Effect of structures of bipyridinium salts on redox potential and its application to CO_2 fixation

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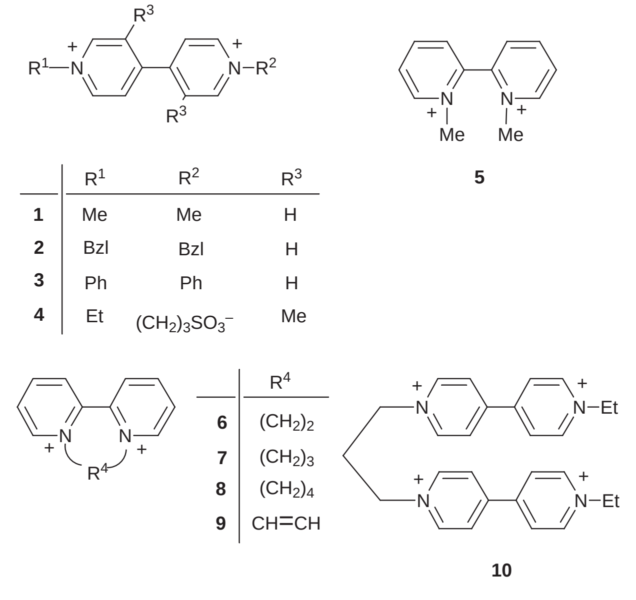
The relation between the structures and the redox potentials in electron carriers, 1,1′-dialkyl-4,4′-bipyridinium salts (**4,4′-BP**) and 1,1′-dialkyl-2,2′-bipyridinium salts (**2,2′-BP**), is theoretically analyzed by AM1 calculation. Relatively good linearity is obtained between the Gibbs free energies and the redox potentials. These electron carriers are used in a CO_2 fixation reaction using enzyme (formate dehydrogenase), in which formic acid is obtained as a final product. It is found that the efficiency of CO_2 fixation is dominated by the relative magnitude of redox potentials of the electron carriers, a photosensitizer and CO_2.

1,1′-Dialkyl-4,4′-bipyridinium salts (viologens; **4,4′-BP**) have been used as electron carriers in some redox reactions such as hydrogen evolution,[1] CO_2 fixation,[2–7] amongst others.[8,9] The oxidized form of viologens can be converted to the reduced form by receiving an electron from electron sources such as photosensitizers, electrodes and photoelectrodes, and the reduced form can give an electron to catalysts or enzymes for subsequent reactions. Though the redox potentials of viologens are thought to substantially affect their efficiency in the electron mediating process, there have been few systematic studies on the relation between the redox potentials and the structures. It is expected that the torsion angle between the two bipyridinium rings and the positions of the nitrogen atoms play an important role in determining the redox potentials. In this study, therefore, attention has been focused on two types of bipyridinium salts, **4,4′-BP** and 1,1′-dialkyl-2,2′-bipyridinium salts (**2,2′-BP**), shown in Scheme 1, to reveal the correlation between their redox potentials and structures. Further, we have applied these electron carriers to the CO_2 fixation system, which is a similar system to that reported by Mandler *et al.*,[6] and studied the relation between the redox potentials of the electron mediators and the yield of formate produced by the reduction of CO_2. It is revealed in the present study that the efficiency of CO_2 reduction is dominated by the relative magnitude of redox potentials of the electron carriers, the photosensitizer and CO_2.



	R1	R2	R3
1	Me	Me	H
2	Bzl	Bzl	H
3	Ph	Ph	H
4	Et	$(CH_2)_3SO_3^-$	Me

5

	R4
6	$(CH_2)_2$
7	$(CH_2)_3$
8	$(CH_2)_4$
9	CH=CH

10

Scheme 1 Structures of 2,2′ and 4,4′ type bipyridinium salts.

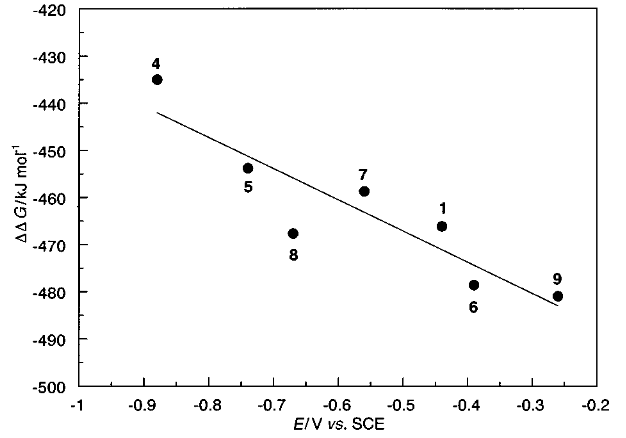


Fig. 1 Relation between calculated Gibbs free energy difference between the oxidized and the reduced forms ($\Delta\Delta G$) and experimental redox potentials (E).

Results and discussion

Redox potentials

The difference in free energy of formation ($\Delta\Delta G$) between the reduced and the oxidized forms of the bipyridinium salts have been calculated by the AM1 method.[10] The relation between the calculated $\Delta\Delta G$ and the experimental redox potentials (E) for some of them is depicted in Fig. 1, where the E values (in MeCN *vs.* SCE) were cited from the literature.[11–13] It is worth noting that there is an almost linear relationship between these two quantities with the slope −76.5 kJ mol^{-1} V^{-1}, which is relatively close to the theoretical value, −96.5 kJ mol^{-1} V^{-1}.[14] It is instructive therefore that $\Delta\Delta G$ can be an index of redox potential when new electron mediators are designed. Fig. 2 shows the relation between the dihedral angles (θ) of the two pyridinium rings and the redox potentials (E), where the θ values were obtained by AM1 method. The θ values of the oxidized form of the **4,4′-BP** are largely independent of the type of compound, while the θ values of the reduced form change to a greater extent. As a result, the difference in the θ

Table 1 Dihedral angle of oxidized form of bipyridinium salts obtained by AM1 and MMX methods

	θ/°	
Compound	AM1	MMX
1	42.9	37.2
5	89.3	76.1
6	19.7	21.6
7	39.3	38.7
8	56.7	62.2

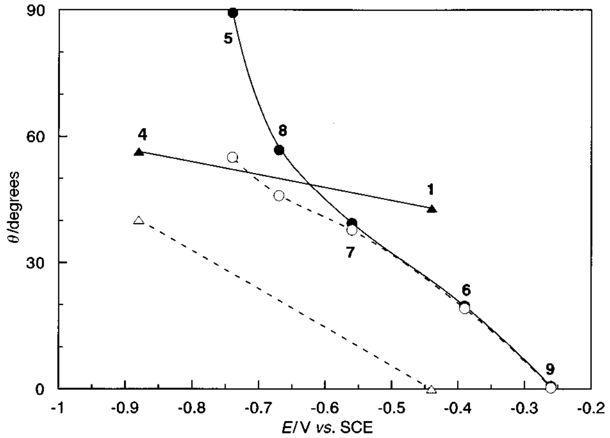


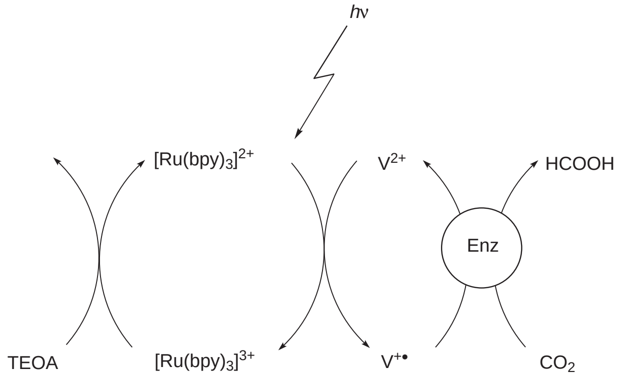
Fig. 2 Relation between dihedral angles (θ) and redox potentials (E); oxidized form (●) and reduced form (○) of 4,4′-type bipyridinium salts, oxidized form (▲) and reduced form (△) of 2,2′-type bipyridinium salts.

values between these two forms becomes large as the redox potential increases. A planar conformation is more stable in the reduced form than a twisted one, because the bond connecting the two pyridinium rings bears more double-bond character in the reduced form than in the oxidized form. In contrast to the reduced forms, the oxidized forms of **1** and **4** have a tendency to adopt more twisted conformations, 43° and 56°, respectively, which are accounted for by the fact that in the oxidized forms the electronic stability due to resonance becomes smaller and thus steric repulsion becomes the more dominant effect. The behavior of **2,2′-BP** derivatives is different from that of **4,4′-BP** ones. Namely, some difference is observed in the θ values between the oxidized and the reduced forms of **5** and **8** in the highly negative redox potential region (around −0.7 V), but the angles decrease and coalesce as the redox potential shifts to the more positive region, as in **6**, **7** and **9**. The molecular flexibility of **6**, **7** and **9** must be restricted by the alkyl ring structures, which accounts for the small difference in θ values between the reduced and oxidized forms of these compounds. In **5**, the restriction by alkyl rings is absent and the oxidized forms can have more twisted conformations ($\theta = 89°$) to relieve the steric repulsion. It should be also noted that as a whole the compounds which are apt to adopt more planar conformations give more positive redox potentials in both homologous series of **2,2′-BP** and **4,4′-BP**.

A similar conclusion was drawn by Willner *et al.* in the relation between the dihedral angle θ of the oxidized forms calculated by a molecular mechanics method (MMX force field method) and the experimental redox potentials.[15] In Table 1 the θ values of the oxidized forms of **1**, **5**, **6**, **7** and **8** obtained by the AM1 method are compared with those obtained by the MMX force field method. As a whole, the values obtained by these two different methods are similar. It is reasonable to consider that a bipyridinium salt whose torsion angle (θ) in the oxidized form is large due to steric hindrance will also show a significant deviation from the coplanar conformation in the corresponding reduced form. The energy of the reduced form is increased to a greater extent than that of the oxidized one when θ becomes large, because the double-bond character between the two pyridinium rings of the reduced form contributes largely to the stability of the coplanar conformation. Therefore, since the difference in Gibbs free energy ($\Delta\Delta G$) has a theoretical linear relationship with the redox potential (E) as shown in Fig. 1, some correlation between θ and E is observed, as shown in Fig. 2 and as reported by Willner *et al.*[15] This correlation between θ and E, however, seems to hold only in the homologous bipyridinium salts, which also suggests that some correlation exists between θ and $\Delta\Delta G$ only in homologous series. Since θ reflects the individual characteristics of relatively intricate structures while $\Delta\Delta G$ is related to the energy terms, it seems very difficult to correlate these two quantities with each other in theory. This accounts for the above findings that the relation between θ and $\Delta\Delta G$ depends on the type of bipyridinium salts; *i.e.*, **2,2′-BP** or **4,4′-BP** (Fig. 2), and on to which position the substituents are bound.[15] Contrary to the relation between θ and E, $\Delta\Delta G$ and E have a theoretical basis for the linear relationship shown in Fig. 1.

CO_2 fixation

The CO_2 fixation reaction was undertaken using the bipyridinium salts as electron carriers and formate dehydrogenase (FD) as a catalyst, as illustrated in Scheme 2. Though this system is similar to that studied by Mandler *et al.*,[6] we used this system to investigate the correlation between the redox potentials of bipyridinium salts and the efficiency of the CO_2 fixation. Here triethanolamine (TEAO) and $[Ru(bpy)_3]^{2+}$ were used as an electron donor and a photosensitizer, respectively. Since FD was not very stable under irradiation, the reaction temperature was lowered to 15 °C. A time-course of the formation of formic acid is shown in Figs. 3–5. The yields of formic acid were found to depend on the type of electron carrier. In **4,4′-BP** series, **3** had a similar efficiency to **1**, whereas **2** was less efficient (Fig. 3). In **2,2′-BP**, **7** showed the highest yield and **8** the lowest yield (Fig. 4). Bipyridinium salt **6** appears to have a similar ability to **1** as an electron carrier. It is apparent that FD has an essential role in the fixation of CO_2, since the yield was reduced when denatured FD was used instead of the active FD (Fig. 5). These results seem to be closely correlated to the redox potentials of the bipyridinium salts. Fig. 6 illustrates the dependency of the yield of formic acid on the redox potentials of the bipyridinium salts. It is worth noting that the most active electron mediator **7** has a redox potential



TEOA (Triethanolamine) : Electron donor
$[Ru(bpy)_3]^{2+}$ (Tris(2,2'-bipyridyl)ruthenium(II)) : Photosensitizer
V^{2+} (Bipyridinium) : Electron carrier (oxidized form)
$V^{+\bullet}$ (Bipyridinium) : Electron carrier (reduced cation radical)
Enz (Formate dehydrogenase) : Catalyst

Scheme 2 Photochemical CO_2 fixation.

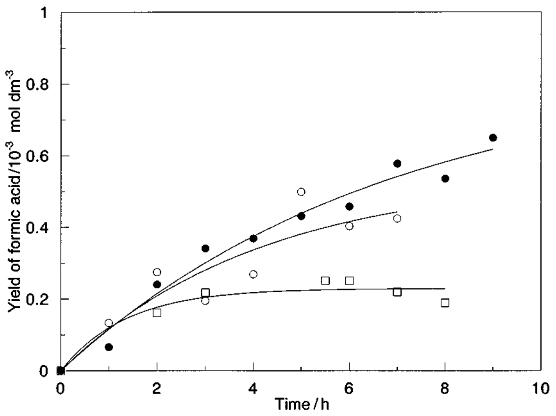


Fig. 3 Time course of the formation of formic acid; **1** (●), **2** (□), **3** (○).

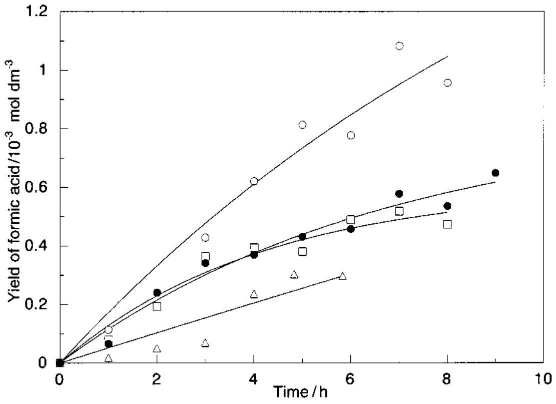


Fig. 4 Time course of the formation of formic acid; **1** (●), **6** (□), **7** (○), **8** (△).

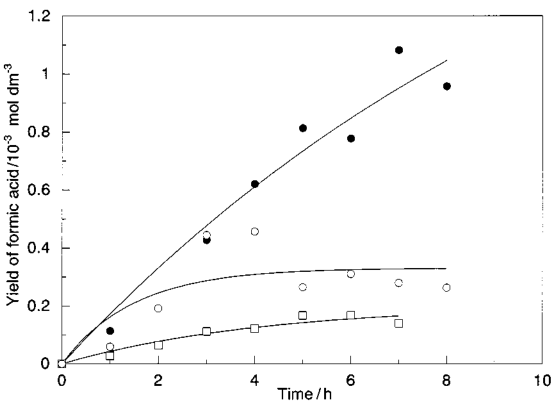


Fig. 5 Time course of the formation of formic acid; **7** (●), denatured enzyme (○), enzyme free (□).

located between those of $[Ru(bpy)_3]^{2+*}/[Ru(bpy)_3]^{3+}$ (−0.83 V *vs.* NHE)[16] and $CO_2/HCOO^-$ (−0.61 V *vs.* NHE at pH 7).[17] This phenomena can be explained qualitatively as follows. The electron transfer reaction [eqn. (1)] from excited $[Ru(bpy)_3]^{2+}$

$$[Ru(bpy)_3]^{2+*} + B^{2+} \longrightarrow [Ru(bpy)_3]^{3+} + B^{+\bullet} \qquad (1)$$

to 2 + bipyridinium salts (B^{2+}) depends on their reduction potentials.

According to the theory of Marcus,[18,19] the electron-transfer rate is proportional to $\exp[-(\Delta G^\circ + \lambda)^2]$, where ΔG° corresponds to the difference in redox potential between $[Ru(bpy)_3]^{2+*}$ (an electron donor) and B^{2+} (an electron acceptor) and λ is the energy of reorganization of solvents. This theory indicates that in the normal region (*viz.*, $-\Delta G^\circ < \lambda$) the rate increases as $-\Delta G^\circ$ increases, that is, the redox potential of

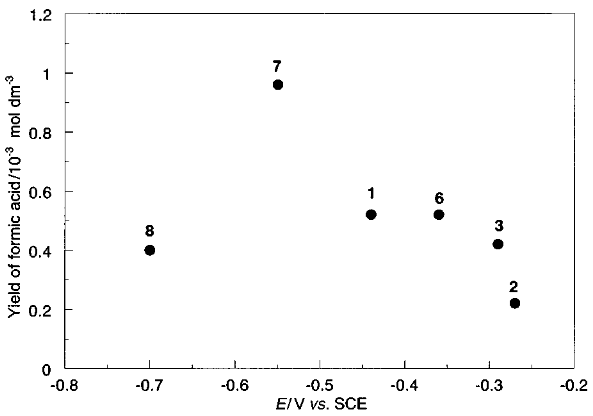


Fig. 6 Relation between yield of formic acid after 7 h reaction and redox potentials of bipyridinium salts (*E*).

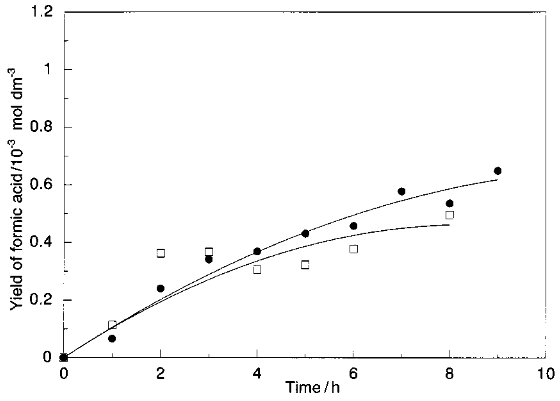


Fig. 7 Time course of the formation of formic acid; **1** (●), **10** (□).

bipyridinium salts becomes more positive. Therefore, bipyridinium salts with more positive redox potentials are favorable in this reaction step. According to the same theory, however, the efficiency of electron transfer [eqn. (2)] from the reduced

$$2B^{+\bullet} + CO_2 + H^+ \longrightarrow 2B^{2+} + HCOO^- \qquad (2)$$

bipyridinium salts ($B^{+\bullet}$) to the enzyme (FD) decreases as the redox potentials of bipyridinium salts become less negative.

It can be concluded therefore that the whole yield of formic acid is dominated by the relative magnitude of redox potentials of the photosensitizer, the electron mediator and the enzyme and that there is an optimum redox potential of bipyridinium salts to produce formic acid most efficiently, though the effect of the difference in interaction between the reduced bipyridinium salts and the enzyme (FD) cannot be excluded.

Since the reduction of CO_2 to formic acid is a two-electron process, we investigated the behaviour of a dimeric compound, **10**, in which two **4,4′-BP** units are linked to each other by a propyl chain. This compound was expected to receive and give two electrons using the two bipyridinium units. As shown in Fig. 7, however, the yield of formic acid was similar to that of **1**, probably due to the lack of reducing power of **10**. The weaker reducing ability of **10** may be caused by the higher stability of the reduced form, in which the two bipyridinium planes are aligned in parallel, as shown in Fig. 8, and consequently electrons are more delocalized over the π-conjugated skeleton of **10**. This folded conformation of **10** is also reflected in the visible spectra of **1** and **10**, which were very different.[20] Compound **1** gives one large absorption at 603 nm ($\varepsilon = 1.20 \times 10^4$ dm^3 mol^{-1} cm^{-1}), while **10** has two main peaks at 533 nm ($\varepsilon = 2.36 \times 10^4$ dm^3 mol^{-1} cm^{-1}) and *ca.* 850 nm ($\varepsilon =$ *ca.* 10^4 dm^3 mol^{-1} cm^{-1}). To prove that the differences in the visible spectra are caused by the folding conformation of **10**, we calculated the electronic spectra of **1** and **10** by INDO/1 and found that **1** has a large

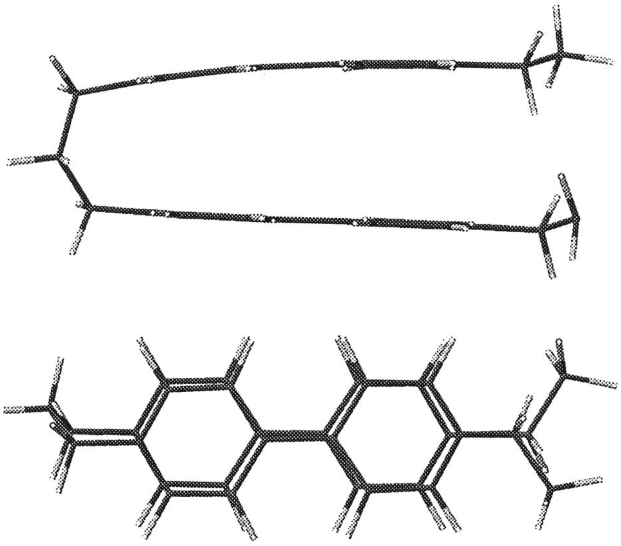


Fig. 8 Possible structure of the reduced form of **10**.

absorption peak ($\varepsilon = 1.2 \times 10^4$ dm^3 mol^{-1} cm^{-1}) at *ca.* 730 nm and **10** has two absorption peaks at *ca.* 440 nm ($\varepsilon = 7.0 \times 10^4$ dm^3 mol^{-1} cm^{-1}) and *ca.* 930 nm ($\varepsilon = 1.1 \times 10^4$ dm^3 mol^{-1} cm^{-1}). As a whole, the calculated spectra qualitatively reproduce the characteristics of the observed spectra.

Experimental

Materials

Bipyridinium salts **1**, **2** and **3** were purchased from Tokyo Kasei Co., and **6**, **7**, **8** and **10** were synthesized following a literature method.[20] Formate dehydrogenase (FD; EC1.2.1.2, from yeast) was obtained from Sigma Chemical Co. All other reagents used were of the highest grade commercially available.

AM1 calculations

Torsion angle θ and the thermodynamic quantities of the bipyridinium salts were obtained using AM1 method in MOPAC of CAChe system (ver. 3.6, SONY TEKTRONIX Co.). AM1 is a semi-empirical molecular orbital calculation method developed by Dewar,[10] which was based on the Roothaan-Hall (RH) SCF-LCAO-MO method.[21,22] The following terms are considered in the Fock matrix of AM1: (a) one-center one-electron energies (U_{rr}), (b) one-center two-electron repulsion integrals, *viz.*, Coulomb integrals ($\mu\mu,\nu\nu$) and exchange integrals ($\mu\nu,\mu\nu$), (c) two-center one-electron core resonance integral ($\beta_{\mu\lambda}$), (d) two-center one-electron attraction ($V_{\mu\nu}$), (e) two-center two electron repulsion integrals ($\mu\nu,\lambda\sigma$). In AM1 method, the standard enthalpy of formation, ΔH_f is obtained by eqn. (3), where E_{el} is electronic energy, $E_{AB}{}^{core}$ is repulsion

$$\Delta H_f = E_{el} + \Sigma\Sigma\, E_{AB}{}^{core} + \Sigma\,\{-E_{el}{}^{A} + \Delta H_f{}^{A}\} \qquad (3)$$

energy between the core of atoms A and B, $E_{el}{}^{A}$ is electronic energy of atom A, and $\Delta H_f{}^{A}$ is heat of formation of atom A. The kinetic energy terms are neglected in eqn. (3), because they are taken into account by the parameterization in AM1 method.[23] On the other hand, the standard entropy of formation, ΔS_f, can be represented by eqn. (4), where S_{vib} is entropy

$$\Delta S_f = S_{vib} + S_{rot} + S_{tra} + \Sigma\, S^A \qquad (4)$$

for vibration, S_{rot} is entropy for rotation, S_{tra} is entropy for translation, and S^A is standard entropy of formation for atom A. Though S_{vib}, S_{rot}, and S_{tra} can be obtained by AM1 method, S^A is unknown. It is not necessary, however, to know S^A, since only the difference in standard entropies of formation between two states (reduced and oxidized states) is focused here and thus $\Sigma\, S^A$ is canceled [*cf.* eqn. (5)]. The torsion angles (θ) were those of the structures optimized by AM1 method, which correspond to the minimum heat of formation.

Calculation of Gibbs free energy and torsion angle

The difference in free energy of formation ($\Delta\Delta G$) between the reduced and the oxidized forms in acetonitrile (MeCN) was calculated by AM1 according to eqn. (5), where $\Delta G_{f(red)}$ and

$$\begin{aligned}\Delta\Delta G &= \Delta G_{f(red)} - \Delta G_{f(ox)}\\ &= \{\Delta H_{f(red)} - T\Delta S_{f(red)}\} - \{\Delta H_{f(red)} - T\Delta S_{f(red)}\} \qquad (5)\end{aligned}$$

$\Delta G_{f(ox)}$ are standard Gibbs free energy of formation, $\Delta H_{f(red)}$ and $\Delta H_{f(ox)}$ are standard enthalpy of formation, $\Delta S_{f(red)}$ and $\Delta S_{f(ox)}$ are standard entropy of formation, and the subscripts "red" and "ox" signify the reduced state and the oxidized state, respectively. The AM1 calculation was undertaken in MeCN at 298 K, where the solvent effect was considered using the conductor-like screening model (COSMO) included in MOPAC of CAChe system with a relative permittivity 37.5 and an effective radius of the solvent molecule 2.0 Å.

Fixation of CO_2

Into the aqueous solution including the electron donor triethanolamine (0.5 mol dm^{-3}), $[Ru(bpy)_3]^{2+}$ (5×10^{-4} mol dm^{-3}) and bipyridinium salts (3×10^{-3} mol dm^{-3}), CO_2 was bubbled and FD (8 mg) was added. The reaction system was illuminated using an ultra high pressure Hg lamp (500W USHIO, UI-501H) with cut-off filters to remove UV region shorter than 370 nm and infrared region. Samples of the solution were analyzed at intervals by a Shodex organic acid analyzer (Shodex RS pak column: KC-811, eluant: 3 mM $HClO_4$).

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