Control of electron transfer and its utilization

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Abstract: In order to get information on the controlling factors of photosynthetic electron transfer and to apply the principle for the construction of artificial photosynthesis and molecular electronics, we have so far prepared various model compounds from which particular factors can be extracted. Among them our recent results on 1) mutual orientation effect, 2) effect of the nature of intervening bonds, 3) effect of inserted π-system, 4) effect of coordination bond between a redox pair, 5) size and shape effect of an acceptor, are described. In order to utilize charge separated state, C60-linked porphyrin with SMe group at the terminal position was synthesized and fixed it on gold surface using S-Au bond as self-assembled monolayer. When the sample was irradiated, photocurrent was observed.

INTRODUCTION

The conversion of solar energy into useful chemical energy in photosynthesis is the basis of the life of all organisms. Among various processes of photosynthesis photoinduced electron transfer (ET) plays a crucial role in the utilization of photon energy. The natural ET process is quite skillfully controlled to achieve stable charge separation by the combination of the acceleration of forward ET and the retardation of back ET. The high selectivity in ET is achieved by both the selection of suitable chromophores and their arrangement in membrane protein. Recent X-ray analysis (1) on the bacterial reaction center has revealed that the arrangement of chromophores in protein matrix play an important role in the achievement of the efficient and stable charge separation. However, we can not control ET like in natural system until now, since all of the controlling factors of ET are not well understood. Since the pictures drawn by X-ray analysis are the final result of evolution in several billion years, we do not know what points were improved during the evolution. If we could see the intermediate pictures in the course of evolution, we could get information about the controlling factors of ET in more detail and apply the principle to develop molecular based sensors, electronic devices, and so on. One of the most useful strategy to get such information without seeing the intermediates is to prepare suitable compounds from which the particular factor can be extracted. Based on this idea pioneering works of preparing model compounds, where a porphyrin and a benzoquinone chromophore was connected by a linkage of covalent bonds, were carried out independently by two groups in 1979 (2). We came into this field two years later (3). After the publication of X-ray analysis on bacterial reaction center in 1984, various kinds as well as huge number of model compounds have been so far prepared and factors of interchromophore distance and free energy change associated with ET reaction have been quantitatively analyzed (4). However, still many factors remain unsolved. Recently, we have synthesized various model compounds to shed light on the unsolved problems described below.

CONTROLLING FACTORS OF ELECTRON TRANSFER

Effect of Donor-Acceptor Orientation

In order to extract the effect of donor-acceptor orientation upon ET, we need a set of compounds where the same redox pair are separated by a rigid spacer with the same distance and have different orientation. Furthermore, there should be no interaction between two chromophores in the ground state and the number of intervening bonds between the redox pair should be the same to make discussion clear. Bearing these in mind, we designed and synthesized a pair of **1** (**5**) and **2** (**6**) and that of **3** (**7**) and **4** (**8**) (5). The center-to-center (edge-to-edge) distances between the porphyrin and the quinone in these eight molecules based on MM2 calculations are as follows: **1** and **5**, 12.5 Å (8.2 Å); **2** and **6**, 12.9 Å (8.6 Å); **3** and **7**, 9.0 Å (6.4 Å); **4** and **8**, 9.3 Å (6.3 Å). The rotation of the spacer-quinone unit relative to the porphyrin is strongly restricted by the steric effects of the methyl groups adjacent to the porphyrin *meso* position to which the spacer is attached. One can see from the structures of **1** - **8** that the above requirements are satisfied in each pair. The rigid structure of **1** - **8** was confirmed by ^{1}H NMR spectra. Thus, ring current effects due to the porphyrin ring were experimentally obtained by subtracting the chemical shifts of the corresponding protons of reference compounds lacking porphyrin rings. On the other hand, this effect was calculated by the well established method in which 8 point dipoles in a porphyrin ring are assumed. The calculation was carried out assuming that the structures have the dihedral angle of 90° between porphyrin and *meso*-substituted phenyl rings. Quite good agreement between the calculated and observed values clearly indicates that the orthogonal conformation is frozen in a solution at room temperature.

1 :   M = 2H
5 :   M = Zn

2 :   M = 2H
6 :   M = Zn

3 :   M = 2H
7 :   M = Zn

4 :   M = 2H
8 :   M = Zn
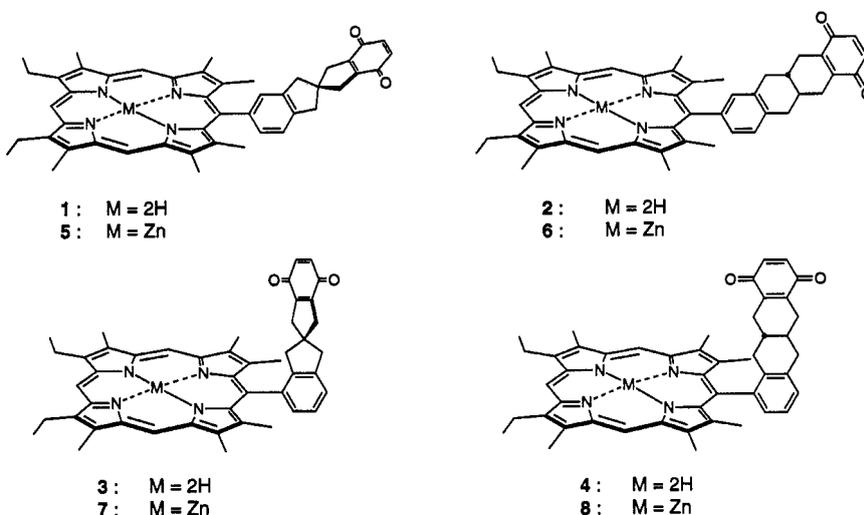
Redox potentials of **1** - **8** show that the driving force for the intramolecular ET are actually the same in each pair. Electronic spectra of **1** - **8** are superimposable to those of reference compounds, indicating that there is no special interaction between the porphyrin and quinone moieties in **1** - **8** and hence, ET rates can be estimated on the basis of fluorescence lifetimes. Fluorescence lifetimes of **1** - **8** and the corresponding reference compounds, where quinone is replaced by 1,4-dimethoxybenzene, are measured by a correlated photon counting in two solvents with different polarity. The values are in good agreement with the lifetimes of the excited singlet states which were determined by analyzing the time dependence of the transient $S_0 \leftarrow S_1$ absorbance excited with a picosecond dye-laser system at 590 nm. Using these data ET rates for charge separation (k_{CS}) were evaluated for **1** - **4** by the equation (1)

$$k_{CS} = 1/\tau - 1/\tau_o \qquad (1)$$

where τ and τ_o are lifetimes of porphyrin-quinone and reference compounds, respectively. On the other hand, k_{CS} and k_{cr} values of **5** - **8** were obtained by monitoring directly the appearance and decay of characteristic band at 670 nm for zincporphyrin cation radical. The k_{CS} values of the compounds having a spiro spacer are larger than those having a *trans*-decalin spacer by 2 - 9 times in THF and DMF. The observed orientation dependent differences in k_{CS} and k_{cr} are explained by the orientation dependent

changes in electronic coupling, especially non-covalent indirect interaction through the solvent molecules that lie between the donor and acceptor.

Effect of the Nature of Intervening Bonds

In order to evaluate the effect of the nature of chemical bonds between a redox pair we synthesized compounds **9 - 10** (6). In these compounds a three-membered ring with two halogen atoms was introduced into the spacer of **2**. The energy minimized structures of **2, 9**, and **10** by MM2 and AM1 calculations indicate that the edge-to-edge distances are 8.5 Å for **9** and **10** and 8.6 Å for **2** and the dihedral angles between the quinone and the benzene rings are 122° for **9** and **10** and 176° for **2**. On the basis of fluorescence lifetimes k_{CS} values were obtained. The k_{CS} values of **9** and **10** with three-membered ring in the spacer are 50 to 60 times (in THF) or 20 times (in DMF) larger than that of **2**. Since the key factors which control ET, that is, separation distance, free energy change associated with

the reaction, mutual orientation, and the number of the intervening bonds between the redox pair are the same or almost the same for **2, 9**, and **10**, the observed large differences in k_{CS} can be attributed to the existence of the dihalosubstituted three-membered ring in the spacer. The large rate acceleration of **9** and **10** is explained by the electronic effect of the three-membered ring. Thus, new lower lying LUMO, which appears by the mixing of three-membered ring and halogen orbitals, are responsible for the rate acceleration by super exchange mechanism.
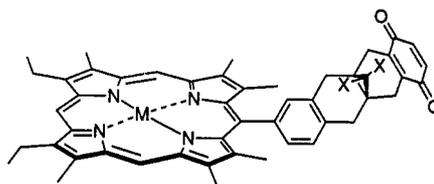
9 : M = 2H, X=Cl
10 : M = 2H, X=Br

Effect of Inserted π-System Between a Redox Pair

In order to distinguish between through-space and through-bond ET mechanism, a model compound **11**, where a phenyl ring is inserted into the spacer of **3**, was designed and synthesized (7). If the through-space mechanism is mainly operating, ET rate of **11** is expected to be larger than that of **3**, because the inserted phenyl ring would accelerate ET by super exchange mechanism. The values of k_{CS} were determined by using eq. (1). No difference between ET rates of **3** and **11** indicates clearly that the through-bond mechanism is operating in these compounds. One possible reason why the phenyl ring is not used as a "stepping stone" in intramolecular ET is that the LUMO level of the phenyl ring is not low

enough. The contribution of virtual state P⁺-Ph⁻-Q to the charge separation process is determined by the energy difference between this state and P*-Q state. The estimated difference (2.3 eV) may be too large to compete with facile through-bond ET. Another possible reason for the non-participation of the inserted π-system to ET may be that the relative orientation of the phenyl ring is not adequate. Although the partial overlap of p-orbitals in the two chromophores is possible for the present geometry, the overlap may not be enough for the strong participation of the phenyl ring for the through-space ET pathways.
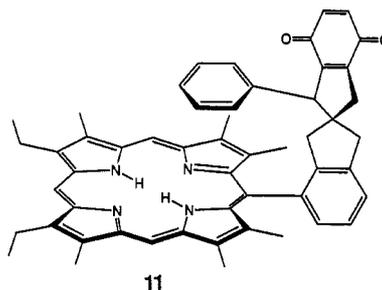
11

Effect of Coordination Bond Between a Redox Pair

In order to get information on the effect of coordination bond between a redox pair, we designed and constructed a porphyrin-quinone supramolecule **12** where a host **13**, zincporphyrin dimer with phenanthrene spacer and a guest **14**, dipyridine-linked quinone can be assembled with two coordination bonds (8). Binding constants in CH_2Cl_2 were obtained from UV-visible spectroscopic titration of the porphyrins for various concentrations of the ligands by using the shift of Soret band on ligation. The
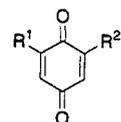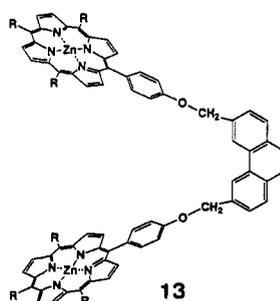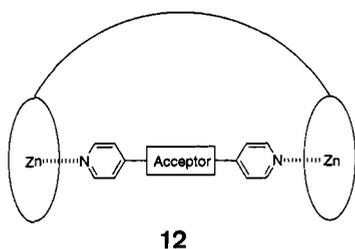
14 : $R^1=R^2=CH_2O\text{-Py}$
15 : $R^1=H$, $R^2=CH_2O\text{-Py}$

binding constant of **13 - 14** is estimated to be around 1.0×10^7 M^{-1}, which is three orders of magnitude larger than that for the binding of **13** and monopyridine-linked quinone **15**. The structure of the supramolecule was obtained by conformational analysis using molecular mechanics method and the result is shown in Fig. 1. Based on the time-resolved, single-photon counting fluorescence studies , k_{CS} of **13 - 14** in CH$_2$Cl$_2$ was obtained to be 1.6×10^{10} s^{-1}. This indicates that the coordination bonds between the donor (D) and acceptor (A) do not make significant influence on ET. Therefore, supramolecular ET systems by using coordination bonds can be treated in a similar manner as for covalently linked ET systems. One of the advantage of supramolecular D-A system is the ease of preparation since D and A parts can be synthesized separately. Furthermore, in well-designed supramolecular D - A systems the breaking of coordination bond will take place immediately after ET, so that charge-separated state with long lifetime will be achieved.
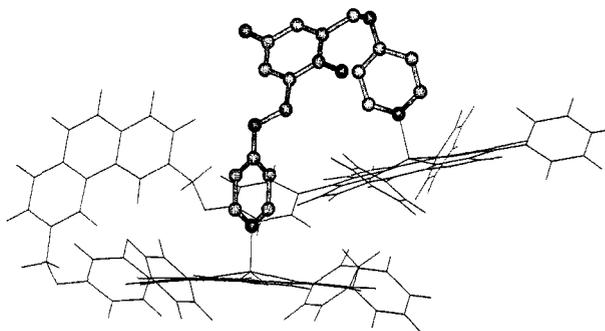
Fig. 1 Calculated structure of supramolecule **13 - 14**.

Size and Shape Effect

One of the major controlling factor of ET in Marcus theory is reorganization energy (λ). In the theoretical expression D and/or A with large size is expected to have small λ value. Experimental verification has not been carried out since no suitable building block was not known. Newly emerged C$_{60}$ has large size (7.0 Å in diameter in carbon skeleton or 11 Å including π-cloud) as well as relatively high electron-accepting ability equivalent to small size of acceptor, benzoquinone (BQ). Therefore, we synthesized a pair of compounds **16** and **17**. where donors are kept constant (porphyrin) and spacers are similar with each other (9). On the basis of molecular modeling, edge-to-edge (or center-to-center) distances are 12.6 Å (18.6 Å) for **16** and 12.7 Å (16.8 Å) for **17**. Free energy charge for charge separation

Ar=3, 5-(t-Bu)$_2$C$_6$H$_3$
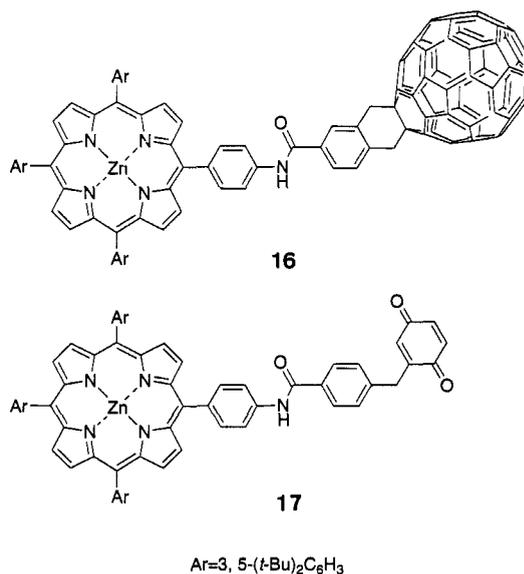
and subsequent charge recombination processes were calculated based on the redox potentials measured in CH_2Cl_2. Values of k_{CS} and k_{cr} in **16** and **17** were obtained in THF from time constants for the decay of the porphyrin fluorescence and decay of the absorbance of the ion pair, respectively. The value of k_{CS} for **16** is faster than that for **17** by about a factor of 6, which is in good agreement with the relative fluorescence quantum yields of **16** and **17**. The rate acceleration of **16** is highly remarkable considering that the energy gap in **16** is somewhat smaller than in **17**. On the other hand, pronounced deceleration (less than 1/25 times) was observed for k_{cr} of **16** compared with that for **17**. Accelerate charge separation and retarded charge recombination can be interpreted by the smaller λ value in C_{60} compared with those in typical acceptors such as quinones and pyromellitic diimides. In general, total λ value is express by the sum of solvent reorganization energy (λ_s) and intramolecular reorganization energy (λ_i). The both value of λ_s and λ_i for C_{60} are expected to be small. The small λ_i value can be explained by the followings. Thus the unit charge in C_{60}^- is spread over the whole C_{60} framework, while BQ π system is small and the charge in BQ anion radical is concentrated on the oxygen atoms. In addition, the small structural change from C_{60} to C_{60}^- due to the rigid framework also contributes to the small value of λ_i. Our conclusion that C_{60} has small reorganization energy has opened the possibilities that artificial photosynthetic systems with a function of efficient and long-lived charge separation can be engineered with less number of ET steps and less energy loss by using a new building block, C_{60}.

In order to carry out further systematic study for ET dynamics of intramolecular photophysical processes including C_{60} chromophore, we synthesized three kinds of porphyrin-linked C_{60} **18** - **20** in addition to **16** (10). Regardless of the linkage between the two redox pair, photoinduced charge separation and subsequent charge recombination were observed by picosecond fluorescence lifetime measurements and time-resolved transient absorption spectroscopy. ET dynamics of these four compounds showed solvent dependence. In THF the charge separation occurs from both the excited singlet states of the porphyrin and C_{60} moieties. On the other hand, in benzene the charge separated state, which was generated by the photoinduced charge separation from the excited singlet state of the porphyrin moiety to the C_{60} part, produces or energetically equilibrates with the locally excited state of the C_{60} moiety. Among the four porphyrin-C_{60} compounds, k_{CS} and k_{cr} values of **18** are much slower than those for the other compounds. This was explained by the spacer superexchange interaction the extent of which is greater at the *ortho* and *para* positions than at *meta* position.

Ar=3,5-(t-Bu)$_2$C$_6$H$_3$
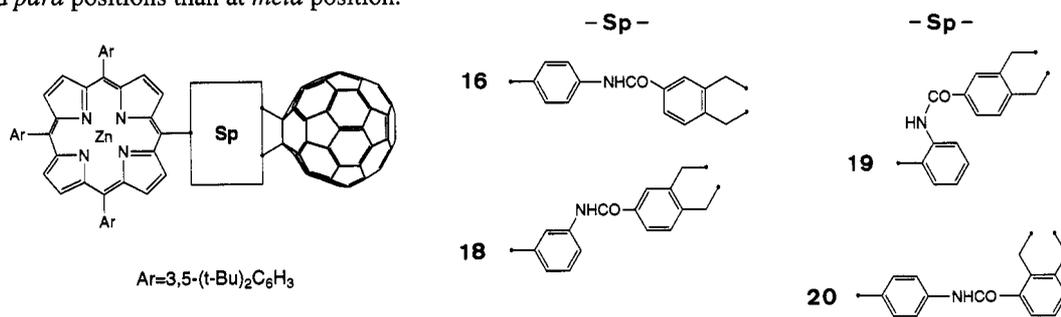
UTILIZATION OF CHARGE SEPARATED STATES

Much information has been accumulated how to prolong the lifetime of charge-separated states in photosynthetic ET models. The next step toward artificial photosynthesis is how to utilize the charge-separated state. So far various donor-acceptor linked molecules have unidirectionally arranged by using lipid bilayer membrane (11), LB films (12), and self-assembled monolayer (13). Among the three techniques the last one where thiolates are assembled on gold surface seems to be most promising from the view points of higher stability and less defects. Along with this line we designed and synthesized compound **21** (14). We employed C_{60} as an acceptor in **21**, since we found that C_{60} is an excellent building block for producing stable charge separated state. Compound **21** was deposited on the surface of gold electrode by soaking a solution of **21** in CH_2Cl_2. Upon irradiation, large photocurrent was observed only for the modified electrode. The schematic diagram of ET is shown in Fig. 2.

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Ar = 3,5 - (t-Bu)₂ C₆H₃
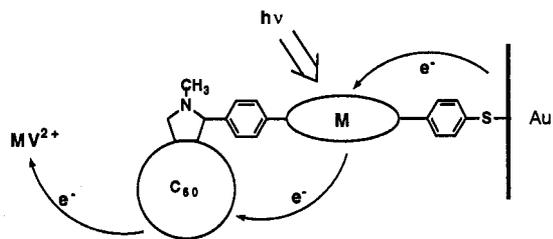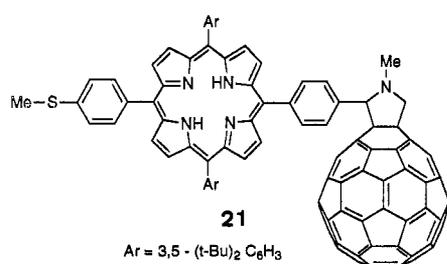
Fig. 2 Schematic diagram of photocurrent in **21**-Au.

Acknowledgments

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