A chemical approach towards photosynthetic reaction center (2)

Kazuhiro Maruyama, Atsuhiro Osuka, and Noboru Mataga[#]

Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan

[#]Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka 560, Japan

Abstract—Pyromellitimide(Im)-linked porphyrin arrays were prepared and their intramolecular electron-transfer reactions were studied by picosecond time-resolved transient absorption spectroscopy. In pyromellitimide-linked zinc porphyrin (M-Im), the rates of the photoinduced charge separation (CS) and charge recombination (CR) of the product ion pair (IP) states, k_{CS} and k_{CR}, were precisely determined by tracing a characteristic sharp absorption band around 715 nm due to $(Im)^-$. k_{CS} is essentially solvent polarity independent, while k_{CR} increases with solvent polarity. In 1,2-phenylene-bridged zinc diporphyrin-zinc porphyrin-pyromellitimide (D-M-Im) triads, $^1(M)^*$ is competitively quenched by D through energy transfer to give $^1(D)^*$-M-Im and by Im through CS to give D-$(M)^+$-$(Im)^-$. Secondary IP states $(D)^+$-M-$(Im)^-$ are formed via hole transfer from $(M)^+$ to D. Sequential electron-transfer reactions that are the same type of the reaction mode of the reaction center are realized in zinc porphyrin-pyromellitimide-quinone (M-Im-Q) triads; $^1(M)^*$-Im-Q —> $(M)^+$-$(Im)^-$-Q —> $(M)^+$-Im-$(Q)^-$. Finally, a more long-lived IP state is generated from D-M-Im-Q tetrads.

1. INTRODUCTION

The appearance of the X-ray structure of bacterial photosynthetic reaction center (RC)(ref. 1) has exerted a great impact on mechanistic as well as synthetic approaches toward this natural charge separation (CS) apparatus(ref. 2 and 3). In the RC, six tetrapyrrolic pigments and two quinones are positioned at precise distances and orientations to achieve a highly efficient CS. In order to understand the detailed mechanisms in the RC, ultrafast laser photolysis investigations on the electron-transfer (ET) reactions of elaborated models consisting of acceptor-linked porphyrin arrays are highly desirable. However, it is not necessarily easy to identify a charge-separated ion pair (IP) state when the acceptor is quinone, since the absorption spectra of the porphyrin cation radical are quite similar to those of S_1-state or T_1-state of porphyrin and the spectral characteristics of the quinone anion radical are rather obscure. We report here the picosecond excited-state dynamics of pyromellitimide- and/or quinone-linked porphyrin models, 1(M-Im), 2(D-M-Im), 4(M-Im-Q), and 6(D-M-Im-Q), where M represents a monomeric zinc-porphyrin, D represents a 1,2-phenylene-bridged diporphyrin, and Im and Q represent pyromellitimide and quinone acceptors, respectively. In the D moiety, strong electronic interactions between the two porphyrins results in the lowering of the S_1 excitation energy by 0.16 eV in THF, and also in the decrease of the one-electron oxidation potential by 0.24 V in DMF in comparison to those of M(ref. 4). These properties, which may be directly compared to those of the special pair in the RC, make the D moiety a promising excitation-energy acceptor from M and a potential electron donor to $(M)^+$. The Im moiety is an effective electron acceptor toward the singlet excited state of M and has been proven to be quite useful for analysis of electron-transfer kinetics because of the characteristic sharp absorption at ca. 715 nm(ref. 5 and 9). The Im unit was used earlier by Sanders et al. as an electron acceptor toward the singlet excited state of porphyrins(ref. 6). They have also conducted picosecond time-resolved transient absorption spectroscopy on the pyromellitimide-capped porphyrins. However, they monitored the transient absorption spectra only in a narrow range of 420-540 nm, and thus missed observing the characteristic absorption of $(Im)^-$(ref. 7). Since the Im moiety is a weaker electron acceptor than usual Q moieties, there exist energy gradients, which are favorable for formations of $(M)^+$-Im-$(Q)^-$ and $(D)^+$-M-Im-$(Q)^-$ in 4 and 6, respectively. Photosynthetic models studied here were prepared according to our improved porphyrin cyclization method(ref. 8). Synthetic details are described elsewhere.(ref. 9 and 10).
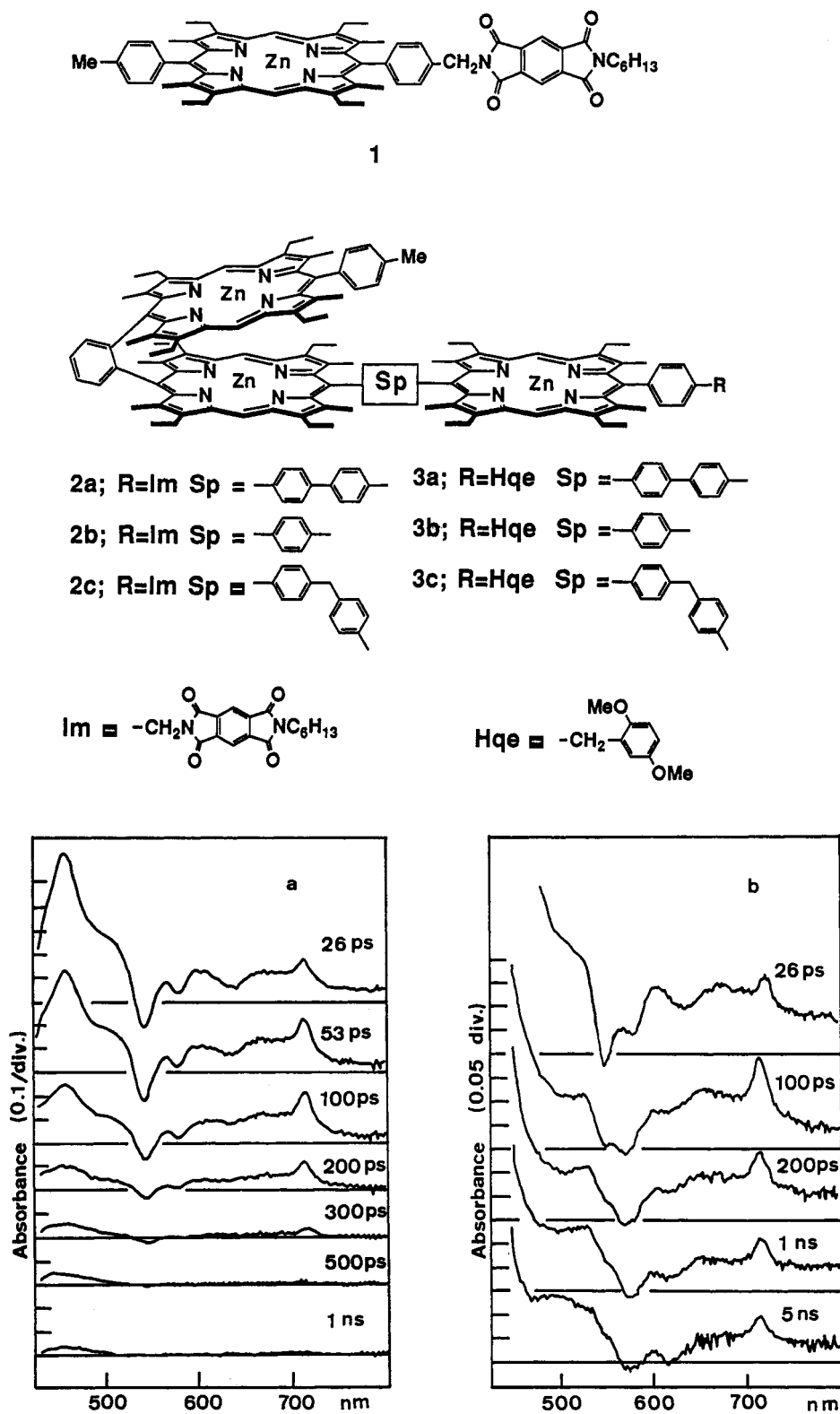
1

2a; R=Im Sp =

2b; R=Im Sp =

2c; R=Im Sp =

3a; R=Hqe Sp =

3b; R=Hqe Sp =

3c; R=Hqe Sp =

Im = −CH₂N...NC₆H₁₃

Hqe = −CH₂...

Fig. 1. Picosecond transient absorption spectra of 1 (a) and 2a (b) for excitation at 532 nm in THF.

2. M-IM DYADS

First, we examined intramolecular electron-transfer reactions of $\underline{1}$, in which the Im moiety can rotate around the CH_2 group but the center-to-center distance between the Im and porphyrin is restricted at ca. 13 Å. The picosecond time-resolved transient absorption spectra of $\underline{1}$ for excitation at 532 nm in THF are shown in Fig. 1a. As the $S_n \longleftarrow S_1$ absorption band of M at 460 nm decays with $\tau = 60$ ps, a sharp absorption band at 715 nm appears with rise time of 60 ps and decays with $\tau = 100$ ps. A broad absorption band around 670 nm exhibits the same time-profile as that of the 715 nm band. The absorption bands at 670 nm and 715 nm were assigned to $(M)^+$ and $(Im)^-$, respectively, on the basis the spectra obtained by electrochemical oxidation or reduction of the relevant chromophores. The long-lived absorption band around 460 nm can be assigned from its band shape to the $^3(M)^*$, which may be produced by the intersystem crossing competing with the CS between the $^1(M)^*$ and Im. From the above results, the reaction scheme for $\underline{1}$ may be depicted as summarized in Scheme 1. This reaction scheme gives eq(1) for the time dependence of the absorbance $A\lambda(t)$ at a wavelength of λ, where $1/\tau_S = k_{CS} + 1/\tau_0$, $1/\tau_0 = k_F + k_d + k_{ISC}$, $1/\tau_{IP} = k_{CR}$, and α, β, and γ are constant independent of time (t) and include initial concentration of $^1(M)^*$, intersystem crossing yield of $^1(M)^*$, yield of IP state formation, etc. By simulation of the observed time profiles at 715 nm and 460 nm with eq(1), k_{CS} and k_{CR} values have been obtained to be 1.7×10^{10} and 9.3×10^9 s^{-1}, respectively. Similarly, k_{CS} and k_{CR} values in other solvents were determined to be 1.9×10^{10} and 3.6×10^8 s^{-1} in benzene, and 8.0×10^9 and 5×10^{10} s^{-1} in DMF, respectively(ref. 4). It is evident that k_{CS} does not show large solvent polarity dependence but k_{CR} shows a large decrease with decrease of the solvent polarity. In general, with decrease of the solvent polarity, the free energy gap for the CR reaction of IP state increases and that for the photoinduced CS reaction decreases, while the solvent reorganization energy decreases. Therefore, k_{CS} is not much affected by solvent polarity on the one hand, while k_{CR} shows a rather drastic decrease with the decrease of the solvent polarity. Consequently, the IP state from $\underline{1}$ is longer-lived in benzene but is rather shorter-lived in DMF in comparison with that in THF. Dramatic increase of the lifetime of the IP state upon lowering the medium polarity stresses the importance of a relatively apolar environment in slowing down undesirable CR reaction as well as maintaining a high level of the charge separated state for a simple 1:1 donor-acceptor linked compound.

$$A\lambda(t) = \alpha exp\,(-t/\tau_S) + \beta exp\,(-t/\tau_{IP}) + \gamma \qquad (1)$$
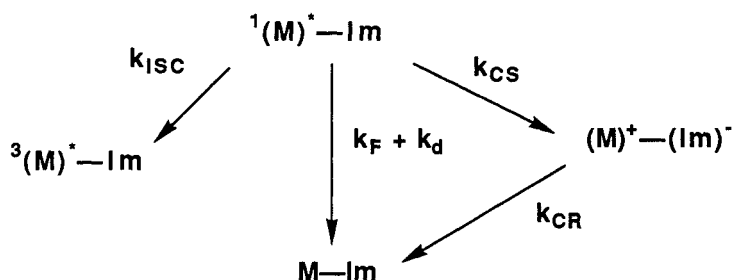
Scheme 1

We have also examined the energy gap dependencies of the photoinduced CS and CR of the product IP states in a series of porphyrin-diimide dyads (ref. 12). It should be noted here that investigations on various factors regulating the electron transfer by employing fixed distance dyads are of crucial importance not only for the construction of artificial photosynthetic apparatus but also for the further development of the electron transfer theory. The obtained results are quite similar to those obtained for related porphyrin-quinone dyads bearing the same bridge. By using the latter molecules, we have made critical examinations on energy gap, temperature and solvent polarity dependence of the photoinduced CS and CR of the product IP states and have obtained interesting results which seem to provide some important new physical insights into the electron transfer mechanism (ref. 13). However, we do not get into details here.

3. D-M-IM TRIADS

In the steady-state fluorescence spectrum of the acceptor-free model $\underline{3a}$, the fluorescence intensity of M (λ_{em} = 586 nm and 638 nm) decreases significantly whereas that of D (λ_{em} = 680 nm) is enhanced,

indicating the occurrence of the efficient intramolecular excitation energy transfer (EN) from M to D in 3a. The rate of this energy transfer (k_{EN}) was calculated from the following eq(2),

$$k_{EN} = (\tau(M))^{-1} - (\tau_0(M))^{-1} \qquad (2)$$

where $\tau(M)$(68 ps) is the fluorescence lifetime of the $^1(M)^*$ in 3a and $\tau_0(M)$ (1.35 ns) is the fluorescence lifetime of the reference zinc porphyrin monomer. The k_{EN} value thus calculated is 1.4 x 10^{10} s^{-1}. In a similar manner, the k_{EN} values have been obtained for 3b(2.0 x 10^{11} s^{-1}) and 3c(2.5 x 10^{10} s^{-1})(ref. 9). To the best of our knowledge, this is the first example of one-directional singlet-singlet energy transfer from a monomeric porphyrin to a diporphyrin comprising the same chromophore. We assumed the occurrence of similar energy transfer in 2a-c. The transient absorption spectra of 2a in THF are shown in fig. 1b. In the triads 2a-c, the $^1(M)^*$ should be competitively quenched by the D through the intramolecular singlet-singlet energy transfer to give $^1(D)^*$-M-Im and by the Im through the CS to give D-(M)$^+$-(Im)$^-$. In fact, the decay of $^1(M)^*$ in 2a-c is faster than that in 3a-c. It is interesting to note that the absorbance at 715 nm due to (Im)$^-$ persists even at 5-ns delay time. Deconvolution of the time dependence of the absorbances at 715 nm reveals the decay curve to be composed of two exponentials with lifetime of 70 ps and 2.5 μs, which can be ascribed to CR process from IP states, D-(M)$^+$-(Im)$^-$ and (D)$^+$-M-(Im)$^-$, respectively. On the basis of these results, the rate of the hole transfer from the (M)$^+$ to the (D) in 2a in THF is estimated to be 4.3 x 10^9 s^{-1}. In benzene solution the hole transfer from the (M)$^+$ to the (D) does not occur. The failure of the hole transfer in nonpolar benzene solution would be ascribed to the much reduced electrostatic stabilization-energy acquired by the IP state (D)$^+$-M-(Im)$^-$ compared with that in THF. In THF or DMF, the long-lived IP states are formed from 2a-c, and their lifetimes have been determined as follows, 2.5, 0.25, and 5.3 μs for 2a, 2b, and 2c, in THF, and 8.2, 0.39, and 23 μs for 2a, 2b, and 2c, in DMF, respectively(ref. 9). In contrast to the results for 1, the lifetime of the (D)$^+$-M-(Im)$^-$ increases upon increase of the solvent polarity. This marked difference between solvent effect on the lifetime of the (D)$^+$-M-(Im)$^-$ and (M)$^+$-(Im)$^-$ may have an important practical implication on design of artificial photosynthetic models. Another result of mechanistic importance is that selective excitation at the D moiety (λ_{ex} = 620 nm) in 2 does not lead to the formation of (Im)$^-$. This result implies that long-distance ET from the $^1(D)^*$ to the (Im) does not take place in D-M-Im. The reaction scheme of 2a in THF was summarized in Scheme 2 (ref. 9).

**Scheme 2**
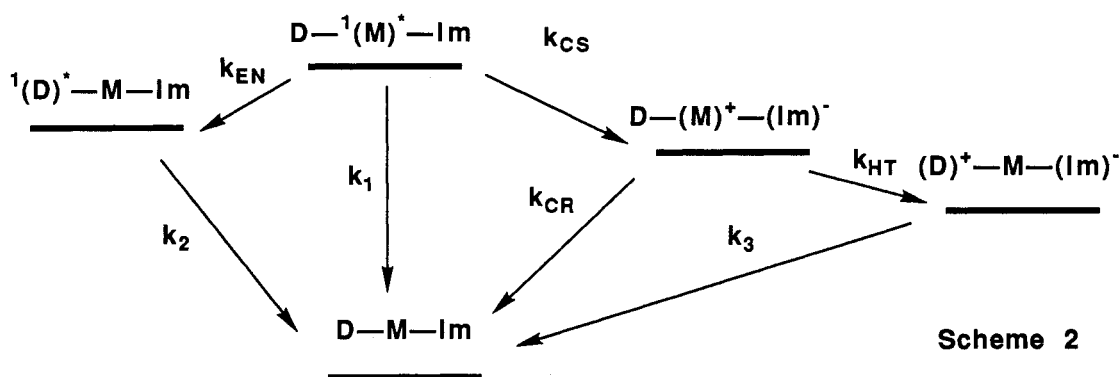
4. M-IM-Q TRIADS

Advantage of the Im acceptor as an electron probe has been more clearly demonstrated in the study of M-Im-Q triads, in which there exists a energy gradient favorable for a charge-shift (CSH) reaction (M)$^+$-(Im)$^-$-Q —> (M)$^+$-Im-(Q)$^-$. By tracing the rise and decay kinetics of the absorbance of (Im)$^-$, it is possible to determine the rate of charge-shift (CSH) reaction; (M)$^+$-(Im)$^-$-Q —> (M)$^+$-Im-(Q)$^-$. In the triad 5, the CSH does not occur in THF, probably due to a long distance between the Im and Q moieties. On the other hand, in the triads 4a-c, the CSH reactions were directly observed by the transient absorption spectroscopy and their rates were determined to be 3.0 x 10^{10}, 2.5 x 10^9, and >2 x 10^{11} s^{-1}, respectively (ref. 10). In 4c, a nearly quantitative quantum yield for the formation of (M)$^+$-

4a; R=   **4b; R=**   **4c; R=**

5
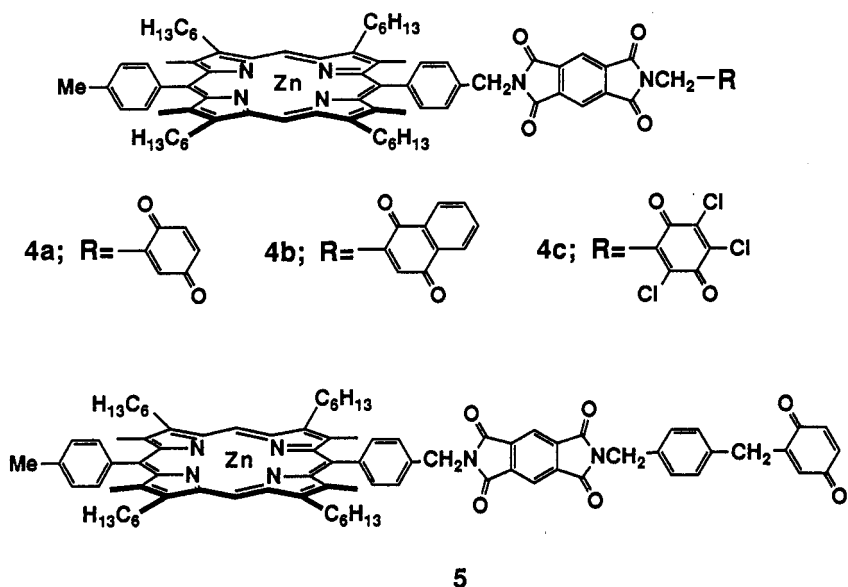
Im-(Q)⁻ is achieved, since the k_{HT} value is much larger than the k_{CR} value (9.3×10^9 s⁻¹). It should be stressed here that this sequential electron-transfer reactions (the initial CS reaction between the ^{1}(M)* and Im followed by the CSH reaction from (Im)⁻ to Q) is the same reaction mode occurring in RC but is quite rare in the literature(ref. 11), although many examples have been reported where the other sequence results in the formation of long-lived IP states: (the initial CS followed by the hole transfer being the same as reported for the D-M-Im models)(ref. 2).

5. D-M-Im-Q TETRADS

Finally, it is expected that a more longer-lived IP state would be formed from a D-M-Im-Q tetrad such as 6. Thus we studied its excited-state dynamics. The photoexcited-state dynamics of the Q-free molecule 7 was virtually the same as those of 2b; (D)⁺-M-(Im)⁻ IP state is formed in a substantial quantum yield and its lifetime is 260 ns. In contrast, no indication of the absorbance due to (Im)⁻ was detected in the transient absorption spectra of 6, indicating immediate formation of (D)⁺-M-Im-(Q)⁻ from (D)⁺-M-(Im)⁻-Q as expected from the results obtained for M-Im-Q. The lifetime of the final IP state thus formed is 2.7 μs.
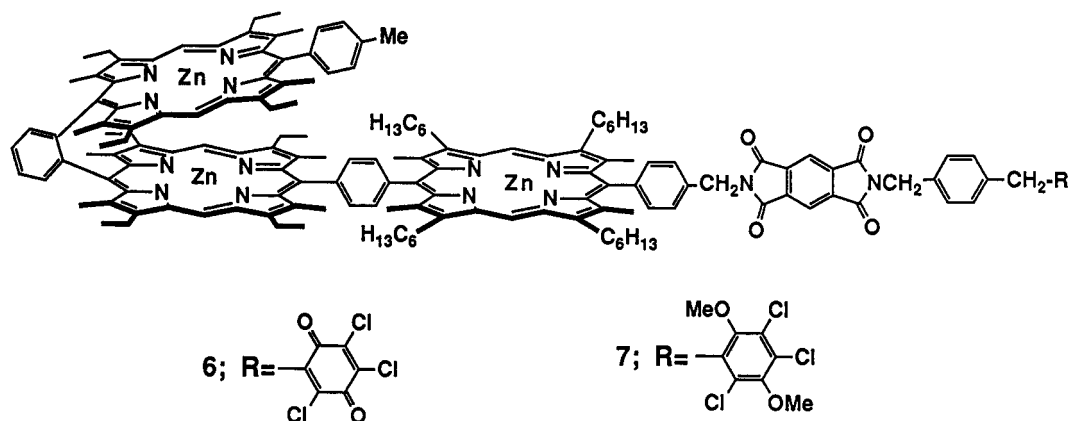
6; R=   **7; R=**

Acknowledgment

REFERENCES

1. J. Deisenhofer, O. Epp, K. Miki, R. Huber, and H. Michel, J. Mol. Biol. 180, 385-398 (1984).
2. M. R. Wasielewski, Chem. Rev. 92, 435-461 (1992).
3 K. Maruyama, and A. Osuka, Pure Appl.Chem. 62, 1511-1520 (1990).
4. A. Osuka, S. Nakajima, T. Nagata, K. Maruyama, and K. Toriumi, Angew. Chem.. Int. Ed. Engl. 30, 582-584 (1991).
5. A. Osuka, S. Nakajima, K. Maruyama, N. Mataga, and T. Asahi, Chem. Lett., 1003-1006 (1991).
6. J. A. Cowan and J. K. M. Sanders, J. Chem. Soc.. Perkin Trans 1, 2435-2437 (1985).
7. R. J. Harrison, B. Pearce, G. S. Beddard, J. A. Cowan, and J. K. M. Sanders, Chem. Phys. 116, 429-448 (1987).
8 T. Nagata, A. Osuka, and K. Maruyama,J. Am. Chem. Soc. 112, 3054-3059 (1990).
9. A. Osuka, S. Nakajima, K. Maruyama, N. Mataga, T. Asahi, I. Yamazaki, Y. Nishimura, T. Ohno, and K. Nozaki, J. Am. Chem. Soc. 115, in press (1993).
10. M. Ohkohchi, A. Takahashi, N. Mataga, T. Okada, A. Osuka, H. Yamada, and K. Maruyama, J. Am. Chem. Soc., submitted.
11. S. Nishitani, N. Kurata, Y. Sakata, S. Misumi, A. Karen, T. Okada, and N. Mataga, J. Am. Chem. Soc. 105, 7771-7773.
12. Y. Tanaka, T. Okada, N. Mataga, A. Osuka, H. Yamada, and K. Maruyama, unpublished results.
13. T. Asahi, m. Ohkohchi, R. Matsuzaka, N. Mataga, R. P. Zhang, A. Osuka, and K. Maruyama, J. Am. Chem. Soc. 115, in press (1993).