A STRATEGY FOR MIMICKING PHOTOSYNTHESIS

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ABSTRACT   A strategy for mimicking the unit functions of photo-
synthesis was described. Enhancement of photoabsorption cross-
section was achieved by the use of polymer- or surfactant-bonded
electron transfer sensitizers. Energy migration among the sen-
sitizers is the reason for this, which is equivalent to the
action of antenna pigments. Efficient charge separation after
primary electron transfer process was made possible by means of
either utilizing Coulombic effects to assist the dissociation
of an ion radical pair or incorporating an irreversible process
in the electron transferring cycle. For example, photooxida-
tion of leuco crystal violet by excited benzophenone deriva-
tives proceeded with a 100 % efficiency when the sensitizer
contained quaternary ammonium ions. Also the kinetic mechani-
stic study on electron transfer photochemistry of ruthenium(II)
complexes led us to establish an efficient photoreduction
system of methylviologen with a 100 % efficiency in homogeneous
solution. Photofixation of carbon dioxide was demonstrated
either by direct reduction of carbon dioxide to formic acid
mediated by methylviologen cation radical (maximum quantum
yield: 5 %) or by reductive coupling with aromatic hydrocarbons
to aromatic carboxylic acids (maximum quantum yield; 20 %).
Thus, the functional but not machanistic mimicry of photo-
synthesis seems to be a promising approach.

INTRODUCTION

Photosynthesis consists of a series of brilliant photochemical processes.
Mimicry of photosynthesis has been consequently a dream of all photochemists.
The completeness of photosynthesis however is based on the fact that all
processes from the initial photoabsorption to the final product separation and
storage are expediently linked. Furthermore the self reproduction function
is included in the system. Although total mimicry of this combination of
subtle functions is far beyond the ability of human being, each function
provides a good model to be mimicked. This standpoint of mimicking functions
of photosynthesis may not be as ambitious as mimicking the total chemistry
involved in photosynthesis but definitely more practical.
The unit functions of photosynthesis are divided as follows. i) Photoabsorp-
tion by antenna pigments and excitation energy transfer to reaction centre
chlorophyll. ii) Electron transport from donor to acceptor via the excited
reaction centre. iii) Charge separation on both sides of thylakoid membrane.
iv) Oxidation and reduction processes involving enzymatic dark processes even-
tually coupling the oxidation of water to oxygen and proton and the reduction
of carbon dioxide to organic compounds. In the beginning of the special pro-
ject research in 1977(Ref. 1) we set up the following research strategy. i)
Mimicry of the function of antenna pigments by the use of sensitizers in a
form of molecular aggregate so that excitation energy migration is expected
to increase the crosssection of photoabsorption. ii) Development of highly
efficient electron transfer sensitization by coupling a sensttizer(S) with an
electron donor(D) and an electron acceptor(A) which are capable of quenching
the singlet excited state of S. iii) Reductive photofixation of carbon di-
oxide. iv) Survey on self-supporting electron transporting membrane to mimic
thylakoid membrane. We are trying to mimic the functions but not the chemi-
stry of photosynthesis.

MIMICRY OF ANTENNA PIGMENTS

When aromatic hydrocarbons are aggregated, the singlet excited state energy
can migrate according to the Förster mechanism. The molecular aggregate could
be either polymer, micelle, membrane or else on the condition that molecular
association does not bring about deep energy traps preventing excitation
energy migration. Previously we showed the capability of aromatic hydro-
carbons as electron transfer sensitizers(Ref. 2 & 3). For example, when pyrene,
anthracene, or perylene is exclusively photoexcited in a polar solvent in the
presence of leuco crystal violet(LCV) and an electron acceptor such as 1,4-
dicyanobenzene or air, LCV is readily oxidized to crystal violet cation(CV^+)
whereas the sensitizer is recycled. Several molecular aggregated form of the
sensitizer are depicted in Fig. 1. The effect of molecular aggregation is
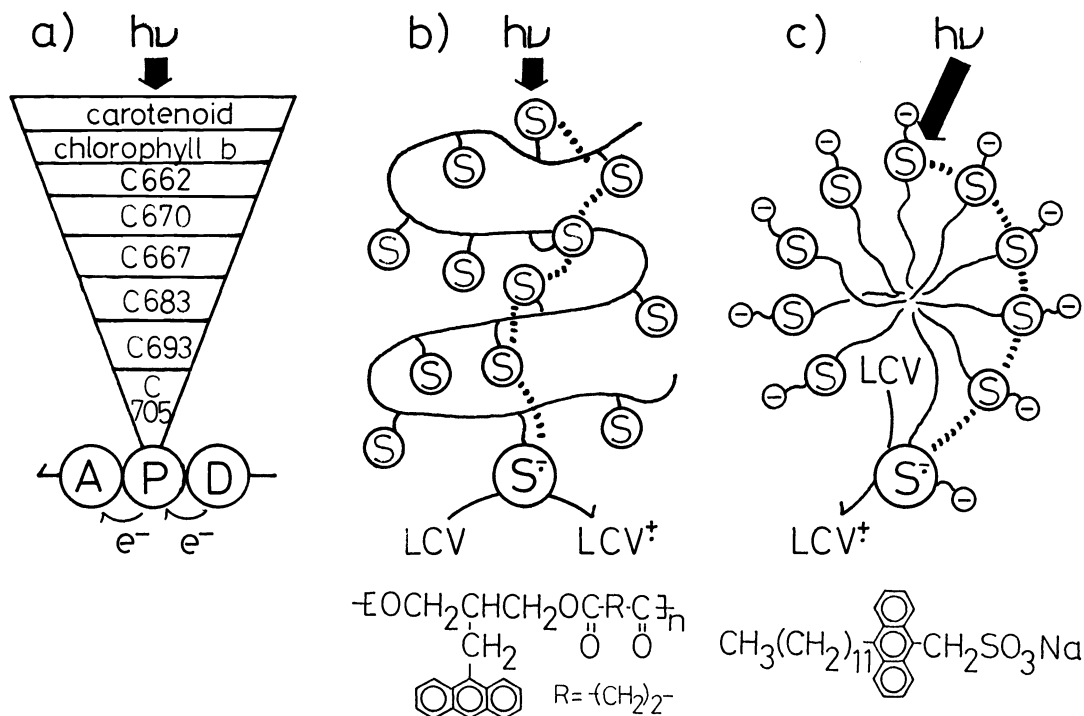

Fig. 1 A schematic representation of molecular aggregated
       sensitizers. a) natural photosynthesis, b) polymer,
       c) micelle.

to increase the photoabsorption crosssection so that the quantum yield($\emptyset$) of
electron transfer sensitization increases. Thus, polyesters containing
anthryl groups as side chain are a better sensitizer than their monomer model
compound(Ref. 4). Efficient excitation energy migration in the polymers was
evidenced by complete depolarization of fluorescence in 2-methyltetrahydro-
furan(MTHF) matrix at 77K. In fluid solution, energy migration and excimer
formation are in competition. For the purpose of taking advantage of energy
migration and avoiding excimer formation, chromophores having a short natural
lifetime of singlet excited state(τ_f) are favoured. Probability of excimer
formation is reduced with decreasing τ_f whereas energy migration probability
according to the Förster mechanism increases with the transition moment namely
with decreasing τ_f provided that intersystem crossing and other side reactions
are neglected(Ref. 5). Consequently, pyrene bonded to polymers exhibits
strong excimer emission and is an inferior sensitizer than their monomer model.
Example of micellar system is shown in Fig. 2. When anthracene containing
surfactant, sodium 9-dodecyl-10-anthrylmethanesulfonate(SDAS), is used as a
sensitizer for photooxidation of LCV, the addition of sodium dodecylsulfate
(SDS) greatly reduces $\emptyset(CV^+)$. The effect is apparently attributed to the loss
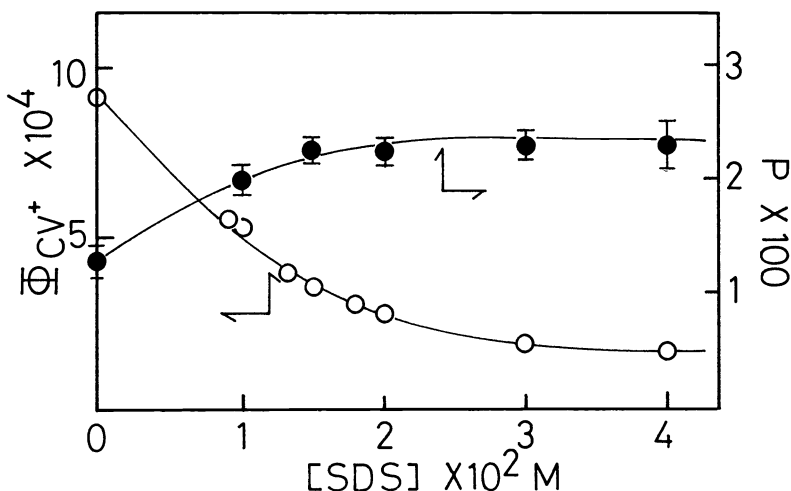of energy migration when anthryl unit is diluted in micelle as manifested by

Fig. 2 Quantum yields of LCV photooxidation ($\bar{\Phi}_{CV^+}$) and the
        degree of fluorescence polarization of SDS (P) as a
        function of SDS concentration.
        [SDS] = 1 x 10^{-4} M, [LCV] = 2 x 10^{-5} M in H_2O.

the increase of fluorescence polarization(P) with increasing the concentration
of SDS. Although the absolute value of P is small owing to rotational diffu-
sion, the effect of added SDS is clear. Furthermore, the viscosity within the
micelle decreases with increasing [SDS] so that the effect of energy migration
on P should have been much more prominent than observed if the effect of
enhanced rotational diffusion in the SDAS-SDS mixed micelle on reducing P were
subtracted. Reduced viscosity in the SDAS-SDS mixed micelle was confirmed by
fluorescence depolarization experiments using perylene as a probe. The P
vs [SDS] plots in Fig. 2 exhibit an opposite trend against the decreasing
tendency of viscosity in support of efficient energy migration in neat SDAS
micelle. The reduced viscosity by the addition of SDS was confirmed by the
finding that the P value of perylene in SDAS micelle([SDAS] = 1 x 10^{-4} M) was
0.134 whereas it decreased to 0.016 by the addition of SDS([SDS] = 2 x 10^{-2} M).
These may be called prototype mimicry of antenna pigments using excitation
energy migration instead of the oriented excitation energy transfer in photo-
synthesis. Arrangement of chromophores possessing slightly different energy
levels from each other in the order of energy level is still beyond our
synthetic ability. For the purpose of chemical conversion of photoenergy,
mimicry of antenna pigments is however not an essential target. Simply in-
creasing sensitizer concentration is enough to increase the efficiency of
photoabsorption. Utilization of absorbed photons depends on the subsequent
reactions. The most imminent subject is therefore to increase the quantum
efficiency of subsequent redox processes.

HOW TO IMPROVE THE EFFICIENCY OF ELECTRON TRANSFER SENSITIZATION ?

Electron transfer sensitization as mimicry of reaction centre chlorophyll
is schematized in Fig. 3. The process ① is the matter of photoabsorption.
The process ② is essentially electron transfer quenching of excited sensitizer
(*S), which is not a synonym of generating reducing and oxidizing species.
Provided that the process ② is exoergonic by more than -5 kcal/mol(Ref. 6),
electron transfer quenching is expected to proceed with a diffusion controlled
rate in fluid media. Consequently, practically quantitative quenching of *S
is attainable if we use high concentration of a strong donor or acceptor. The
real problem lies in the fact that dissociation of the transient ion radical
pair($S^+ \cdots Q^-$ or $S^- \cdots Q^+$) is always in competition with back electron transfer
to the ground state of S(process ③). This situation becomes immediately
clear if one realizes examples of efficient fluorescence quenching by D or A
which results very little or no net chemical change(Ref. 7). Basic principle
of increasing charge separation efficiency is straight forward, namely, re-
duction of the probability of back electron transfer ③ by means of increasing
the efficiency of the subsequent reactions ④ leading to products or of the
reaction with O_2 to reduce the stationary concentration of S^- or S^+. In
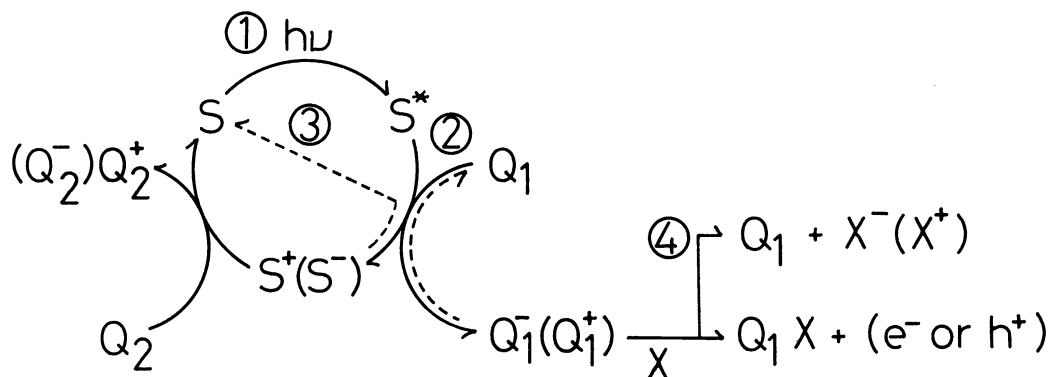
Fig. 3 A generalized sketch of electron transfer sensitization.

practice, use of Coulombic effect, neutral salt effect and/or heterogeneous reaction system, and incorporation of irreversible redox processes in the electron transferring cycle are envisaged. Among these, heterogeneous systems such as micelles, vesicles and semiconductor particles are best studied(Ref. 8). In the following we will show that many simple homogeneous systems can meet the requirement of efficient charge separation.

Role of Coulombic effects

As a way of suppressing back electron transfer we chose the use of Coulombic repulsive effect and synthesized various sensitizers bearing quaternary ammonium salt. The first example was photooxidation of LCV by benzophenone bearing quaternary ammonium ion so that the cation radical of LCV was re-pulsed by the positive charge around the sensitizer whereas the benzophenone anion radical was stabilized by the attached cationic atmosphere as shown in Fig. 4(Ref. 9). Thus, the quantum yield of LCV photooxidation $\emptyset(CV^+)$ was as high as 0.5 when the cation bearing benzophenone was used. With unsubstituted benzophenone itself, $\emptyset(CV^+)$ was less than 0.1. Incidentally, the theoretical maximum of $\emptyset(CV^+)$ is 0.5 since two photons are required to oxidize one molecule of LCV to CV^+.

The concept of using electrostatic repulsion to promote charge separation is not new. Micellar systems have been proposed to meet the purpose(Ref. 10). Our results indicate that the use of molecular aggregate systems is not an essential condition and a simple solution system can be used to bring about complete charge separation.

stabilization of an ion radical pair by counter ion exchange.

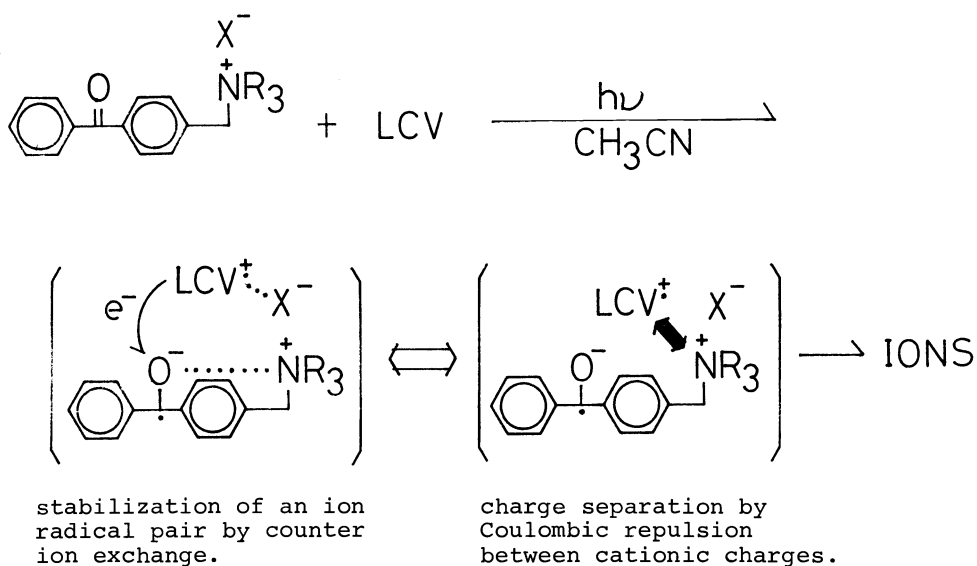charge separation by Coulombic repulsion between cationic charges.

Fig. 4 Schematic representation of effects of ionic atmosphere.

When the reacting substrate is neutral like LCV, the forward electron transfer process is not affected by the charge on a sensitizer. However, when the substrate is a charged species such as methylviologen(MV^{2+}), both forward and reverse processes are under the influence of Coulombic effect. Examples are shown in Table 1(Ref. 11). When the sensitizer was anionic, MV^{2+} was attracted to the sensitizer and the rate of forward electron transfer (fluorescence quenching rate) exceeded the diffusion controlled limit. The Stern-Volmer plots deviated upwards from linearity indicating the overall yield of MV^{2+} reduction to its cation radical ($MV^{\dot{+}}$) was practically zero. On the other hand, the fluorescence quenching rate constant of cationically charged sensitizer by MV^{2+} was smaller than that of anionically charged one whereas $\emptyset(MV^{+})$ was higher. These results manifest that the back electron transfer process is mainly responsible for reducing the efficiency of electron transfer sensitizers provided that the substrates have enough chance to encounter the excited sensitizer.

Table 1   Quenching of the excited state of pyrene by MV^{2+} and MV^{+} formation.

Sensitizer	k_q (M^{-1})	$(\emptyset_{MV^+})_i^*$
1	17.5	0.061**
2	2×10^4	0.0

*[pyrene]=5×10^{-5}M, [EDTA]=1×10^{-3}M, [MV^{2+}]=5×10^{-4}M.
**$\emptyset_{MV^+}$ 0.2 at [MV^{2+}]=[EDTA]=1×10^{-2}M.

1   R=$-CH_2N^+Et_3\cdot Cl^-$

2   R=$-SO_3^-\cdot Na^+$
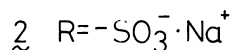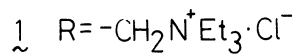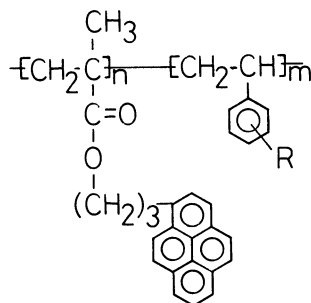
Another series of experiments reducing MV^{2+} by excited phenothiazine derivatives reveal distinctive Coulombic effects(Ref. 12). The formal charge on both sensitizer and quencher is controlled by the introduction of either quaternary ammonium group or sulfate group. Since each combination shows different quenching efficiency, the observed quantum yield was corrected for the quenched fraction of the excited sensitizer. The ordinate in Fig. 5 represents therefore the probability of charge separation after primary electron transfer. The good linear correlation of the probability with $(W_p - W_r)$, where W_p and W_r are the Coulombic work required to bring together the products and reactants to form the ion pair or encounter complex, respectively, indicates the importance of the Coulombic effect. In Fig. 5, all combinations of charged reactants fall on a straight line for a solvent system.

$$w = \frac{z_A z_B}{\epsilon d(1 + \beta d\sqrt{\mu})} \qquad \beta = \left(\frac{8\pi N^2 e^2}{1000\epsilon RT}\right)^{1/2}$$

z_A, and z_B are the ion charges, d is the distance between the ion centers, ϵ and μ are the dielectric constant and the ionic strength of the medium, respectively.
Along the context of Coulombic interaction, photoinduced electron transfer processes should be subjected to neutral salt effect. For example, photooxidation of LCV by neutral benzophenone is subjected to positive neutral salt effect. As the first approximation, the salt effect may be interpreted as a result of reducing Coulombic attraction after electron transfer. However, the behaviour of added salt could not be fully explained within the framework of the Debye-Hückel theory. Photochemically produced ion radicals are in pair and furthermore in non-equilibrium state. We are not sure if the Debye-Hückel theory is applicable to such transient phenomena. In addition, effective dielectric constant between and in the periphery of paired ion radicals is uncertain. The present theory on the assumption of uniform distribution of ions dilute enough to avoid overlapping of the ionic atmospheres is apparently inadequate. We often observed very specific salt effect depending on

the cation and anion of the added salt. We know for sure from quenching of
exciplex emission by neutral salts that dipole or ion paired state is in-
fluenced by neutral salts(Ref. 13). Neutral salt effect is undoubtedly a
useful approach to improve the quantum efficiency of electron transfer
although the details ought to be further investigated.
An important conclusion is the possibility of efficient charge separation
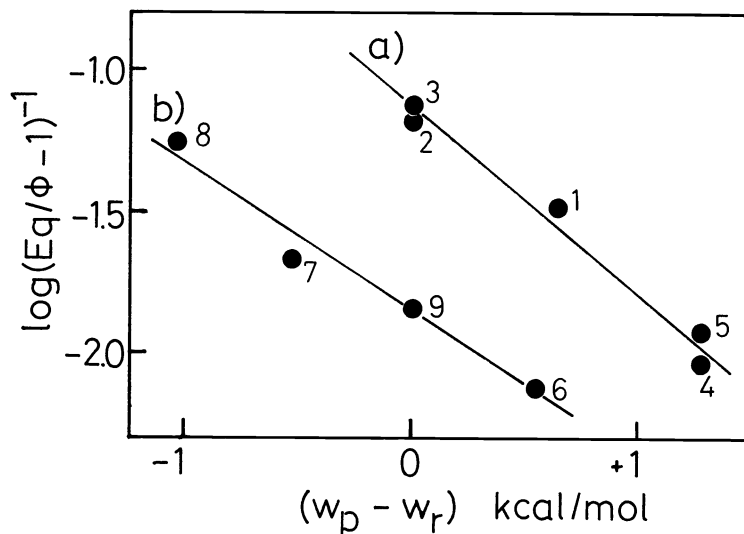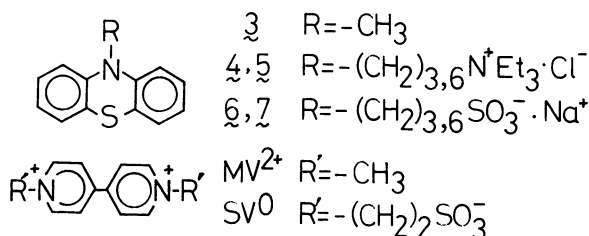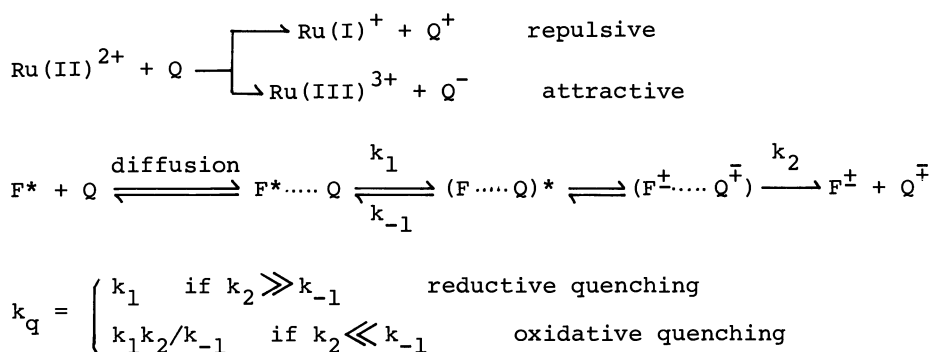in homogeneous solution by proper choice of charged reactants.

Fig. 5 Photoreduction of MV^{2+} or SV^0 by phenothiazine
derivatives bearing ionic atmosphere.
a) in $CH_3CN/H_2O=4/1$, 1 : $3-MV^{2+}$, 2 : $4-MV^{2+}$,
3 : $5-MV^{2+}$, 4 : $6-MV^{2+}$, 5: $7-MV^{2+}$.
b) in $CH_3CN/H_2O=1/1$, 6 : $3-MV^{2+}$, 7 : $3-SV^0$,
8 : $4-SV^0$, 9 : $6-SV^0$
[phenothiazine]$=5\times10^{-4}$M, [MV^{2+} or SV^0]$=5\times10^{-3}$M.
E_q=quenching efficiency.

Highly efficient photoreduction of methylviologen by tris(bis-diazadiimine)-
ruthenium(II) complex.
We have learned the importance of charge balance before and after electron
transfer. Ruthenium(II) complexes represented by tris(2,2'-bipyridine)
ruthenium(II) ($Ru(bpy)_3^{2+}$) are subjected to both oxidation and reductive
quenching in the excited state. Quenching experiments of *$Ru(bpy)_3^{2+}$ by
various organic donors and acceptors indicated that oxidative quenching
involved a back electron transfer process exhibiting a negative temperature
dependence whereas reductive quenching was a normal activation enthalpy
controlled process as shown below (Ref. 15).

$$Ru(II)^{2+} + Q \underset{\searrow Ru(III)^{3+} + Q^- \quad \text{attractive}}{\overset{\nearrow Ru(I)^+ + Q^+ \quad \text{repulsive}}{\longrightarrow}}$$

$$F^* + Q \underset{\text{diffusion}}{\rightleftharpoons} F^*\cdots Q \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (F\cdots Q)^* \rightleftharpoons (F^{\pm}\cdots Q^{\mp}) \overset{k_2}{\longrightarrow} F^{\pm} + Q^{\mp}$$

$$k_q = \begin{cases} k_1 & \text{if } k_2 \gg k_{-1} \quad \text{reductive quenching} \\ k_1 k_2/k_{-1} & \text{if } k_2 \ll k_{-1} \quad \text{oxidative quenching} \end{cases}$$

If the sequence could claim generality, the extensively studied oxidative quenching of $*Ru(bpy)_3^{2+}$ by MV^{2+} leading to the generation of MV^+ would not be an ideal system. Since the choice of oxidative or reductive quenching of Ru(II) complexes is relevant to the relative magnitude of oxidation and reduction potentials of the fluorescer and the quenchers, modification of ligand structure is expected to change the reaction path when the quenchers are fixed. Although several ruthenium complexes of bis-diazadiimine ligands were prepared and their spectroscopic and electrochemical properties were studied, these new complexes have been scarcely examined for the ability of photocatalyst except for tris(2,2'-bipyrazine)ruthenium(II) complex which photoreduces MV2+ in a 77 % yield in the presence of triethanolamine (TEOA) (Ref. 16).

We prepared Ru(II) complexes with diazadiimine ligands (RuL_3^{2+}, the structures of L are shown in Table 2)(Ref. 17). Their absorption and emission spectra are nearly identical whereas their oxidation and reduction potentials vary with L (Ref. 18).

Table 2 shows the quantum yields of MV^{2+} photoreduction in the system of RuL_3^{2+} (6×10^{-5}) – MV^{2+} (0.02 M) – TEOA (0.6 M) in aqueous solution deaerated by several freeze-pump-thaw cycles, $\emptyset$(vac), or Ar-gas purging, $\emptyset(N_2)$ and the quenching rate constants (k_q) of the excited state of RuL_3 ($*RuL_3^{2+}$) by MV^{2+} and TEOA in 0.5 M of aqueous KCl solution. For comparison, $Ru(bpy)_3^{2+}$ was also reexamined under same conditions. The photosensitizer efficiency of $Ru(bpy)_3^{2+}$ was confirmed to be in good agreement with the reported values (0.19 (Ref. 16) – 0.24 (Ref. 20)). The most important results are as follows.

Table 2 Quantum yields of MV^{2+} photoreduction and rate constants for the quenching of $*RuL_3$ emission by MV^{2+} and TEOA.
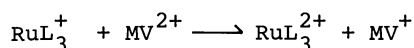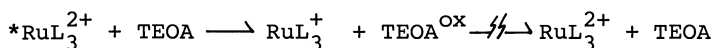
RuL_3	$\emptyset_{vac}$	$\emptyset_{N2}$	k_q (M^{-1}s^{-1})		$E_{1/2}$ (V vs. SCE)[a]		(μs)[f]
			MV^{2+}	TEOA	$Ru^{3+/2+}$	$Ru^{2+/+}$	(in water, at 298 K)
8	0.98	0.75	8.6×10^6	2.5×10^8	$+1.86$[d]	-0.80[d]	1.02
9	0.85	0.44	b)	3.6×10^7	——	-1.40[e]	0.06
10	0.27	0.16	7.6×10^7	1.3×10^6	$+1.58$[f]	-1.00[f]	0.70
11	0.03	——	c)	c)	$+1.48$[f]	-0.78[f]	c)
12	0.02	——	3.9×10^8	b)	$+1.38$[f]	-1.18[f]	0.21
13	0.22	0.19	2.1×10^9	b)	$+1.27$[f]	-1.34[f]	0.64

a) In CH$_3$CN. b) No emission quenching was observed in the concentration region of [MV^{2+}] < 0.02M or [TEOA] < 0.6M. c) Not determined owing to the low emission quantum yield and the short excited lifetime. See also ref [18]. d) Ref. [16]. e) Ref. [19]. f) Ref. [18].
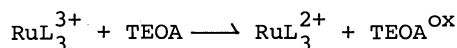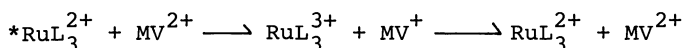

8   9   10   11   12   13
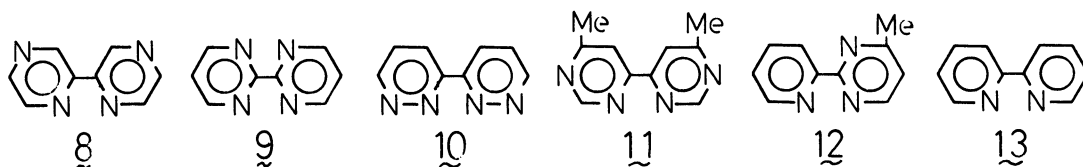
i) ϕ(vac) are 0.98 for $\underset{\sim}{8}$ and 0.85 for $\underset{\sim}{9}$, which are 4 times as large as the value for Ru(bpy)$_3^{2+}$. For $\underset{\sim}{8}$, ϕ(vac) is larger than the reported value (0.77) determined under N_2 atmosphere (Ref. 16). We observed strong oxygen effect on MV^{2+} photoreduction yield by $\underset{\sim}{8}$ and $\underset{\sim}{9}$. The $\phi(N_2)$ values are 0.75 for $\underset{\sim}{8}$ and 0.44 for $\underset{\sim}{9}$, and the former is in excellent agreement with the result by Crutchley and Lever (Ref. 16). ii) $\underset{\sim}{10}$ is less effective for MV^{2+} photo-reduction than $\underset{\sim}{8}$ and $\underset{\sim}{9}$, but is more efficient then Ru(bpy)$_3^{2+}$. iii) The other RuL$_3^{2+}$, $\underset{\sim}{11}$ and $\underset{\sim}{12}$, are almost inefficient for MV^{2+} photoreduction. iv) The absorption spectra of RuL$_3^{2+}$ before and after photoreaction are identical, in-dicating good turn-over of RuL$_3^{2+}$ as a photocatalyst.

These results are explainable by the following observations. The quenching rate contants of the excited state of $\underset{\sim}{8}$ by MV^{2+} and TEOA are 8.6 x 10^6 M^{-1} s^{-1} and 2.5 x 10^8 M^{-1} s^{-1}, respectively. Consequently, the photoexcited $\underset{\sim}{8}$ is mainly reduced by TEOA to Ru(I) but scarcely oxidized by MV^{2+}. The excited state of $\underset{\sim}{9}$ is also reduced by TEOA with the rate constant of 3.6 x 10^7 M^{-1} s^{-1} but not oxidized by MV^{2+} at all. Since the oxidation of TEOA is an irreversi-ble process, back electron transfer from Ru(I) to oxidized TEOA (TEOA^{OX}) is unlikely and consequently, the fate of Ru(I) is to reduce MV^{2+} to MV^+ to attain the high quantum yield (Scheme I). On the other hand, the excited state of Ru(bpy)$_3^{2+}$ is oxidized by MV^{2+} to Ru(III) as shown in Scheme II. Back electron transfer from MV^+ to Ru(III) is inevitable so that the overall quantum yield of MV^{2+} photoreduction is lower than that by $\underset{\sim}{8}$ or $\underset{\sim}{9}$.

Scheme I.

$$*RuL_3^{2+} + TEOA \longrightarrow RuL_3^+ + TEOA^{OX} \xrightarrow{\;/\!\!/\;} RuL_3^{2+} + TEOA$$

$$RuL_3^+ + MV^{2+} \longrightarrow RuL_3^{2+} + MV^+$$

Scheme II.

$$*RuL_3^{2+} + MV^{2+} \longrightarrow RuL_3^{3+} + MV^+ \longrightarrow RuL_3^{2+} + MV^{2+}$$

$$RuL_3^{3+} + TEOA \longrightarrow RuL_3^{2+} + TEOA^{OX}$$

Strong oxygen effect as manifested by the difference between ϕ(vac) and $\phi(N_2)$ for $\underset{\sim}{8}$ and $\underset{\sim}{9}$ (and also $\underset{\sim}{10}$) is suggested as due to oxidation of Ru(I) by oxygen. This is supported by the fact that oxidation of Ru(I) is highly exothermic process with a free energy change of -5.3 kcal/mol and -19.1 kcal/mol for $\underset{\sim}{8}$ and $\underset{\sim}{9}$, respectively. Furthermore, the electron transfer from Ru(I) to oxygen has been directly demonstrated by a laser photolysis study of the Ru(bpy)$_3^{2+}$ - N,N-dimethylaniline - O_2 system by Meyer et al (Ref. 21).

The ϕ(vac) value is larger for $\underset{\sim}{10}$ than that for Ru(bpy)$_3^{2+}$, whereas the quench-ing rate constant by MV^{2+} for $\underset{\sim}{10}$ is smaller than that for Ru(bpy)$_3^{2+}$. The larger ϕ(vac)/$\phi(N_2)$ value and the samll but finite quenching rate constant by TEOA for $\underset{\sim}{10}$ suggest that MV^+ is produced partly by the reductive quenching mechanism (Scheme I). On the other hand, although $\underset{\sim}{11}$ and $\underset{\sim}{12}$ have strong re-ducing and oxidizing powers (Ref. 18) and the reductive and oxidative quench-ing from the exicted state of $\underset{\sim}{11}$ or $\underset{\sim}{12}$ by TEOA and MV^{2+}, respectively, are both thermodynamically favorable, these complexes can scarcely photoreduce MV^{2+}. The short excited lifetimes of $\underset{\sim}{11}$ and $\underset{\sim}{12}$ may be responsible for such low yield.

In conclusion, $\underset{\sim}{8}$, $\underset{\sim}{9}$, and $\underset{\sim}{10}$ are superior photocatalysts to Ru(bpy)$_3$ for MV^{2+} photoreduction whereas $\underset{\sim}{11}$ and $\underset{\sim}{12}$ are almost inactive, indicating that the photoredox ability of RuL$_3$ is highly sensitive to the ligand property. Now, photoreduction of MV^{2+} with a 100 % efficiency is possible in homogeneous solution.

PHOTOCHEMISTRY OF CARBON DIOXIDE

The marrow of photosynthesis is reductive fixation of carbon dioxide. In the previous sections we demonstrated quantitative utilization of absorbed photons to generate reducing or oxidizing species. If the reducing power of an electron carrier can be coupled with reduction of carbon dioxide, it should be justifiably called a prototype of artifical photosynthesis.

Reductive fixation of carbon dioxide
A few years ago we succeeded to reduce carbon dioxide to formic acid and

oxalic acid by means of electron transfer sensitization. When pyrene or perylene(S), 1,4-dicyanobenzone(A), and N,N-dimethylaniline(D) were irradiated in aqueous acetonitrile solution in the presence of carbon dioxide, very poor yields($\emptyset < 10^{-4}$) of the acids were obtained (Ref. 22). Recently we found a much better reaction system using MV^{2+} as an electron carrier to reduce carbon dioxide to formic acid(Ref. 23).

The well-known photochemical formation and accumulation of MV^+ when the $Ru(bpy)_3^{2+}$ - MV^{2+} - TEOA system is irradiated under anaerobic conditions is suppressed under CO_2 atmosphere. This quenching action is expected to involve reduction of CO_2.

Formic acid was analysed by isotachophoresis and identified by comparing the potential unit (PU) value with authentic sample. The PU value is defined by $(P_{si} - P_L)/(P_T - P_L)$ where P_{si}, P_L and P_T are the potential gradient values of formic acid, leading electrolyte and terminating electrolyte, respectively. As shown in Fig. 6, we confiemed that formic acid and two unknown carboxylic acids were produced. The yield of formic acid was 4.5×10^{-3} M after 4 h irradiation and the quantum yield of CO_2 reduction to formic acid was calculated to be 0.01. We confirmed by the following observations that CO_2 was photochemically reduced to formic acid. i) Dark reaciton of the system under CO_2 atmosphere gave no carboxylic acid. ii) photoreaction of the $Ru(bpy)_3^{2+}$ - MV^{2+} - CO_2 system did not bring about the formation of any carboxylic acids (Fig. 6c), indicating that formic acid was not the decomposition product of MV^{2+} and that a sacrificial electron donor such as TEOA was necessary for the photoreduction of CO_2 to formic acid. iii) After photo-irradiation of the system under CO_2 atmosphere for 4 h, MV^{2+} was recovered in
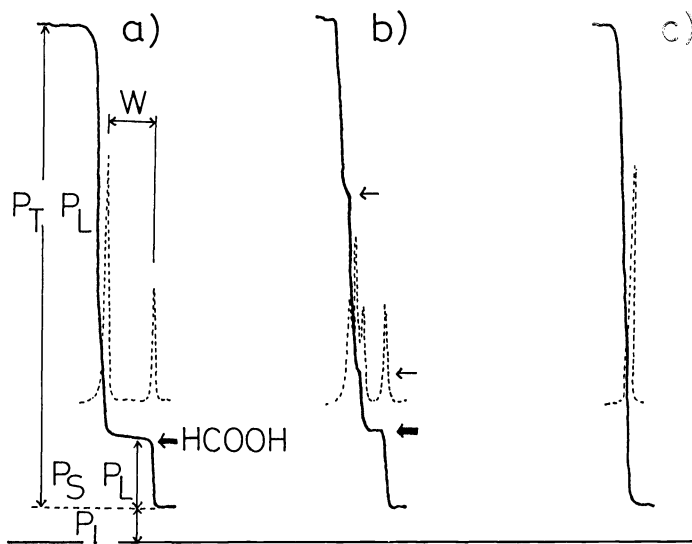

Fig. 6 Isotachopherograms of a) authentic formic acid,
b) the reaciton mixture ($Ru(bpy)_3$ - MV^{2+} - TEOA - CO_2,
irradiated for 4 h), and c) the reaction mixture
($Ru(bpy)_3$ - MV^{2+} - CO_2, irradiated for 4 h).

92 % yield, corresponding to the decomposition of 1.6×10^{-3} M of MV^{2+}, which is about one third of formic acid produced. Consequently, MV^{2+} was proved to act as a restorable electron relay for the CO_2 reduction. iv) Although TEOA is known to be oxidatively decomposed by electron transfer to $Ru(bpy)_3^{3+}$, our controlled experimants showed that formic acid was not a decomposition product of TEOA (see Note a).

Note a. Photoreactions of the $Ru(bpy)_3^{2+}$ - TEOA - CO_2, $Ru(bpy)_3^{2+}$ - TEOA - $K_2S_2O_8$ - N_2, 8 - TEOA - CO_2, and $Ru(bpy)_3^{2+}$ - TEOA - MV^{2+} - N_2 or Ar systems did not lead to the formation of formic acid. In the last system, intensive coloration occured due to accumulation of MV^+ and the photoirradiation conditions could not be identical with other systems.

From these results, we conclude that formic acid is produced by reduction of CO_2 by MV^+. However, direct electron transfer from MV^+ to CO_2 is energetically impossible, The redox potential of CO_2 is about or more negative than -2.0 V (vs. SCE) whereas that of MV^{2+} is -0.44 V (vs. NHE)(Ref. 24). Providing that the mechanism involving CO_2 prevails similar to the previous pyrene(or perylene) - N,N-dimethylaniline -1,4-dicyanobenzene system(Ref. 22), it seem to be a contradiction that the present highly endoergic reaction proceeds with an efficiency more than 100 times better than the previous nearly thermoneutral system. We must seek for another possible reaction pathway. Reduction of CO_2 occurs at a lower potential when protons participate as shown below. Coupling with oxidation of MV^+ to MV^{2+}, the reaction is still

$$CO_2 + 2H^+ + 2e^- \longrightarrow HCOOH$$
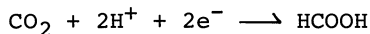
$$E^{0'} = -0.61 \text{ V (vs. NHE at PH 7)(Ref. 26)}$$

slightly endoergic. However, bubbling of CO_2 will shift the pH towards acidic side so that the E^0 value may become more positive. If the participation of proton is considered, the reducing power of MV^+ is nearly sufficient and the magnitude of $\emptyset$(HCOOH) will be controlled kinetically. Simultaneous two-electron reduction reacting with two MV^+ species in a homogeneous system would not be efficient. This is probably a partial reason for rather poor quantum yield of CO_2 reduciton to formic acid ($\emptyset$(HCOOH) = 0.01) while the formation of MV^+ is an efficient process ($\emptyset_{MV^+}$ = 0.22).
Now we have better systems for reduction of MV^{2+}. Using 8 instead of Ru(bpy)$_3^{2+}$ the maximum quantum yield of formic acid formation reahed 5 %. The time-conversion relation in Fig. 7 is linear for at least initial several
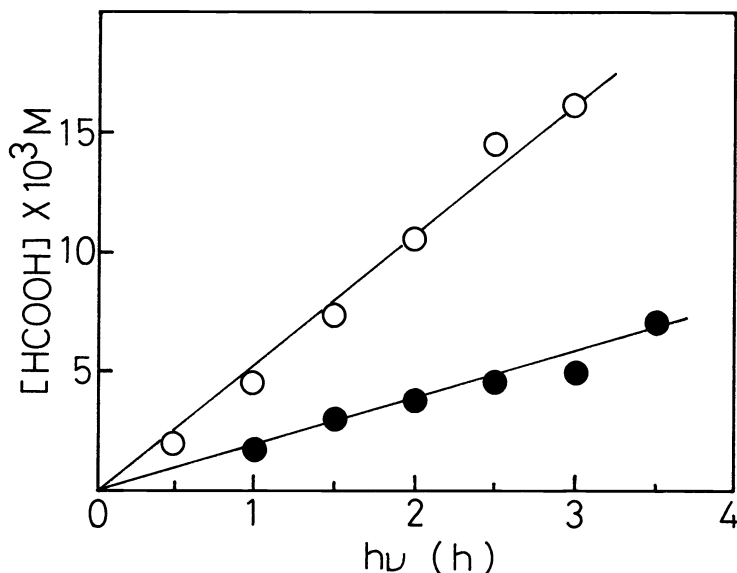

Fig. 7 Time - conversion curves of formic acid production.
8 ($\bigcirc$), 13 ($\bullet$).
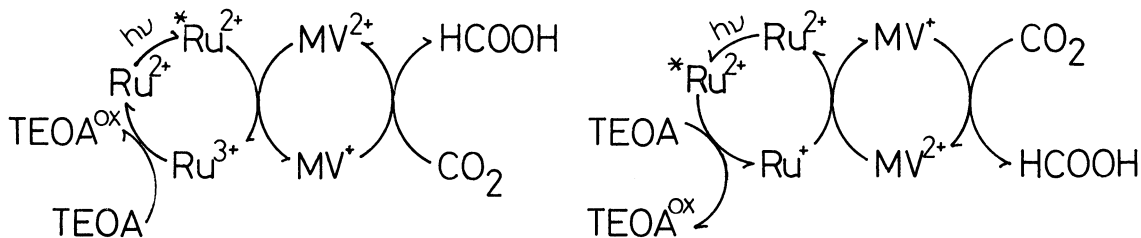[RuL$_3$]=6x10^{-5}M, [MV^{2+}]=0.02M, [TEOA]=0.6M, in aqueous solution. CO_2 gas purging : 50 ml/min.

Fig. 8 Photoreduction of carbon dioxide to formic acid mediated by a methylviologen electron relay.

hours indicating good turn-over of the sensitizers. The reaction profiles are schematized in Fig. 8.

Reductive C-C coupling with carbon dioxide

In 1975 one of us showed for the first time that reductive photocarboxylation of aromatic hydrocarbon. The reaction proceeded with a fair yield in the presence of tertiary amine and carbon dioxide in dipolar aprotic solvents (Ref. 27). Although the reaction is not directly relevant to photosynthesis, reductive C-C coupling with carbon dioxide and reduction of carbon dioxide to formic acid are very similar from mechanistic viewpoint. The only difference between the two is the fact that the reducing species is stabilized by C-C bond formation with carbon dioxide or by giving one electron to carbon dioxide. Indeed, same anion radical of aromatic hydrocarbon may conduct both reactions. The factors deciding the reaction path are not yet understood. However, for the reductive C-C coupling with carbon dioxide is favoured in solvents of large donor number (DN) in the absence of water (Ref. 27,28) whereas the presence of water seems essential for formic acid formation (Ref. 22,23). Among aromatic hydrocarbons so far examined phenanthrene is most reactive. The reaction mechanism is suggested as follows (Ref. 28). The intermediate anion radical should couple with carbon dioxide before back electron transfer to amine cation radical or protonation. This is the reason for the choice of dipolar aprotic solvents. Also the use of secondary and primary amines as reductants should be avoided since they are proton donors in particular after loosing one electron (Ref. 29). On the other hand the presence of hydrogen donors is advantageous. Coupling of anion radical with carbon dioxide yields unstable carboxylate which might decompose unless it is stabilized by hydrogenation to complete the reductive carboxylation. Addition of hydrogen donors such as dihydrophenanthrene, dihydroanthracene, cumene, and others increases the quantum yield as shown in Table 3. High carbon dioxide pressure is also effective to increase the yield. Under optimized condition, the quantum yield

Table 3   Photocarboxylation of phenanthrene using carbon
          dioxide as a carboxylating agent.

Run	Φ COOH	Φ-phen	selectivity %
N,N-dimethylaniline	0.087	0.11	82
N-methylaniline	0.042	0.14	29
aniline	0	0.16	0
DMPT*	0.17	0.20	86
DMPT* +cumene(0.5M)	0.20	0.25	80
N,N-dimethylaniline** 5 atom	$(6.56 \times 10^{-3} M)$	$(7.29 \times 10^{-3} M)$	90
N,N-dimethylaniline** 1 atom	$(3.41 \times 10^{-3} M)$	$(4.87 \times 10^{-3} M)$	70

*DMPT = N,N-dimethyl-p-toluidine
**The reaction was carried out in a pressurized bottle and
   the quantum yield was not determined.
Reaction conditions : [phenanthrene] = $1 \times 10^{-2} M$,
[amine] = 0.5M in DMSO.

is 0.20 with the selectivity of 9,10-dihydrophenanthrene-9-carboxylic acid of over 80 %. This is astonishingly high value considering inertness of carbon dioxide. Use of carbon dioxide as a carbon source in synthetic photochemistry will be another legitimate target originating from mimicry of photosynthesis.

CONCLUSION AND FUTURE PROBLEMS

Partial mimicry of the individual functions of photosynthesis is now possible. Comparing the efficiency of each process, the efficiency of artificial reaction system is even better than photosynthesis. For example, the efficiency of carbon dioxide fixation using methylviologen as an electron relay is better than that of photosynthesis in Nature. Magnificence of photosynthesis is the harmony and completeness as a total system. To approach this goal, the next step is to integrate the partial success of mimicking the unit functions and to establish a photochemical production system including product separation process. Heterogeneous reaction systems separating the oxidizing and reducing sites will then be essential. A promising candidate is electron transporting

membrane with sufficient mechanical strength. This is the fourth target
proposed in the introduction which has not been achieved. We commenced photo-
induced electron transfer reactions on polymer membrane and the factors decid-
ing the reaction efficiency are being investigated (Ref. 30).

REFERENCES

1. S. Tazuke, N. Kitamura, H. Tomono, Y. Kawasaki, and T. Inoue,
    Reports on Chemical Conversion and Storage of Solar Energy (to the
    Ministry of Education, Science and Culture, Japan)., 98-105 (1980).
2. S. Tazuke, and N. Kitamura, J. Chem. Soc., Chem. Commun. 515-516 (1977).
3. N. Kitamura and S. Tazuke, Bull. Chem. Soc. Jpn. 53, 2594-2597 (1980);
    53, 2598-2604 (1980).
4. S. Tazuke, H. Tomono, N. Kitamura, K. Sato, and N. Hayashi, Chem. Lett.
    85-88 (1979).
5. N. Mataga and T. Kubota, Molecular Interactions and Electronic Spectra.
    Marcel Dekker, New York (1970).
6. D. Rehm and A. Weller, Israel J. Chem. 8, 259-271 (1970).
7. For example, H. Schomburg, H. Staerk, and A. Weller, Chem. Phys. Lett.
    22, 1-4 (1973).
8. N. J. Turro, M. Grätzel, and A. Braun, Angew. Chem. Int. Ed. Engl. 19,
    675-696 (1980); M. Grätzel, Acc. Chem. Res. 14, 376-384 (1981); D. G.
    Whitten, Angew. Chem. Int. Ed. Engl. 18, 440-450 (1979).
9. S. Tazuke, Y. Kawasaki, N. Kitamura, and T. Inoue, Chem. Lett. 251-254
    (1980) and unpublishied results.
10. Y. Waka, K. Hamamoto, and N. Mataga, Chem. Phys. Lett. 53, 242-246
    (1978); B. Katusin-Rozem, M. Wong, and J. K. Thomas, J. Am. Chem. Soc.
    100, 1679-1686 (1978); S. S. Atik and J. K. Thomas, J. Am. Chem. Soc.
    103, 3550-3555 (1981).
11. S. Tazuke and N. Kitamura, Reports of Asahi Glass Foundation for
    Industrial Technology. 41, 133-142 (1982).
12. Y. Kawanishi, N. Kitamura, and S. Tazuke, manuscript in preparation.
13. N. Kitamura, S. Imabayashi, and S. Tazuke, Chem. Lett. 455-458 (1983).
14. N. Sutin and C. Creutz, Pure Appl. Chem. 52, 2717-2738 (1980).
15. N. Kitamura, S. Okano, and S. Tazuke, Chem. Phys. Lett. 90, 13-16 (1982).
16. R. J. Crutchley and A. B. P. Lever, J. Am. Chem. Soc. 102, 7128-7129,
    (1980).
17. N. Kitamura, Y. Kawanishi, and S. Tazuke, Chem. Lett. 1185-1188 (1983).
18. N. Kitamura, Y. Kawanishi, and S. Tazuke, Chem. Phys. Lett. 97, 103-106
    (1983).
19. M. Hunziker, and A. Ludi, J. Am. Chem. Soc. 99, 7370-7371 (1977).
20. C. Creutz, A. D. Keller, N. Sutin, and A. P. Zipp, J. Am. Chem. Soc.
    104, 3618-3627(1982).
21. C. P. Anderson, D. J. Salmon, T. J. Meyer, and R. C. Young, J. Am. Chem.
    Soc. 99, 1980-1982 (1977).
22. S. Tazuke and N. Kitamura, Nature. 275, 301-302 (1978).
23. N. Kitamura and S. Tazuke, Chem. Lett. 1109-1112 (1983).
24. N. Rysselberghe and G. J. Alkire, J. Am. Chem. Soc. 68, 2050-2051 (1946).
25. E. Amouyal and B. Zidler, Israel J. Chem. 22, 117-124 (1982).
26. J. -M. Lehn and R. Ziessel, Proc. Natl. Acad. Sci., USA. 79, 701-704 (1982).
27. S. Tazuke and H. Ozawa, J. Chem. Soc., Chem. Commun. 237-238 (1975).
28. S. Kazama, N. Kitamura, H. Ozawa, and S. Tazuke, unpublished results.
29. T. Okada, T. Mori, and N. Mataga, Bull Chem. Soc. Jpn. 49, 3398-3402 (1976)
30. S. Tazuke and R. Takasaki, J. Polym. Sci., Polym. Chem. Ed. 21, 1517-1527;
    1929-1534 (1983).