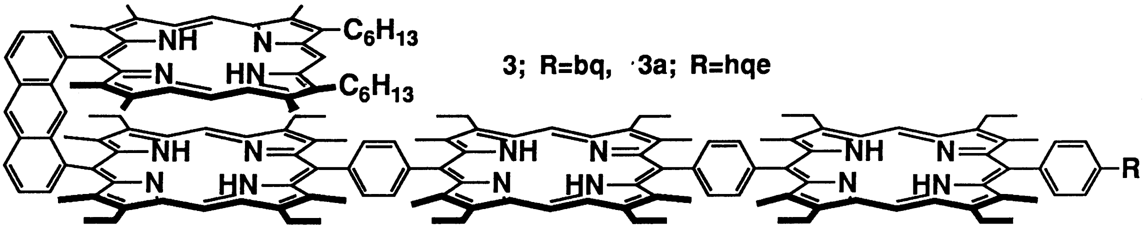
1a; R=hqe





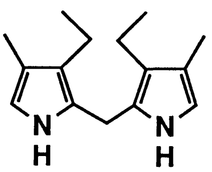


2; R=bq, 2a; R=hqe



3; R=bq, 3a; R=hqe

are particularly effective in studying the geometry-dependence of electron transfer reactions.[3,4] Synthetic model compounds consisting of two or more porphyrins linked with electron acceptors have already been prepared.[5] However, linking three, four, or more photosynthetic pigments with electron acceptor in appropriately designed and fixed geometries is still a challenging synthetic task.[6] In this paper, we will describe the synthesis of conformationally restricted quinone-linked porphyrin dimer **1**,[7] trimer **2**, and tetramer **3**. In the model **1**, the coplanarly arranged diporphyrin unit is directly connected to the quinone moiety, while the coplanar diporphyrin and quinone are bridged by one or two additional porphyrins in the models **2** and **3**, respectively. The model **3** can be regarded as a formal duplication of the photochemically active L-branch in the purple bacterial photosynthetic reaction center.



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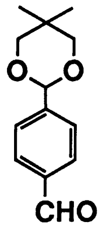

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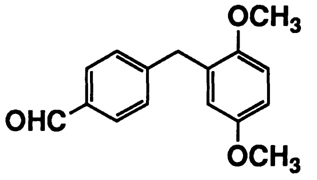

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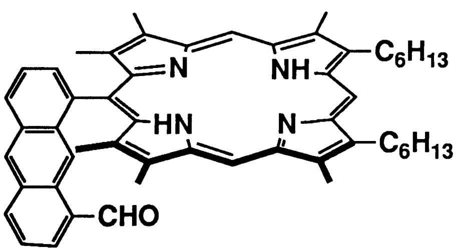

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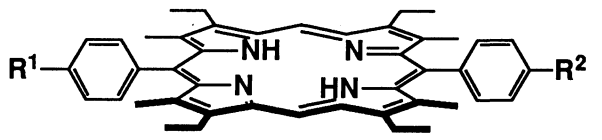
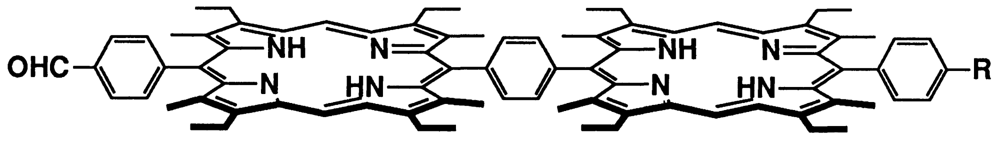


7; $R^1=R^2=$hqe

8; $R^1=$hqe, $R^2=$CHO

9; $R^1=R^2=$CHO



10; R=hqe

Typically, the synthesis of the tetrameric model **3** is outlined. Acid-catalyzed cross condensation (trichloroacetic acid/acetonitrile)[8] of **4**, **5**, and **6** in a ratio of 2:1:1 followed by acidic hydrolysis (trifluoroacetic acetic and 10% H_2SO_4) gave porphyrins **7**, **8**, and **9** in 28, 42, and 22% yields, respectively. Mono-formyl-substituted porphyrin **8** was again cyclized with **4** and **5** in a ratio of 1:5:4 to give formyl-substituted dimeric porphyrin **10** in 48% yield based on the used amount of **8**.[8] Then, the cross condensation of **10**, the anthracene-linked porphyrin **11**,[6] and **4** in a ratio of 1:1:2 gave **3a** in 15% yield.[9] Demethylation of **3a** with BBr_3 followed by oxidation with PbO_2 in CH_2Cl_2 gave **3** in 80% yield (FAB mass; m-nitrobenzyl alcohol matrix, 10 keV, 2520 (M^+ + 1); $C_{173}H_{182}N_{16}O_2$ requires 2519).[10] In a similar manner, the model **1** was prepared from the cross condensation of **4**, **6**, and **11** in a ratio of 3:2:1 followed by the demethylation and oxidation in overall 38% yield (FAB mass, 1414 (M^+ + 1), $C_{97}H_{102}N_8O_2$ requires 1413). The model **2** was similarly prepared from the cross condensation of **4**, **8**, and **11** in overall 18% yield (FAB mass, 1966;

$C_{135}H_{142}N_{12}O_2$ requires 1966). The zinc complexes of these models were prepared by the reaction with $Zn(OAc)_2$ in refluxing $CHCl_3$.

In Fig. 1, the absorption spectra of the zinc complexes **1(Zn_2)**, **2(Zn_3)**, and **3(Zn_4)** in THF were presented. These spectra are essentially same with those of the zinc complexes **1a(Zn_2)**, **2a(Zn_3)**, and **3a(Zn_4)**, respectively. The coplanar dimer **1(Zn_2)** displays blue-shifted Soret band at 407 nm compared with the corresponding monomer at 416 nm, while the trimer **2(Zn_3)** and the tetramer **3(Zn_4)** exhibit rather red-shifted and split Soret bands . Split width observed for **3(Zn_4)** is larger than that for **2(Zn_3)**. These spectral changes can be understood in terms of the exciton coupling of the neighboring porphyrin chromophores.[6, 11] The relative fluorescence intensities of **1(Zn_2)**, **2(Zn_3)**, and **3(Zn_4)** to the corresponding **1a(Zn_2)**, **2a(Zn_3)**, and **3a(Zn_4)** in THF, are 0.02, 0.08, and 0.12, respectively. Thus, even the fluorescence from the distal coplanar diporphyrin unit in **3** is significantly quenched by the quinone. These results indicates the efficient electron transfer from the porphyrin array to the attached quinone as well as the efficient singlet energy transfer between the porphyrin arrays. Ultrafast photoexcited dynamics revealed by picosecond time-resolved fluorescence and transient absorption spectroscopy will be reported elsewhere.

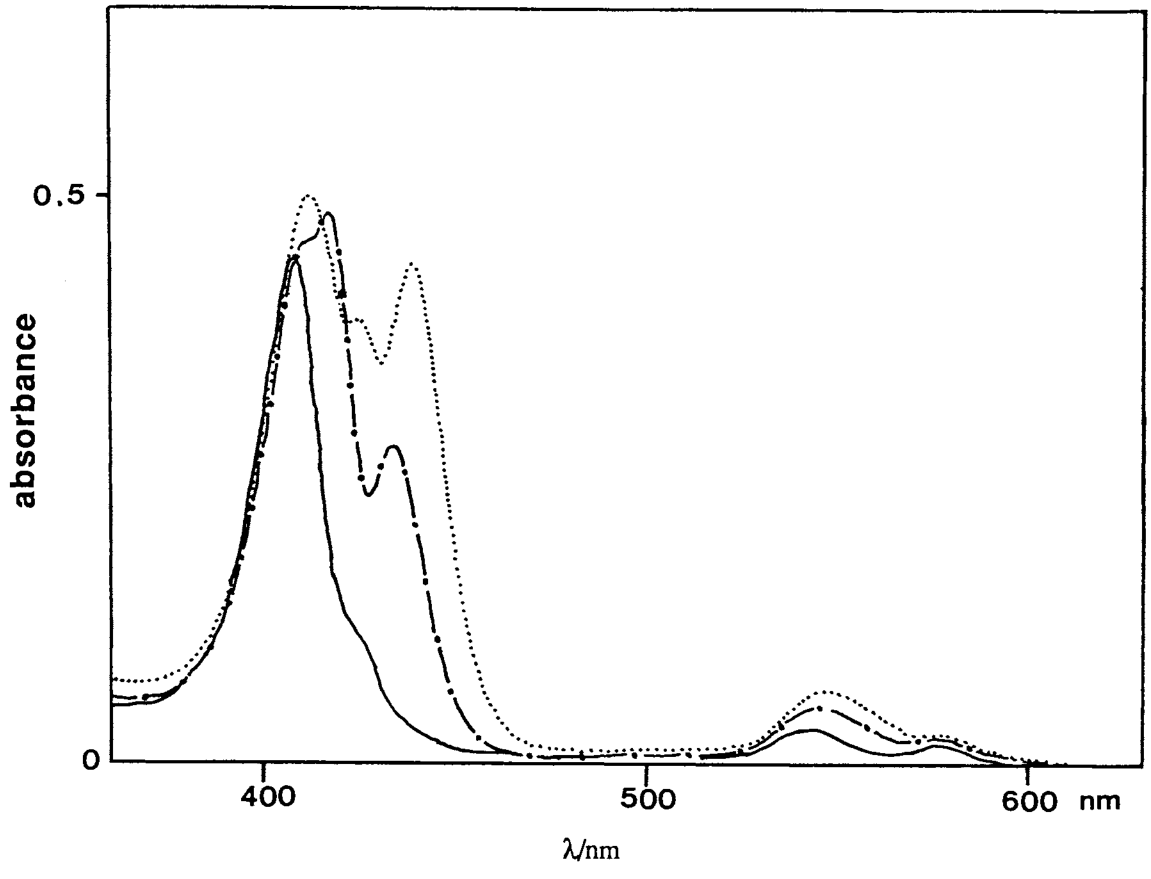


Fig. 1. Absorption spectra of **1(Zn_2)** (——), **2(Zn_3)** (— - —), and **3(Zn_4)** (·······) in THF at 25 °C. Concentrations are 1.0×10^{-6} M.

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References

1) C. Kirmaier and D. Holten, *Photosynth. Res.*, **13,** 225 (1987).
2) R. A. Friesner and Y. Won, *Photochem. Photobiol.*, **50,** 831 (1989).
3) M. R. Wasielewski, "Distance Dependencies of Electron Transfer Reactions," in "Photoinduced Electron Transfer," ed by M. A. Fox and M. Chanon, Elsevier, Amsterdam (1988), Part A. pp.161-206.
4) K. Maruyama and A. Osuka, *Pure Appl. Chem.*, **62,** 1511 (1990).
5) J. L. Sessler and V. L. Capuano, *Angew. Chem. , Int. Ed. Engl.*, **29,** 1134 (1990); U. Rempel, B. von Maltzan, and C. von Borczyskowski. *Chem. Phys. Lett.*, **169,** 347 (1990), D. Gust, T. A. Moore, A. L. Moore, L. R. Makings, G. R. Seely, X. Ma, T. T. Trier, and F. Gao, *J. Am. Chem. Soc.*, **110,** 7567 (1988); D. Gust, T. A. Moore, A. L. Moore, S.-J. Lee, E. Bittersmann, D. K. Luttrull, A. A. Rehms, J. M. DeGraziano, X. C. Ma, F. Gao, R. E. Belford, and T. T. Trier, *Science*, **248,** 199 (1990); J. A. Cowan, J. K. M. Sanders, G. S. Beddard, and R. J. Harrison, *J. Chem. Soc., Chem. Commun.*, **1985,** 55.
6) T. Nagata, A. Osuka, and K. Maruyama, *J. Am. Chem. Soc.*, **112,** 3054 (1990).
7) Anthracence-pillared diporphyrin was first synthesized by Chang et al., C. K. Chang and I. Abdalmuhdi, *J. Org. Chem.*, **48,** 5388 (1983).
8) A. Osuka, T. Nagata, F. Kobayashi, and K. Maruyama, *J. Heterocycl. Chem.*, **27,** 1657 (1990).
9) In this cross condensation reaction, the anthracence-pillared trimeric porphyrin and the linearly-linked pentameric porphyrin were obtained in 8 and 7% yields, respectively.
10) All new compounds described in this paper gave satisfactory spectral data consistent with the assigned structures.
11) A. Osuka and K. Maruyama, *J. Am. Chem. Soc.*, **110,** 4454 (1988).

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