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1,3-Dioxane-Bridged Pyromellitimide-Pyropheophorbide and Pyropheophorbide Dimer

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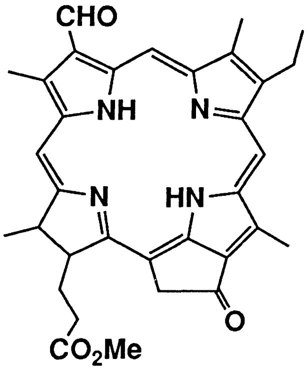
1,3-Dioxane-bridged pyromellitimide-pyropheophorbide dyads were synthesized by simple acid-catalyzed reaction of methyl pyropheophorbide-*d* and a pyromellitimide-substituted diol. A bis-1,3-dioxane-bridged pyropheophorbide dimer was similarly prepared by the reaction of methyl pyropheophorbide-*d* and pentaerythritol. Intramolecular electron-transfer and energy-transfer reactions in these models have been studied by picosecond fluorescence measurements.

In the bacterial photosynthetic reaction centers (RC), the cyclic tetrapyrrole pigments are held at precise distances and orientations by the protein matrix. With a view to better understanding the mechanism of electron and/or energy transfer in the RC, a large number of artificial models, mainly based on porphyrin molecules, have been studied.$^{1-3)}$ Recently, increasing attention has been focussed on those with well-defined geometries and energies, since such models allow to quantify the distance, orientation, energy-gap dependencies of electron-transfer reactions. There are however only a few conformationally restricted models based on natural chlorin-pigments such as chlorophyll or pyropheophorbide.$^{4)}$ This class of pigments stands in marked contrast to symmetric porphyrin pigments due to fairly stabilized S_1-energies, prominet Qy-absorption bands, and unique reactivities in one-electron oxidation or reduction reactions.

Here, we describe the synthesis of 1,3-dioxane-bridged pyromellitimide-pyropheophorbide (Im-P) dyads **4** and **5** and pyropheophorbide dimer (P-P) **6**, in both of which the relative geometries of each chromphore are held at well-defined. An Im moiety is employed here as an electron acceptor because of its pertinent redox properties, thermal stabilities, and a sharp absorption band of its anion radical.$^{5)}$

When methyl pyropheophorbide d (**1**)$^{4)}$ was treated with 2,2,-dimethyl-1,3-propanediol in the presence of *p*-toluenesulfonic acid in CH_2Cl_2, the acetal **2a**$^{6)}$ was formed in quantitative yield. The 9-keto group does not react with the diol even under rather forcing conditions. When a solution of **1** in CH_2Cl_2 was heated in the presence of pyromellitimide-linked diol **3**,$^{7)}$ Im-P dyads were formed as a mixture of stereoisomers in 79% yield; the ratio of major to minor product was ca. 2/1. These dyads were easily separated by flash column chromatography on silica gel. Since the spectroscopic data including ^{1}H-NMR, IR, and mass spectra obtained for these isomers are quite similar to each other, we tentatively assigned the major isomer as thermodynamically more stable trans product **4a** and the minor one as cis product **5a**. The N-methine protons in the 1,3-dioxane ring in the both isomers were coupled with the adjacent vicinal protons with coupling constants of 6.1 and 10.7 Hz in **4a** and of 6.2 and 11.5 Hz in **5a**. Observed large coupling constants (> 10 Hz) are typical of those for



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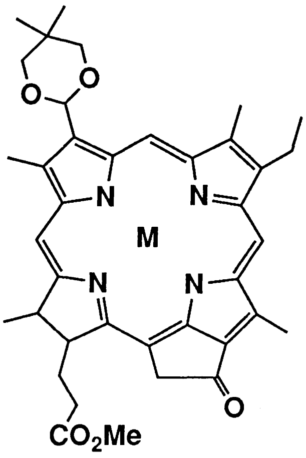
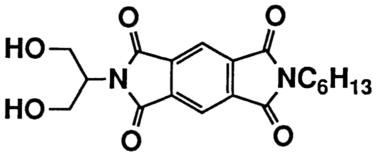


2a; M = H_2

2b; M = Zn



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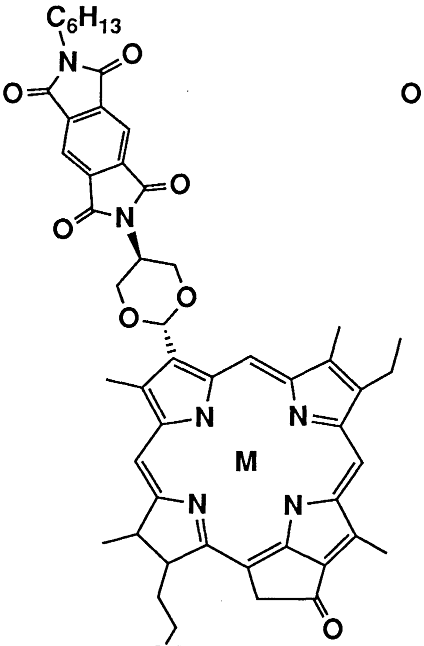
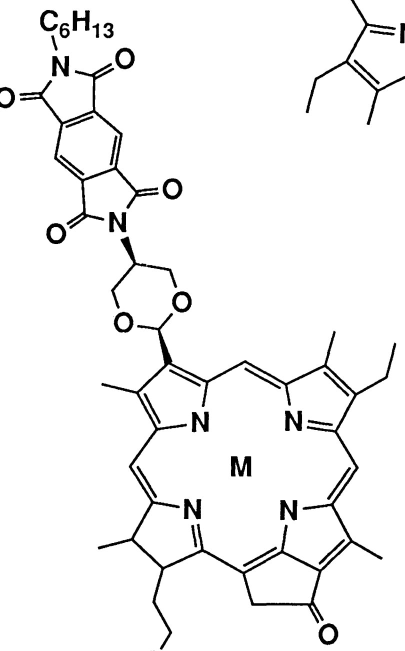


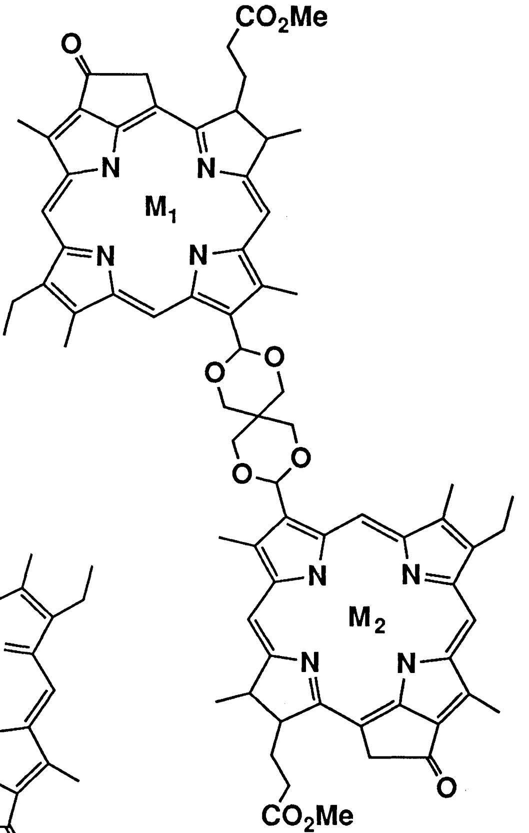
4a; M = H_2

4b; M = Zn



5a; M = H_2

5b; M = Zn



6a; $M_1 = M_2 = H_2$

6b; $M_1 = M_2 = Zn$

6c; $M_1 = H_2$, $M_2 = Zn$

axial-axial coupling, indicating the N-methine protons in the both dyads are axial. Since it is pertinent to assume the equatorial stereochemistry for a large pyropheophorbide macrocycle, it is inferred that the 1,3-dioxane ring in **4a** takes a chair conformation but that in **5a** takes a boat conformation.

The fluorescence intensities of the H_2P in **4a** and **5a** are virtually the same as that in **2a** in solvents of a wide range of polarity, while those of the ZnP in **4b** and **5b** are significantly decreased in comparison to that of **2b**, suggesting the occurrence of intramolecular charge separation between the $^1(ZnP)^*$ and Im.[8] The fluorescence lifetimes of **4b** and **5b** were measured in benzene, THF, and DMF (Table 1). Both the fluorescence decays in THF and DMF can be fit to a single exponential function, while the fluorescence in benzene exhibits biphasic decays. Rates of intramolecular charge separation (k_{CS}) in THF and DMF have been calculated by the equation; $k_{CS} = 1/\tau - 1/\tau_0$, where τ and τ_0 are the fluorescence lifetimes of Im-ZnP and **2b**, respectively.[9] On the other hand, the observed biphasic fluorescence decay in benzene indicates a rapid equilibrium between the excited state Im-$^1(ZnP)^*$ and ion pair state $(Im)^-$-$(ZnP)^+$.[10-12] In nonpolar benzene solution, the ion pair states should be destabilized and their energies come near to that of the excited state. Values of k_{CS} have been calculated according to the well-established procedure,[10-12] assuming thermal repolulation of the Im-$^1(ZnP)^*$ from $(Im)^-$-$(ZnP)^+$. Nearly identical k_{CS} values have been obtained for **4b** and **5b**. More notably, the k_{CS} values are almost independent of the solvent polarity, being the same as those observed for distance-fixed dyads[5,11]. This result can be qualitatively accounted for in a similar manner as follows. In general, a decrease of the solvent polarity is followed by decreases in both of a free energy gap for the CS reaction and solvent reorganization energy. Therefore these two effects compensate each other, resulting in rather constant k_{CS} values independent of solvent polarity.

Finally, the similar reaction of **1** with 0.5 equivalent amount of pentaerythritol gave the dimer **6a** as a single product in 71% yield. In this dimer, the center-to-center distance of the two pyropheophorbide chromophores is fixed to be ca. 25 Å. Biszinc- and monozinc complexes **6b** and **6c** were prepared from **6a** by the reaction with $Zn(OAc)_2$ followed by chromatographic separation. The chemical shifts of **6a** and **6b** are virtually identical with those in **2a** and **2b**, indicating an extended conformation. The absorption and fluorescence spectra of **6a** and **6b** are also identical with those of **2a** and **2b**. In the hybrid dimer **6c**, reversible singlet excitation energy transfer between the ZnP and H_2P has been revealed by the fluorescence lifetime measurements. The fluorescence decays of **6a** and **6b** in THF can be fit with monoexponential functions with time constants of 9.3 and 4.5 ns, respectively, being practically the same as those of **2a** and **2b**. On the other hand, the steady-state fluorescence spectrum of **6c** in THF contains the emissions both from the H_2P and ZnP moieties at 650 and 665 nm, respectively, but its fluorescence decays with a time constant of ca. 6.1 ns at the both wavelength. These results indicate rapid equilibrium between $^1(H_2P)^*$-ZnP and H_2P-$^1(ZnP)^*$, which is consistent with a small energy difference (ca. 260 cm^{-1}) between the $^1(H_2P)^*$ and $^1(ZnP)^*$ states and large spectral overlap of the emission spectra of donors and the absorption spectra of acceptor in both energy transfer processes.

Table 1. Fluorescence Lifetimes and Electron-Transfer Rates in **4b** and **5b**

Model	Solvent	Lifetime[a] ns	k_{CS}[b] s^{-1}	Model	Solvent	Lifetime ns	k_{CS}[b] s^{-1}
4b	benzene	1.13 (47) 2.35 (53)	3.7×10^8	**5b**	benzene	0.99 (52) 2.36 (49)	3.7×10^8
4b	THF	1.50	4.4×10^8	**5b**	THF	1.49	4.4×10^8
4b	DMF	1.62	4.0×10^8	**5b**	DMF	1.65	3.9×10^8

a) Fluorescence lifetimes determined by single photon counting technique. Numbers in parentheses are relative amplitudes of preexponential function. b) Rates of intramolecular charge separation; Im-$^1(ZnP)^*$ —> $(Im)^-$-$(ZnP)^+$ calculated on the basis of the fluorescence lifetimes.

Current efforts are being devoted to incorporation of these units into a more elaborated photosynthetic model.

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References

1) M. R. Wasielewski, *Chem. Rev.*, **92**, 435 (1992).
2) D. Gust, T. A. Moore, and A. L. Moore, *Acc. Chem. Res.*, **26**, 198 (1993).
3) K. Maruyama and A. Osuka, *Pure Appl. Chem.*, **62**, 1511 (1990); K. Maruyama, A. Osuka, and N. Mataga, *ibid.*, **65**, (1993) in press.
4) M. R. Wasielewski, W. A. Svec, and B. T. Cope, *J. Am. Chem. Soc.*, **100**, 1961 (1978); M. R. Wasielewski, D. G. Johnson, and W. A. Svec, "Supramolecular Chemistry," ed by V. Balzani, pp. 255, Reidel Amsterdam; D. G. Johnson, W. A. Svec, and M. R. Wasielewski, *Isr. J. Chem.*, **28**, 193 (1988).
5) A. Osuka, S. Nakajima, K. Maruyama, N. Mataga, T. Asahi, I. Yamazaki, Y. Nishimura, T. Ohno, and K. Nozaki, *J. Am. Chem. Soc.*, **115**, 4577 (1993).
6) All new compounds described in this paper gave satisfactory spectral data consistent with the assigned structures.
7) This diol was prepared in 40% yield by the reaction of pyromellic dianhydride with hexylamine and 2-amino-1,3-propanediol in DMF.
8) This has been actually confirmed by picosecond transient absorption spectroscopy, A. Osuka, S. Marumo, K. Maruyama, S. Taniguchi, Y. Tanaka, T. Okada, and N. Mataga, unpublished results.
9) The fluorescence lifetime of **2b** (τ_0) is 3.7 ns in benzene, 4.4 ns in THF, and 4.7 ns in DMF.
10) J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, London (1970).
11) H. Heitele, S. Finck, S. Weeren, F. Pollinger, and M. Michel-Beyerle, *J. Phys. Chem.*, **93**, 5173 (1989). G. L. Gaines, III, M. P. O'Neil, W. A. Svec, M. P. Niemczyk, and M. R. Wasielewski, *J. Am. Chem. Soc.*, **113**, 719 (1991).
12) T. Asahi, M. Ohkochi, R. Matsusaka, N. Mataga, R. P. Zhang, A. Osuka, and K. Maruyama, *J. Am. Chem. Soc.*, **115**, 5665 (1993).

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