A STRATEGY FOR MIMICKING PHOTOSYNTHESIS

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ABSTRACT A strategy for mimicking the unit functions of photosynthesis was described. Enhancement of photoabsorption cross-section was achieved by the use of polymer- or surfactant-bonded electron transfer sensitizers. Energy migration among the sensitizers 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, photooxidation of leuco crystal violet by excited benzophenone derivatives proceeded with a 100% efficiency when the sensitizer contained quaternary ammonium ions. Also the kinetic mechanistic 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 mechanistic mimicry of photosynthesis 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) Photoabsorption 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 eventually coupling the oxidation of water to oxygen and proton and the reduction of carbon dioxide to organic compounds. In the beginning of the special project 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 sensitizer(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 dioxide. iv) Survey on self-supporting electron transporting membrane to mimic thylakoid membrane. We are trying to mimic the functions but not the chemistry 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 hydrocarbons 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 to increase the photoabsorption crosssection so that the quantum yield (Ø) 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-methyltetrahydrofuran (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 (τₑ) are favoured. Probability of excimer formation is reduced with decreasing τₑ whereas energy migration probability according to the Förster mechanism increases with the transition moment namely with decreasing τₑ 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 Ø(CV⁺). The effect is apparently attributed to the loss of energy migration when anthryl unit is diluted in micelle as manifested by

![Diagram](image_url)
the increase of fluorescence polarization (P) with increasing the concentration of SDS. Although the absolute value of P is small owing to rotational diffusion, 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 SDS-SDS mixed micelle on reducing P were subtracted. Reduced viscosity in the SDS-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 SDS micelle. The reduced viscosity by the addition of SDS was confirmed by the finding that the P value of perylene in SDS micelle ([SDS] = 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 photosynthesis. 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 increasing 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 exoergic 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^{••}−Q^{−} or S^{−•}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 straightforward, namely, reduction 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
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 repulsed 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 $\phi(CV^+)$ was as high as 0.5 when the cation bearing benzophenone was used. With unsubstituted benzophenone itself, $\phi(CV^+)$ was less than 0.1. Incidentally, the theoretical maximum of $\phi(CV^+)$ 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.

[Diagram]

Fig. 3 A generalized sketch of electron transfer sensitization.

<table>
<thead>
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<th><img src="image" alt="Diagram" /></th>
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<tr>
<td>Fig. 3 A generalized sketch of electron transfer sensitization.</td>
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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$^{+}$) was practically zero. On the other hand, the fluorescence quenching rate constant of cationically charged sensitizer by MV$^{+}$ was smaller than that of anionically charged one whereas $\Phi$(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.

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 $(W - W_r)$, where $W$ 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.

$$w = \frac{Z_A Z_B}{\epsilon d (1 + \beta d \mu)} \left(\frac{9\pi N_e^2}{1000\epsilon RT}\right)^{1/2}$$

$Z_A$ and $Z_B$ are the ion charges, $d$ is the distance between the ion centers, $\epsilon$ and $\mu$ 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 influenced 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$_3$CN/H$_2$O=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$_3$CN/H$_2$O=1/1, 6 : 3-MV$^{2+}$, 7 : 3-SV$^{0}$, 8 : 4-SV$^{0}$, 9 : 6-SV$^{0}$

[phenothiazine]=5x10$^{-4}$M, [MV$^{2+}$ or SV$^{0}$]=5x10$^{-3}$M. $E_q$ quenching efficiency.

$$
\begin{align*}
R &
= \text{CH}_3 \\
R &
= -(\text{CH}_2)_3\text{N}^+\text{Et}_3^-\text{Cl}^-
\end{align*}
$$

$$
\begin{align*}
R^- &
= \text{CH}_3 \\
R^- &
= -(\text{CH}_2)_3\text{N}^+\text{SO}_3^-\text{Na}^+
\end{align*}
$$

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)($\text{Ru(bpy)}_3^{2+}$) are subjected to both oxidation and reductive quenching in the excited state. Quenching experiments of $\text{Ru(bpy)}_3^{2+}$ 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).
A strategy for mimicking photosynthesis

\[
\text{Ru(II)}^{2+} + Q \xrightarrow{\text{diffusion}} \text{Ru(I)}^{3+} + Q^+ \quad \text{repulsive}
\]

\[
\text{Ru(II)}^{2+} + Q \xrightarrow{\text{diffusion}} \text{Ru(III)}^{3+} + Q^- \quad \text{attractive}
\]

\[
F^* + Q \xrightarrow{k_1} (F^* + Q)^+ \xrightarrow{k_2} F^+ + Q^-
\]

\[k_q = \begin{cases} 
\frac{k_1}{k}\ if\ k_2 \gg k_1 & \text{reductive quenching} \\
\frac{k_1k_2}{k_1} & \text{oxidative quenching}
\end{cases}\]

If the sequence could claim generality, the extensively studied oxidative quenching of \(*\text{Ru(bpy)}_3^{2+}\) by \(\text{MV}^{2+}\) leading to the generation of \(\text{MV}^+\) 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 fluorogen 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-diazadiine 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 \(\text{MV}^{2+}\) in a 77% yield in the presence of triethanolamine (TEOA) (Ref. 16).

We prepared Ru(II) complexes with diazadiine ligands (RuL3+, 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 \(\text{MV}^{2+}\) photoreduction in the system of RuL3+ (6 \times 10^{-5}) - \(\text{MV}^{2+}\) (0.02 M) - TEOA (0.6 M) in aqueous solution deaerated by several freeze-pump-thaw cycles, \(\phi\text{(vac)}\), or Ar-gas purging, \(\phi\text{(N}_2\text{)}\) and the quenching rate constants (\(k_q\)) of the excited state of RuL3 (*RuL3^+) by \(\text{MV}^{2+}\) 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.

<table>
<thead>
<tr>
<th>RuL_3</th>
<th>(\phi_\text{vac})</th>
<th>(\phi_\text{N}_2)</th>
<th>(k_q) (M^{-1}s^{-1})</th>
<th>(E_{1/2}) (V vs. SCE)</th>
<th>(\mu s)</th>
<th>(in water, at 298 K)</th>
</tr>
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<tbody>
<tr>
<td>8</td>
<td>0.98</td>
<td>0.75</td>
<td>8.6 \times 10^6</td>
<td>2.5 \times 10^8</td>
<td>+1.86</td>
<td>-0.80</td>
</tr>
<tr>
<td>9</td>
<td>0.85</td>
<td>0.44</td>
<td>3.6 \times 10^6</td>
<td>1.3 \times 10^8</td>
<td>+1.58</td>
<td>-1.00</td>
</tr>
<tr>
<td>10</td>
<td>0.27</td>
<td>0.16</td>
<td>3.9 \times 10^6</td>
<td>2.1 \times 10^8</td>
<td>+1.27</td>
<td>-1.34</td>
</tr>
<tr>
<td>11</td>
<td>0.03</td>
<td>0.03</td>
<td>3.6 \times 10^6</td>
<td>1.3 \times 10^8</td>
<td>+1.48</td>
<td>-0.78</td>
</tr>
<tr>
<td>12</td>
<td>0.02</td>
<td>0.19</td>
<td>2.1 \times 10^6</td>
<td>1.3 \times 10^8</td>
<td>+1.38</td>
<td>-1.18</td>
</tr>
<tr>
<td>13</td>
<td>0.22</td>
<td>0.19</td>
<td>3.6 \times 10^6</td>
<td>1.3 \times 10^8</td>
<td>+1.27</td>
<td>-1.34</td>
</tr>
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\[a)\text{ In CH}_3CN. \ b) No emission quenching was observed in the concentration region of \([\text{MV}^{2+}] < 0.02M\) or \([\text{TEOA}] < 0.6M\). 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].

![Image of structures](image_url)
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i) $\Phi(\text{vac})$ are 0.98 for 8 and 0.85 for 9, which are 4 times as large as the value for Ru(bpy)$_2^{2+}$. For 8, $\Phi(\text{vac})$ is larger than the reported value (0.77) determined under N$_2$ atmosphere (Ref. 16). We observed strong oxygen effect on MV$_2^{2+}$ photoreduction yield by 8 and 9. The $\Phi(\text{N}_2)$ values are 0.75 for 8 and 0.44 for 9, and the former is in excellent agreement with the result by Crutchley and Lever (Ref. 16). ii) 10 is less effective for MV$_2^{2+}$ photoreduction than 8 and 9, but is more efficient then Ru(bpy)$_3^{2+}$. iii) The other RuL$_3^{3+}$, 11 and 12, are almost inefficient for MV$_2^{2+}$ photoreduction. iv) The absorption spectra of RuL$_3^{3+}$ before and after photoreaction are identical, indicating good turn-over of RuL$_3^{3+}$ as a photocatalyst.

These results are explainable by the following observations. The quenching rate constants of the excited state of 8 by MV$_2^{2+}$ and TEOA are 8.6 x 10$^6$ M$^{-1}$ s$^{-1}$ and 2.5 x 10$^7$ M$^{-1}$ s$^{-1}$, respectively. Consequently, the photoseceted 8 is mainly reduced by TEOA to Ru(I) but scarcely oxidized by MV$_2^{2+}$. The excited state of 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$_2^{2+}$ at all. Since the oxidation of TEOA is an irreversible 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$_2^{2+}$ to MV$^+$ to attain the high quantum yield (Scheme I). On the other hand, the excited state of Ru(bpy)$_3^{3+}$ is oxidized by MV$_2^{2+}$ 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$_2^{2+}$ photoreduction is lower than that by 8 or 9.

Scheme I.

$*\text{RuL}_3^{2+} + \text{TEOA} \rightarrow \text{RuL}_3^{3+} + \text{TEOA}^{ox} \rightarrow \text{RuL}_3^{2+} + \text{TEOA}$

Scheme II.

$*\text{RuL}_3^{2+} + \text{MV}_2^{2+} \rightarrow \text{RuL}_3^{3+} + \text{MV}^+$

Strong oxygen effect as manifested by the difference between $\Phi(\text{vac})$ and $\Phi(\text{N}_2)$ for 8 and 9 (and also 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 8 and 9, respectively. Furthermore, the electron transfer from Ru(I) to oxygen has been directly demonstrated by a laser photolysis study of the Ru(bpy)$_3^{3+}$ - N,N-dimethylaniline - O$_2$ system by Meyer et al. (Ref. 21). The $\Phi(\text{vac})$ value is larger for 10 than that for Ru(bpy)$_3^{3+}$, whereas the quenching rate constant by MV$_2^{2+}$ for 10 is smaller than that for Ru(bpy)$_3^{3+}$. The larger $\Phi(\text{vac})/\Phi(\text{N}_2)$ value and the small but finite quenching rate constant by TEOA for 10 suggest that MV$^+$ is produced partly by the reductive quenching mechanism (Scheme I). On the other hand, although 11 and 12 have strong reducing and oxidizing powers (Ref. 18) and the reductive and oxidative quenching from the excited state of 11 or 12 by TEOA and MV$_2^{2+}$, respectively, are both thermodynamically favorable, these complexes can scarcely photoreduce MV$_2^{2+}$. The short excited lifetimes of 11 and 12 may be responsible for such low yield.

In conclusion, 8, 9, and 10 are superior photocatalysts to Ru(bpy)$_3^{2+}$ for MV$_2^{2+}$ photoreduction whereas 11 and 12 are almost inactive, indicating that the photoredox ability of RuL$_3^{3+}$ is highly sensitive to the ligand property. Now, photoreduction of MV$_2^{2+}$ 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 artificial photosynthesis.

Reducive 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($\varnothing<10^{-4}$) 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)$_3^+$ - 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 $(P_{5j} - P_1)/P_T$ where $P_{5j}$, $P_1$ and $P_T$ are the potential gradient values of formic acid, leading electrolyte and terminating electrolyte, respectively. As shown in Fig. 6, we confirmed that formic acid and two unknown carboxylic acids were produced. The yield of formic acid was 4.5 x $10^{-3}$ 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 reaction of the system under CO$_2$ atmosphere gave no carboxylic acid. ii) Photoreaction of the Ru(bpy)$_3^+$ - 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 photoirradiation of the system under CO$_2$ atmosphere for 4 h, MV$^{2+}$ was recovered in 92 % yield, corresponding to the decomposition of 1.6 x $10^{-3}$ 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)$_3^+$, our controlled experiments showed that formic acid was not a decomposition product of TEOA (see Note a).

Note a. Photoreactions of the Ru(bpy)$_3^+$ - TEOA - CO$_2$, Ru(bpy)$_3^+$ - TEOA - K$_2$S$_2$O$_8$ - N$_2$, Ru(bpy)$_3^+$ - TEOA - CO$_2$, and Ru(bpy)$_3^+$ - TEOA - MV$^{2+}$ - N$_2$ or Ar systems did not lead to the formation of formic acid. In the last system, intensive coloration occurred due to accumulation of MV$^+$ and the photolirradiation 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 seems 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 slightly endoergic. However, bubbling of CO$_2$ will shift the pH towards acidic side so that the $\mathcal{E}^0$ value may become more positive. If the participation of proton is considered, the reducing power of MV$^+$ is nearly sufficient and the magnitude of $\Phi$(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$_2$ reduction to formic acid ($\Phi$(HCOOH) = 0.01) while the formation of MV$^+$ is an efficient process ($\Phi_{MV^+} = 0.22$).

Now we have better systems for reduction of MV$^{2+}$. Using $\Phi$ instead of Ru(bpy)$^{2+}$ the maximum quantum yield of formic acid formation reached 5%.

The time-conversion relation in Fig. 7 is linear for at least initial several hours.

\[
\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCOOH}
\]

$\mathcal{E}^0' = -0.61$ V (vs. NHE at pH 7) (Ref. 26)

\[
\begin{align*}
\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- & \rightarrow \text{HCOOH} \\
\end{align*}
\]

Fig. 7 Time-conversion curves of formic acid production.

[\text{RuL}_3] = 6 \times 10^{-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.
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 losing 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 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 deciding the reaction efficiency are being investigated (Ref. 30).

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