(TMS) chloride, the silyl ether **12b** (55% yield).

Cyclization of enyne **12a** with catalytic palladium dibenzylideneacetone complex ($Pd_2(dba)_3$)[14] in the presence of tri-*o*-tolylphosphine, dimethylhydrosiloxane, and acetic acid completed the phorbol A ring, giving with impressive 1,3-stereocontrol only diene **13a** (58%). Enyne **12b** exhibited similar behavior with palladium catalysis afFording **13b**, and it also reacted with dibutylzirconocene[15] followed by acetic acid quench of the zirconacyclopentene intermediate to give a 69% yield of **13b**. Despite the different mechanisms operative for these cyclizations the stereochemistry at C2 and of the ethylidene group is the same for both processes.

With the assembly of the tricyclic ABC core of phorbol completed, the latent oxidation at C3 and C12 was unveiled by ozonolysis of both exocyclic alkenes followed by reductive workup with sodium borohydride to afford a triol, again as a single isomer. Selective protection of the C3–C4 *cis*-diol as the acetonide followed by oxidation of the C-12 alcohol to the ketone yielded **2** (24% for three steps), thereby completing a formal synthesis of phorbol.[4b]

In summary, the synthesis of phorbol precursor **2**, possessing all of the putative pharmacophore heteroatoms of the natural products, has been achieved in 16 steps from commercial materials (\$) by a novel group transfer induced cycloaddition and a transition metal mediated cyclization. This shortened route offers improved access to racemic phorbol esters as well as unnatural analogues that are needed to establish the structural requirements for tumor promotion. These studies and the extension of this strategy to ingenane and daphnane diterpenes are in progress.

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Supplementary Material Available: NMR, IR, MS, and elemental analysis data for compounds **7b**, **8**, **11**, and **2** (4 pages). Ordering information is given on any current masthead page.

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Geometry Dependence of Intramolecular Photoinduced Electron Transfer in Synthetic Zinc–Ferric Hybrid Diporphyrins

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Despite the crucial role of photoinduced electron transfer (ET) reactions in photosynthetic energy conversion, the factors that control this reactivity remain poorly understood. Among these, the geometrical factors such as distance and mutual orientation offer important effects in the photoinduced ET reaction. Recent theoretical work indicates the importance of orientation effects on the rates of the nonadiabatic ET process between diporphyrin pairs.[1] Synthetic model compounds with well-defined geometries are particularly effective in probing this problem.[2] Recently McLendon et al. reported the occurrence of intramolecular ET reaction in aryl-linked diporphyrin hybrid complexes.[3] This paper reports more comprehensive geometric effects in an extensive array[4] of hybrid metal complexes consisting of zinc porphyrin (ZnP) and ferric porphyrin chloride ($Fe^{III}PCl$) (Figure 1).[5] Diporphyrin models studied here include a variety of mutual orientations and different kinds of aromatic spacers such as benzene, naphthalene, and spirobiindan.

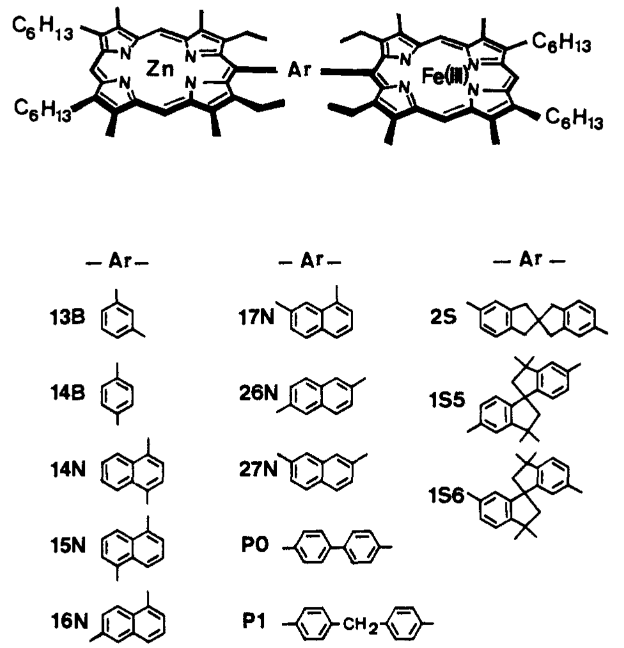

Figure 1. Structure of ZnP–$Fe^{III}P$ hybrid diporphyrins used in this study. Abbreviations are indicated at the left side of the aromatic spacer.

The ground-state absorption spectra of the hybrid diporphyrins ZnP–$Fe^{III}PCl$ in the Q-band region can be adequately described in terms of a superposition of the spectra of the individual chromophores, but those at the B-band displayed slight broadening, indicating very weak interaction in the S_1 states and excitonic interaction in the S_2 states. The fluorescence spectra are that of the unperturbed ZnP alone,[6] but the fluorescence quantum yields for the ZnP in these hybrid diporphyrins decreased dramatically. This decrease in the fluorescence quantum yield can be ascribed to the intramolecular ET from the $^1(ZnP)^*$ to the $Fe^{III}PCl$ on the basis of the picosecond transient absorption measurements.[7] As an example, the transient absorption spectra of 4,4′-diphenylmethylene-bridged diporphyrin **P1** in DMF are shown in Figure 2. The spectrum at the delay time of 26 ps was almost due to

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[5] For intramolecular electron transfer from $^1(ZnP)^*$ to $Fe^{III}P$, see: (a) Fujita, I.; Netzel, T. L.; Chang, C. K.; Wang, C.-B. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 413–417. (b) Brookfield, R. L.; Ellul, H.; Harriman, A. *J. Chem. Soc., Faraday Trans. 2* **1985**, *81*, 1837–1848. (c) Mataga, N.; Yao, H.; Okada, T.; Kanda, Y.; Harriman, A. *Chem. Phys.* **1989**, *131*, 473–480.

[6] It is well-known that $Fe^{III}Cl$ porphyrins are d-type hyperporphyrins and their excited states are very short lived and nonfluorescent: Irrine, M. P.; Harrison, R. J.; Strahand, M. A.; Beddard, G. S. *Ber. Bunsenges. Phys. Chem.* **1985**, *89*, 226–232.

[7] The measurements were done by means of a microcomputer-controlled double-beam ps spectrometer with a repetitive mode-locked Nd^{3+}/YAG laser as the excitation source. Miyasaka, H.; Masuhara, H.; Mataga, N. *Laser Chem.* **1983**, *1*, 357–386.

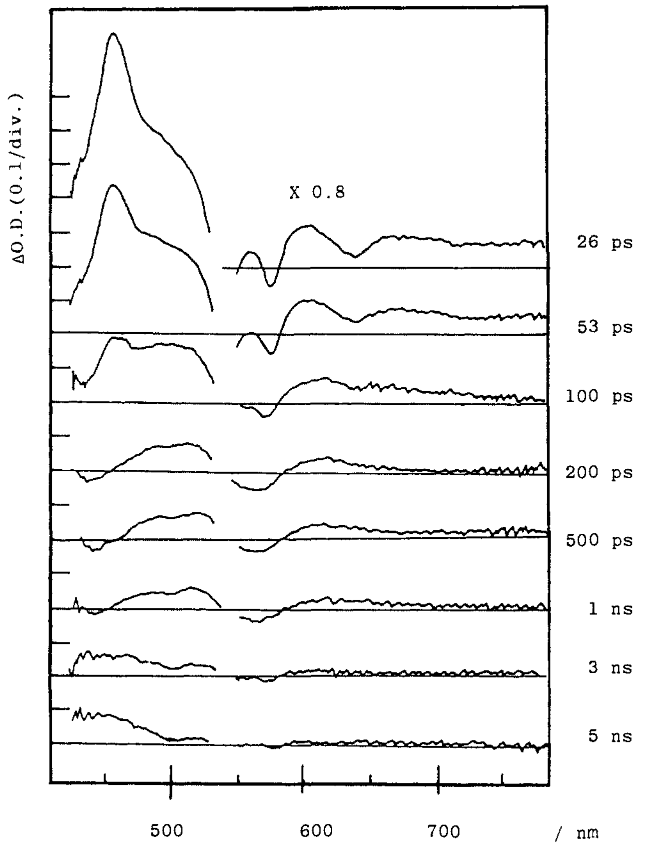

Figure 2. Picosecond time-resolved transient absorption spectra of **P1** in DMF, excited at 532-nm pulse.

the $S_n \leftarrow S_1$ transition of the ZnP. Upon increase of the delay time to 100 ps, the spectra exhibited a drastic change. A rapid decay of the $S_n \leftarrow S_1$ absorption at 460 nm was followed by the rise of a broad absorption in the 480–530- and 590–700-nm regions, which can be ascribed to the formation of $(\mathrm{ZnP})^+$–Fe$^{\mathrm{II}}$P on the basis of the previous studies.[4,8,9] The time constant of the decay at 460 nm (52 ps) agreed satisfactorily with the fluorescence lifetime of the ZnP (50 ps), which was determined by the picosecond time-resolved fluorescence spectroscopy.[10] Upon further increase of the delay time to 3 and 5 ns, the $(\mathrm{ZnP})^+$–Fe$^{\mathrm{II}}$P decayed slowly and the absorption at 450 nm was observed, which was assigned to the absorption spectrum due to the $T_n \leftarrow T_1$ transition of the ZnP.[11] By analyzing a slow decay of the absorption at 512 nm, the rate constant for charge recombination, k_{cr}, was determined to be $6.3 \times 10^8\ \mathrm{s}^{-1}$. In a similar manner, both rate constants for charge separation and recombination were determined in a series of diporphyrin molecules.[11] The rate constants for charge separation were more accurately determined from their respective fluorescence lifetimes, assuming that the sole additional decay route in $^1(\mathrm{ZnP})^*$–Fe$^{\mathrm{III}}$P was due entirely to the formation of $(\mathrm{ZnP})^+$–Fe$^{\mathrm{II}}$P.[12] In Figure 3, these electron transfer rate constants, k_{cs} and k_{cr}, are plotted against the center-to-center distance between two porphyrins, r.

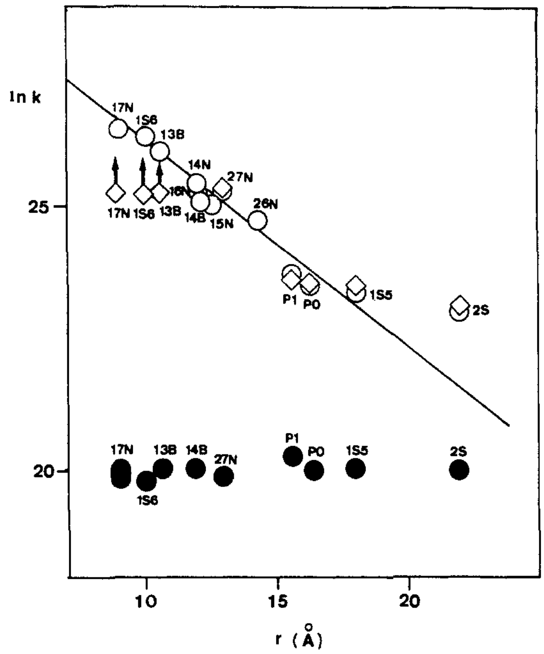

Figure 3. Plots of ln k_{cs} and ln k_{cr} vs the center-to-center distance, r, of two porphyrins: (○) k_{cs} determined by the fluorescence lifetime of ZnP in $\mathrm{CH_2Cl_2}$; (▽) k_{cs} determined by the transient absorption measurement in DMF; (●) k_{cr} determined by the transient absorption measurement in DMF.

A plot of ln k_{cs} vs r showed a good straight line, indicating k_{cs} to be primarily determined by the distance r. Fitting the results

$$k_{\mathrm{cs}} = A_0 \exp(-\beta r) \qquad (1)$$

with eq 1, we calculated the values of $\beta = 0.4\ \text{Å}^{-1}$ as the attenuation factor and $A_0 = 1.4 \times 10^{13}\ \mathrm{s}^{-1}$ as the preexponential factor. It is somewhat surprising that k_{cs} showed no apparent orientation dependence. In marked contrast and more surprisingly, k_{cr} was found to be much smaller than k_{cs} and nearly constant (ca. 4–6 $\times 10^8\ \mathrm{s}^{-1}$) through the series, independent of the orientation, of intervening spacers, and *even of the distance in a range of* $23\ \text{Å} > r > 8\ \text{Å}$. As a result, the increase of the ratio of $k_{\mathrm{cs}}/k_{\mathrm{cr}}$ is brought about on decreasing the center-to-center distance. For example, the ratio of $k_{\mathrm{cs}}/k_{\mathrm{cr}}$ increases ca. 36 times from 18 in **2S** to 650 in **1S6**.

The nearly constant k_{cr} values observed here might be interpreted as accidental compensation of distance effects by other factors such as orientation effects, free energy changes, or spin selection effects. Alternatively, these results suggest that the rate-determining step in the charge-recombination process is not an inter-site ET reaction but a reaction within the Fe$^{\mathrm{II}}$PCl complex site such as the change of ligation.[13]

In conclusion, it is revealed that the charge separation and recombination reactions show quite different distance dependence in these conformationally restricted diporphyrin systems. The charge separation depends primarily on the distance and shows no apparent orientation dependence, while the charge recombination is practically independent of the distance and the orientation.

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(8) The free energy gaps in DMF solution for charge separation and recombination were estimated by using values of the redox potentials, $E_{1/2}(\mathrm{ZnP/ZnP^+}) = 0.29$ eV and $E_{1/2}(\mathrm{Fe^{III}P/Fe^{II}P}) = -0.88$ eV vs Ag/AgCl and the excited singlet state energy of ZnP, 2.14 eV. The work term involved in these electron-transfer reaction was estimated at less than 0.05 eV in DMF. Accordingly, ΔG_{cs} and ΔG_{cr} were roughly calculated to be -1.0 and -1.2 eV, respectively, indicating the high exothermicity of both reactions.

(9) The spectrum of the $(\mathrm{ZnP})^+$–Fe$^{\mathrm{II}}$PCl can be reproduced by superposition of electrochemically generated $(\mathrm{ZnP})^+$ and Fe$^{\mathrm{II}}$PCl. The $(\mathrm{ZnP})^+$ species showed peaks at ca 610 nm in DMF.

(10) Picosecond time-resolved fluorescence spectroscopy revealed that all these models exhibited virtually a single decaying component. The measurements were done with the instruments described in the following paper: Yamazaki, I.; Tamai, N.; Kume, H.; Tsuchiya, H.; Oba, K. *Rev. Sci. Instrum.* **1985**, *36*, 1187–1194.

(11) The triplet $^3(\mathrm{ZnP})^*$–Fe$^{\mathrm{III}}$PCl may be formed via intersystem crossing from $^1(\mathrm{ZnP})^*$, which is competitive with the intramolecular electron-transfer process. This was distinctly observed for diporphyrins **P0**, **1S5**, and **2S** with relatively small k_{cs} values.

(12) We calculated k_{cs} by the following equation

$$k_{\mathrm{cs}} = 1/\tau - 1/\tau_0$$

where τ is the fluorescence lifetime of the ZnP in the ZnP–Fe$^{\mathrm{III}}$P and τ_0 is the fluorescence lifetime of the reference ZnP, 1.5 ns.

(13) Preliminary studies on the ZnP(Im)–Fe$^{\mathrm{III}}$P(Im)$_2$ (Im = imidazole) hybrid complex in DMF revealed a markedly enhanced k_{cr} compared with those in the text, while k_{cs} were similar in both cases. These results indicate the important role of the ligand in the CR process, details of which will be discussed elsewhere.