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The improvement of formic acid production from CO_2 with visible-light energy and formate dehydrogenase by the function of the viologen derivative with carbamoylmethyl group as an electron carrier

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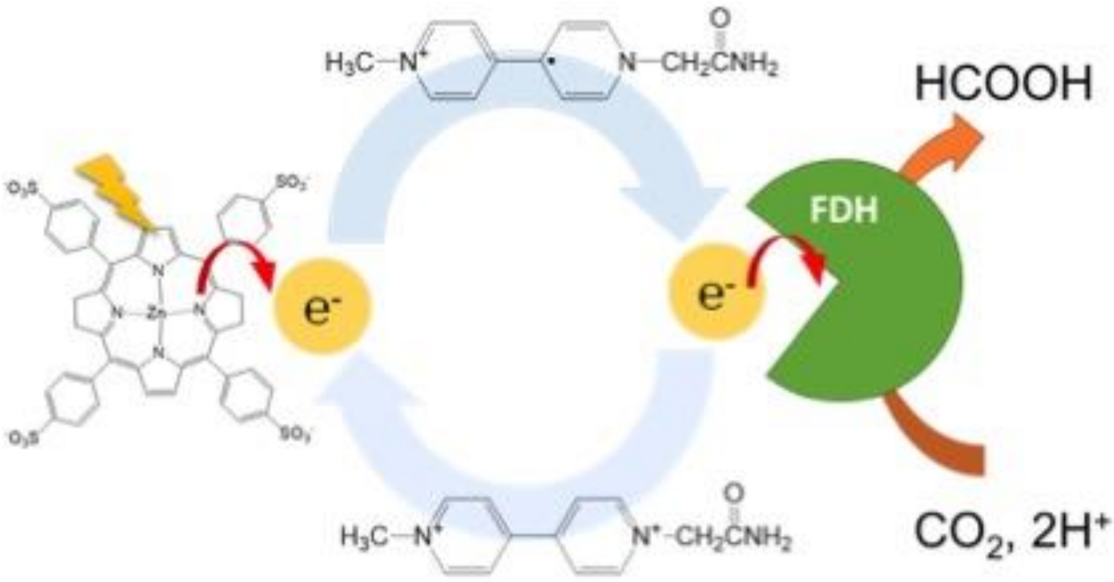
Graphical Abstract



Highlights·

- Viologen derivative (BP) with carbamoyl group was developed and applied as an electron carrier in the visible-light induced CO_2 to formic acid conversion system consisting of the Zn porphyrin and formate dehydrogenase (FDH) for improvement of the formic acid production efficiency.
- The photoreduction efficiency of BP depends on the redox potential and effective photoreduction was observed using 1,1′-dicarbamoylmethyl-4,4′-bipyridinium diiodide with the lowest redox potential among BP's.

- ・The effective formic acid production was observed by using 1-carbamoylmethyl-1’-methyl-4,4′-bipyridinium diiodide, compared with the other BP’s.

Abstract

Formate dehydrogenase (FDH) is an attractive biocatalyst for converting CO_2 to formic acid in ambient conditions. FDH is applied to the catalyst for the visible-light induced CO_2 - formic acid conversion system consisting of an electron donor, a photosensitizaer and an electron carrier. For improvement of the formic acid production efficiency with this system, the enhancement of electron relay processes among a photosensitizer, an electron carrier and FDH has been needed. We aimed to solve this problem by developing novel electron carrier based on the viologen derivative instead of methylviologen (MV), widely used as an electron carreir. In this study, viologen derivatives with carbamoyl group, 1,1’-dicarbamoylmethyl-4,4’-bipyridinium diiodide (CV) and 1-carbamoylmethyl-1’-methyl-4,4’-bipyridinium diiodide (CMV) were synthesized and applied to the electron carrier for photoinduced CO_2-formic acid conversion system consisting of triethanolamine, water-soluble zinc porphyrin and FDH. By using CV and CMV, the effective formic acid production in the system of water-soluble zinc porphyrin and FDH was improved compared with that of MV.

Keywords: Artificial photosynthesis; CO_2 reduction; biocatalyst; formate dehydrogenase; viologen derivative; electron carrier

1. Introduction

The CO_2 based material conversion system with visible light energy has been much paid attention as an artificial photosynthesis, a chemical process that replicates of the natural photosynthesis. To construct the system, the development of the catalyst for CO_2 conversion is important factor. Until now, many catalysts have been reported to apply the photoinduced CO_2 based material conversion system [1-11]. These catalysts are classified into a photocatalyst, molecule catalyst and a biocatalyst. Among various types of catalysts, biocatalyst is an attractive catalyst for CO_2 based material conversion, because it has high selectivity for substrate and product in aqueous solutions at room temperature and ordinary pressure. The photoinduced CO_2 based material conversion system has also been developed in the presence of various biocatalysts such as formate (FDH), aldehyde (AldDH), alcohol dehydrogenase (ADH) and malic enzyme (ME) for the chemical conversion of valuable organic compounds such as formic acid, ethanol, malic acid *etc* [12-20]. Scheme 1 shows the photoinduced CO_2 based material conversion consisting of an electron donor (D), a photosensitizer (P), an electron carrier (C) and biocatalyst. Among various biocatalysts, FDH from *Candida boidinii* with the

CO_2 reduction catalytic activity has been used for the visible-light induced CO_2 - formic acid conversion system. In the system, the electron transfer among a photosensitizer, an electron carrier and FDH is an important process to improve the CO_2 - formic acid conversion. Therefore, the choice of the electron carrier is important for the improvement of the formic acid production efficiency with the system as shown in Scheme 1 .

NAD^+ acts as a natural co-enzyme involving electron transfer for FDH. Therefore, NAD^+ was used as an electron carrier for FDH with the combination of NAD^+ photoreduction scheme [21]. However, the one electron reduced NAD^+ with a photosensitizer such as tris(bipyridine)ruthenium(II), $Ru(bpy)_3^{2+}$ forms a NAD dimer, $(NAD)_2$, and $(NAD)_2$ is an inactive co-enzyme for FDH [22]. From this reason, it is difficult to combine NAD^+ photoreduction into the CO_2 - formic acid conversion system with FDH. To solve this problem, viologen derivative (BP) has been used as an electron carrier instead of NAD^+ [23]. BP is easily reduced to produce the reduced form of BP with organic dye molecule like chlorophyll, porphyrin and so on, so that BP is used as an electron carrier in the visible-light induced CO_2 - formic acid conversion system with FDH. We reported the visible-light induced formic acid production from CO_2 with FDH system consisted of zinc tetraphenylporphyrin tetrasulfonate (ZnTPPS) as a photosensitizer, BP as an electron carrier and FDH [24,25]. BP has the role of the electron acceptor from the excited state of photosensitizer and forms one electron reduced from. In addition, the one electron reduced form of BP acts as electron donor for FDH in CO_2 - formic acid conversion. Thus, the design of the chemical structure of BP is needed for a suitable electron donor for FDH to use the CO_2 reduction catalytic activity efficiently. Until now, various BPs as electron carriers were applied to the improvement of formic acid production efficiency from CO_2 with FDH in the system [26]. But the interaction between the reduced form of BP and FDH was not reported. So we focused on the effect of BP on the catalytic activity of FDH. Through our previous study, the effect of various BP's on the formic acid oxidation catalytic activity and CO_2 reduction catalytic activity of FDH were revealed by enzyme kinetic analysis [27]. Oxidized form of BP doesn't act as an electron acceptor in formic acid - CO_2 conversion. On the contrary, one electron reduced form of BP acts as an electron donor for FDH in CO_2 - formic acid conversion. In addition, we previously reported that the "steric effect" and "ionic effect" of BP affected the function of BP as an electron donor for FDH in CO_2-formic acid conversion [28-30]. The detail mechanism of the interaction between the reduced form of BP and FDH is still unclear. But previous result of enzyme kinetic analysis implies that the reduced form of BP acts as an electron donor in molecular recognition field for FDH as a possibility. In the field, NAD^+ has high affinity for FDH. Hence we aimed to the enhanced the function of the reduced form of BP as an electron donor for FDH in the CO_2 - formic acid conversion with FDH.

In this study, BP’s with carbamoyl group, NAD analogue, shown in Figure 1 were synthesized and applied to the visible-light induced CO_2 - formic acid conversion system consisting of TEOA as an electron donor, ZnTPPS as a photosensitizer and FDH. We assessed those function of novel BP as an electron carrier, as an electron acceptor from ZnTPPS and as an electron donor for FDH in visible-light induced formic acid production from CO_2 system.

2. Experimental

2.1. Materials

FDH from *Candida boidinii* was purchased from Roche Diagnostics K.K.. The molecular weight of FDH from *Candida boidinii* was estimated to be 74 kDa [31]. Methylviologen (MV, $C_{12}H_{14}Cl_2N_2$), iodomethane, and 4,4’-bipyrdyl were purchased from Tokyo Kasei Co. Ltd. Iodoacetamide and sodium pyrophosphate were obtained from Wako Co. Ltd. The other chemical regents were analytical grade or highest grade available.

Zinc tetraphenylporphyrin tetrasulfonate (ZnTPPS) was synthesized according to previous report [32]. The absorption spectrum of ZnTPPS exhibits an intense Soret band at 421 nm and Q bands at 555 and 594 nm in neutral aqueous solution [33].

2.2. Synthesis of BP with carbamoyl group

1-Methyl-4,4’-bipyridinium iodide was synthesized using following method. 4,4’-Bipyridine and iodomethane was stirred at the molar ratio of 1:1 in 200 ml acetone at room temperature. The residue was dried under vacuum overnight.

1-Carbamoylmethyl-1’-methyl-4,4’-bipyridinium diiodide (CMV, $C_{13}H_{15}I_2N_3O$) was synthesized by refluxing 1-methyl-4,4’-bipyridinium iodide with the molar equivalent of iodoacetamide in 200 ml acetonitrile at 90 °C for 48 h.

1,1’-Dicarbamoylmethyl-4,4’-bipyridinium diiodide (CV, $C_{14}H_{16}I_2N_4O_2$) was synthesized by refluxing 4,4’-bipyridine and iodoactamide in 200 ml acetonitrile at 90 °C for 48 h according to the previous report [34].

Reduction potential of BP was measured using cyclic voltammetry (HOKUTO HZ-3000) with a carbon electrode as a working, platinum electrode as a counter; Ag / AgCl electrode as a reference in 50 mM sodium pyrophosphate buffer (pH 7.4). The sample solution consisted of BP (2.0 mM).

The dihedral angle between the pyridine rings of BP was calculated by molecular orbital method (AM-1method).

2.3. Formic acid - CO_2 conversion with FDH and BP with carbamoyl group

The formic acid - CO_2 conversion was carried out as following procedure. The sample solution was consisted of sodium formate (5 mM), FDH (7.5 μM) and BP (0.2 mM) in 50 mM sodium pyrophosphate buffer (pH 7.4) saturated flushed with nitrogen gas. The absorption of the reduced form of BP was detected using UV-visible absorption spectroscopy (SHIMADZU, MaltiSpec-1500).

2.4. Photoreduction of BP with carbamoyl group by photosensitization of ZnTPPS

Photoreduction of BP with ZnTPPS was carried out as follows. The sample solution was consisted of TEOA (0.3 M), ZnTPPS (10 μM), BP (0.1 mM) in 1.0 mM sodium pyrophosphate buffer (pH 7.4). The sample solution was deaerated by freeze-pump-thaw cycles repeated 5 times. The absorption of reduced form of BP was detected by using UV-visible absorption spectroscopy (SHIMADZU, MaltiSpec-1500). The molecular extinction coefficients (ε) of CV, CMV and MV are 7,800 (λ_{max}=595 nm), 12,700 (λ_{max}=600 nm) and 12,000 $M\cdot cm^{-1}$ (λ_{max}=605 nm), respectively. 250 W halogen lamp (TOSHIBA, JD110V85WNP-EHTB) was used as a visible light source.

Fluorescence emission spectrum of ZnTPPS in the presence of BP was measured using fluorescence spectrophotometer (SHIMADZU RF5300PC). The excitation wavelength was 422 nm due to the Soret band of ZnTPPS. In these experiments the absorbance at 422 nm was kept constant to be 0.34 for all the sample solutions.

2.5. Photoinduced formic acid production from CO_2 with ZnTPPS, BP and FDH

Photoinduced formic acid production from CO_2 system with ZnTPPS, BP and FDH was carried out under the following method. The sample solution was consisted of TEOA (0.3 M), ZnTPPS (10 μM), BP (0.1 mM) and FDH (6.4 μM) in CO_2 saturated sodium pyrophosphate buffer (pH 7.4), the sample solution was deaerated by freeze-pump-thaw cycles repeated 5 times and flushed with CO_2 gas. The amount of formic acid was detected by an ion chromatography system (Thermo ICS-1100).

3. Results and discussion

3.1. Characterization of BP with carbamoyl group

Table 1 shows the reduction potentials (*vs* Ag / AgCl) and dihedral angles of BPs. First and second potentials of CV were estimated to be – 0.50 (E_{red1}) and – 0.91 V (E_{red2}), respectively. First and second potentials of CMV were estimated to be – 0.59 (E_{red1}) and – 0.93 V (E_{red2}), respectively. Reduction potential of BP depended on the number of carbamoyl groups. Carbamoyl group is an electron withdrawing substituent, leading these difference of reduction potentials among BPs.

Dihedral angles of CV, CMV and MV were estimated to be 43.9, 43.4 and 43.4 º respectively. There are little differences of dihedral angles between pyridine rings of CV, CMV and MV, indicating that there is little steric effect by introducing carbamoyl group to BP.

3.2. Formic acid - CO_2 conversion with FDH and BP with carbamoyl group

FDH mainly catalyzes formic acid to CO_2 in the presence of NAD^+. Thus the investigation of the function of BP as an co-enzyme in formic acid - CO_2 conversion with FDH is important factor. If the oxidized form of BP acted as a co-enzyme, one electron reduced form of BP was produced with proceeding the formic acid oxidation. In all case, no reduced form of BPs were produced. This result shows that BPs with carbamoyl group do not act as a co-enzyme for FDH in formic acid - CO_2 conversion.

3.3. Photoreduction of BP with carbamoyl group by photosensitization of ZnTPPS

Figure 2 shows the relationship between the photoirradiation time and the concentration of the reduced form of BP produced. The reduced form of CV and CMV were produced with photosensitization of ZnTPPS. The first and second potentials of

BP affect the behavior of the reduced form of BP. Bird and Kuhn reported that ‘dispropportionation’ and ‘conpropportionation’ reaction (equations 1 and 2) occur in solution exist of the reduced form of BP [35].

These equation shows that two one electron reduced form of BPs ($BP^{\cdot +}$) react and divide into oxidize form of (BP^{2+}) and two electron reduced form of BP (BP^0) in the sample solution for the reduction of BP with photosensitization of ZnTPPS. The two one-electron reduced forms of BP used in this study act as a co-enzyme for FDH, however, two electron reduced form of BPs are nearly insoluble in aqueous solution and assumed not to act as co-enzyme of FDH in CO_2 - formic acid conversion. Therefore, the one electron reduced form of BP remain is essentially to proceed the photoinduced formic acid production from CO_2. The conproportionation constant (k_{conp}) for BP has been obtained from those potentials by using equation 3 [36] and the ratio of one electron reduced form of BP in the sample solution can be determined by equation 4, which was expressed by Hunig and Sauer [37].

$$\% \text{ one electron reduced form} = \frac{\sqrt{k_{conp}}}{\sqrt{k_{conp}}+2} \times 100 \quad (4)$$

The obtained k_{conp} values for BPs and the ratio of one electron reduced form of BP (%) were listed in Table 2. In all case, the reduced form of BP with photosensitization of ZnTPPS are assumed to exist at least 99.5 % as one electron reduced form of BP and little disproportionation of the one electron reduced form of BP occurs.

The concentration of the reduced form of CV, CMV and MV after 180 min irradiation were estimated to be 96, 52 and 46 μM, respectively. CV was the easiest likely to be reduced in other BPs.

To investigate the cause of the difference of the amount of reduced form of BP production, the interaction between ZnTPPS and BP was estimated by measurement of the fluorescence of ZnTPPS in the presence of BP. Figure 3 shows the fluorescence spectra changes of ZnTPPS in the presence of BP. The shape of the fluorescence spectrum of ZnTPPS in the presence of BP was the same as that of ZnTPPS without BP, but the fluorescence intensity of ZnTPPS in the presence of BP was lower than that of ZnTPPS without BP, indicating that the fluorescence of the ZnTPPS was quenched by BP.

Figure 4 shows the Stern-Volmer plot for the quenching of fluorescence from the ZnTPPS in the presence of BP.

The ratio of fluorescence intensities of ZnTPPS in the absence of BP and in the presence of BP (I_0/I) increased linearly, indicating that the fluorescence of ZnTPPS was quenched with BP obeyed by Stern-Volmer relationship. Table 3 shows the value of quenching constant (K_{sv}) of ZnTPPS in the presence of each BP. The K_{sv} values of MV, CMV and CV were 0.195, 0.141 and 0.115 μM^{-1}, respectively. The K_{sv} value of MV is the largest in other BPs and the K_{sv} value is lowered with the number of carbamoyl group in BP. This result shows that the interaction between ZnTPPS and BP depends on the chemical structure of BP. By introducing carbamoyl group to BP, the affinity with ZnTPPS is lowered compared with that of MV with methyl group in the molecule.

In this study, CMV and CV with iodide as a counter ion were used as an electron carrier and the counter ion affects the fluorescence quenching of ZnTPPS. Counter ion of CMV and CV was exchanged iodide for chloride according to the previous report [30] and fluorescence emission spectrum of ZnTPPS in the presence of CMV and CV with chloride ion were measured for investigation of the effect of counter ion of BP on the fluorescence emission of ZnTPPS. The K_{sv} values in the presence of CMV and CV with chloride ion were 0.272 and 0.213 μM^{-1}, respectively. The K_{sv} values of CMV and CV with chloride ion are larger than that of CMV and CV with iodide ions, indicating that counter ion of BP affects the fluorescence emission of ZnTPPS. However, BP is not reduced by the electron transfer from the singlet excited sate of ZnTPPS, but by the electron transfer from the triplet excited state of ZnTPPS [38].

The Gibbs free energy change of the photoreduction of BP with photosensitization of ZnTPPS was calculated from the redox potential of BP and ZnTPPS. In the photoreduction of BP, photoinduced electron transfer from the photoexcited triplet state of ZnTPPS (^{3}ZnTPPS*) to BP proceeded. The redox potential of the excited triplet state of ZnTPPS, E (ZnTPPS$^+$ / ^{3}ZnTPPS*) and E (^{3}ZnTPPS* / ZnTPPS$^-$) were reported to be -0.75 and 0.45 V, respectively [33]. The Gibbs free energy change of photoreduction of CV, CMV and MV were estimated to be -24.1, -15.4 and -7.7 kJ·mol^{-1}, respectively. The Gibbs free energy change shifted to negative in the number of carboxyl group in the BP, indicating that the CV and CMV are easy to be reduced than that of MV. Actually, the amount of the concentration of the reduced form of CV was largest, followed in order by CMV and MV after 180 min irradiation. This result shows that the reduced form of BP production depends on that the reduction potential of BP. The reduction potential of CV was the lowest in other BPs, leading the amount of reduced form of CV was the largest in other BPs.

3.4. Photoinduced formic acid production from CO_2 with ZnTPPS, BP and FDH

Figure 5 shows the relationship between the photoirradiation time and formic acid production. The amount of photoinduced formic acid production after 180 min irradiation with MV, CV and CMV were estimated to be 105, 149 and 172 μM, respectively. The formic acid production after 180 min irradiation was increased by using CMV and CV with carbamoyl group than that using MV. By using CMV as an electron carrier, especially, the efficiency of visible-light induced CO_2 - formic acid conversion system with the system consisting of ZnTPPS and FDH in the presence of TEOA was improved approximately 60 % than that using MV. From these results, carbamoyl group in BP affected the electron transfer, leading the improvement of formic acid production with FDH. To explain the cause of result, the detail analysis of mechanism of converting CO_2 - formic acid via FDH and the reduced form of BP is needed. Unfortunately, the CO_2 reduction catalytic mechanism of FDH with the reduced form of BP is still unclear. However, we previously reported the effect of functional group in the reduced form of BP on the CO_2 reduction catalytic activity of FDH. The functional group may have affected the affinity for FDH [28-30]. Molecular recognition of FDH from *Candida boidinii* is consisted of Asp 96, Tyr 194, Asp 195, Tyr 196, Gln 197 and His 232 [39]. Especially, Asp 195 plays an important role in providing specific to co-enzymes such as NAD^+. NAD^+ has high affinity with FDH, indicating that nicotinamide with a role of electron transfer in NAD^+ has little steric hindrance and electrostatic repulsion with Asp 195 in the molecule recognition field. Carbamoyl group in CV or CMV affects the interaction between Asp 195, leading that CV or CMV makes closer contact to Asp 195 via electrostatic effect than that of MV which has only methyl group. From the reason, the reduced form of CV and CMV acted as an electron donor for FDH more efficiency compared with MV. Compared with the ratio of the reduced form of BP production with photosensitization of ZnTPPS, the abundance of reduced form of CV was the largest in other BPs, but the amount of formic acid production with CV was lower than that of CMV. One possible reason of this result, the reduced form of CV may have the higher affinity for FDH than that of CMV. This leads the stabilization of FDH - CV complex and lowering the CO_2 - formic acid conversion reaction rate or the inhibitory effect of CV for FDH in the course of the reaction.

In the photoinduced CO_2 - formic acid production system consisting of ZnTPPS, BP and FDH, the reduced form of CMV acted as the most effective co-enzyme for FDH in other BPs.

4. Conclusion

In this work, BPs with carbamoyl group were developed and the function as an electron transfer was investigated in the visible-light induced conversion of CO_2 to formic acid with the system consisting of ZnTPPS and FDH in the presence of TEOA as an electron donor molecule. In the photoreduction of BP with the photosensitization of ZnTPPS, the reduction efficiency of BP depends on the redox potential of BP and effective photoreduction was observed using CV with two carbamoyl groups. In the photoinduced formic acid production, the amount of formic acid production was improved by using CMV as an electron carrier than that using MV, indicating that carbamoyl group affected the interaction between BP and FDH. By using CV and CMV, the formic acid production was improved compared with that of MV.

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Captions to Figures

Figure 1. Chemical structures of BPs.

Figure 2. The relationship between the photoirradiation time and the amount of the reduced form of CV (◇), CMV (△) and MV (●). The sample solution was consisted of TEOA (0.3 M), ZnTPPS (10 μM), BP (0.1 mM) in 1.0 mM sodium pyrophosphate buffer (pH 7.4).

Figure 3. Change of fluorescence intensity of ZnTPPS in the presence of CV (a), CMV (b) or MV (c). The sample solution was consisted of ZnTPPS (0.5 μM) and BP in pH 7.4 sodium pyrophosphate buffer (1.0 mM). The concentration of BP was changed between 0 to 3.0 μM.

Figure 4. Stern-Volmer plots for the quenching of the fluorescence of ZnTPPS in the presence of CV (◇), CMV (△) or MV (●).

Figure 5. The relationship between the photoirradiation time and the formic acid production with CMV (△), CV (◇) and MV (●). The sample solution was consisted of TEOA (0.3 M), ZnTPPS (10 μM), BP (0.1 mM) and FDH (6.4 μM) in CO_2 saturated 1.0 mM sodium pyrophosphate buffer (pH 7.4).

Scheme 1 Photoinduced material conversion system with biocatalyst consisting of an electron donor (D), a photosensitizer (P), an electron carrier (C^{2+}).

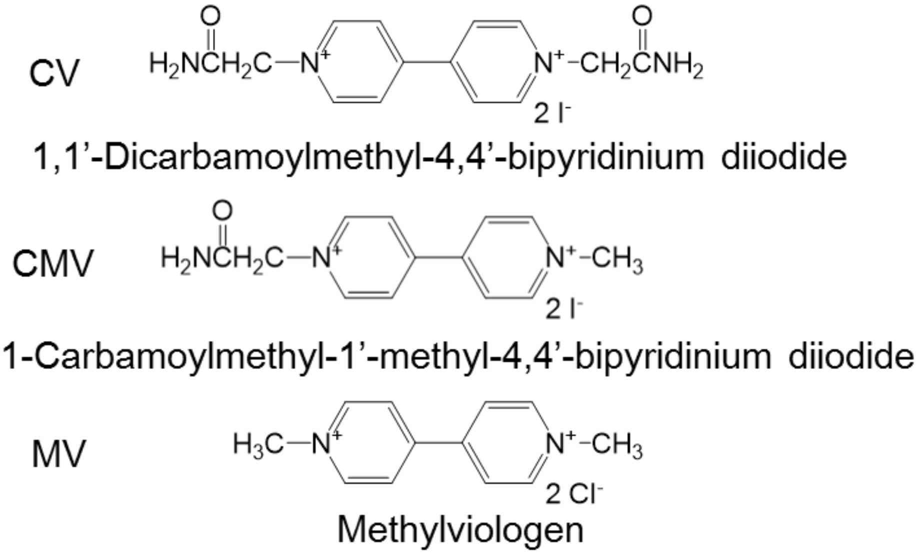


Fig. 1

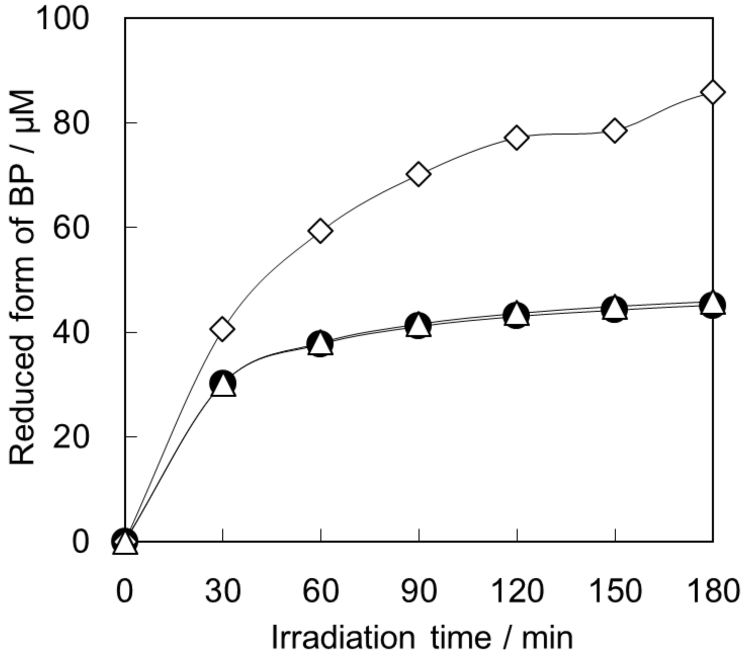
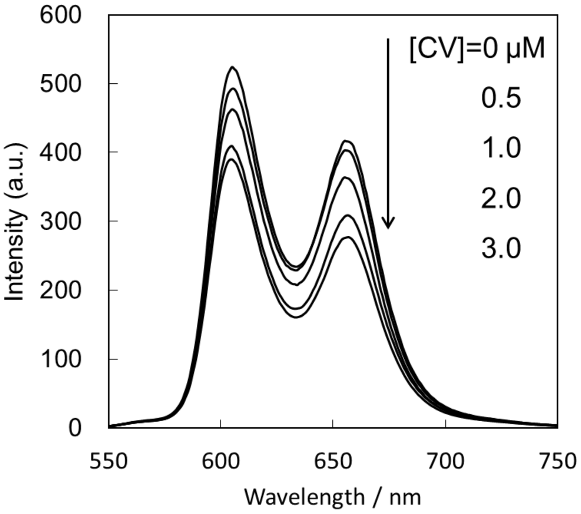


Fig. 2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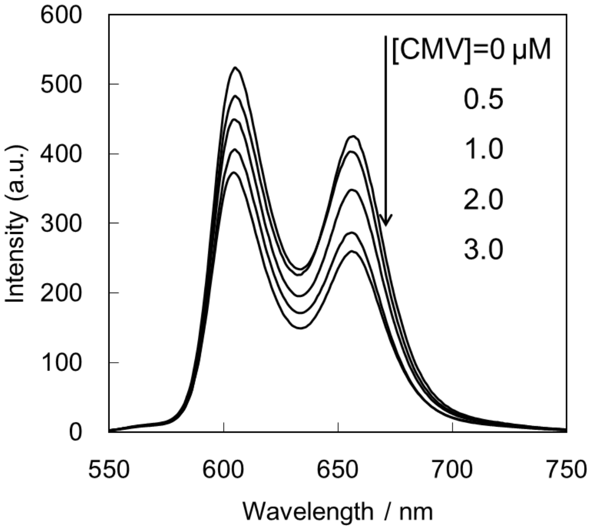
500
400
300
200
100
0
Intensity (a.u.)
550
600
650
700
750
Wavelength / nm
[CV]=0 μM
0.5
1.0
2.0
3.0


600
500
400
300
200
100
0
Intensity (a.u.)
550
600
650
700
750
Wavelength / nm
[CMV]=0 μM
0.5
1.0
2.0
3.0

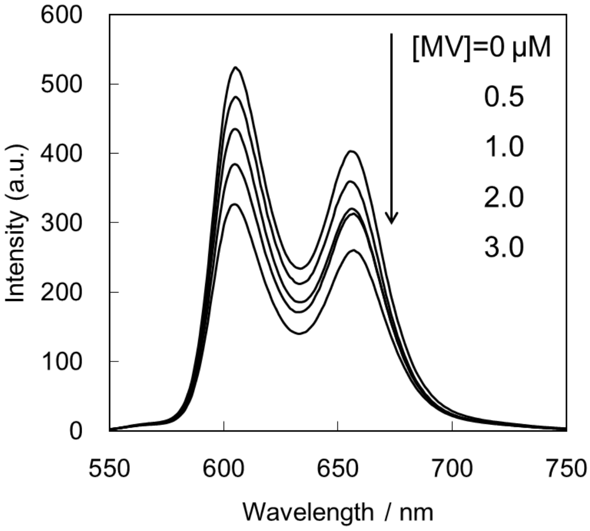

600
500
400
300
200
100
0
Intensity (a.u.)
550
600
650
700
750
Wavelength / nm
[MV]=0 μM
0.5
1.0
2.0
3.0

Fig. 3

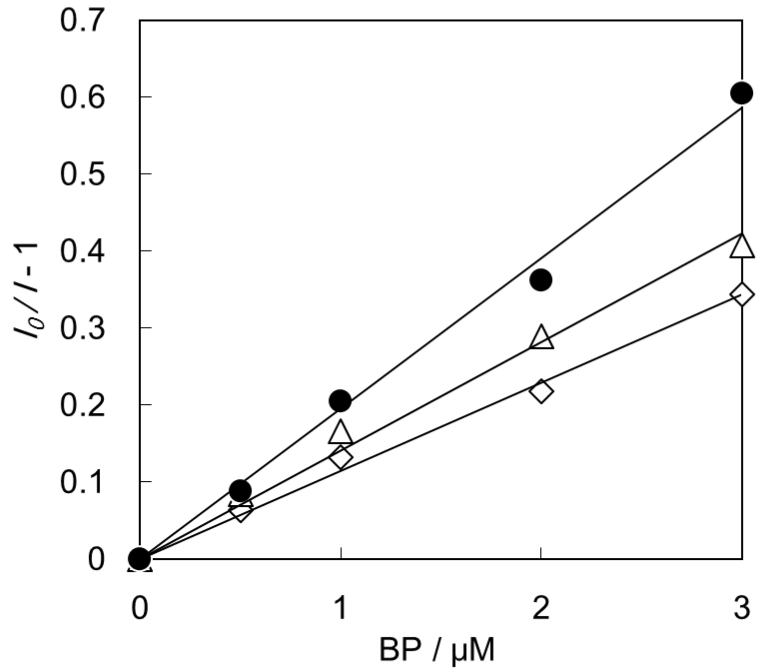


Fig. 4

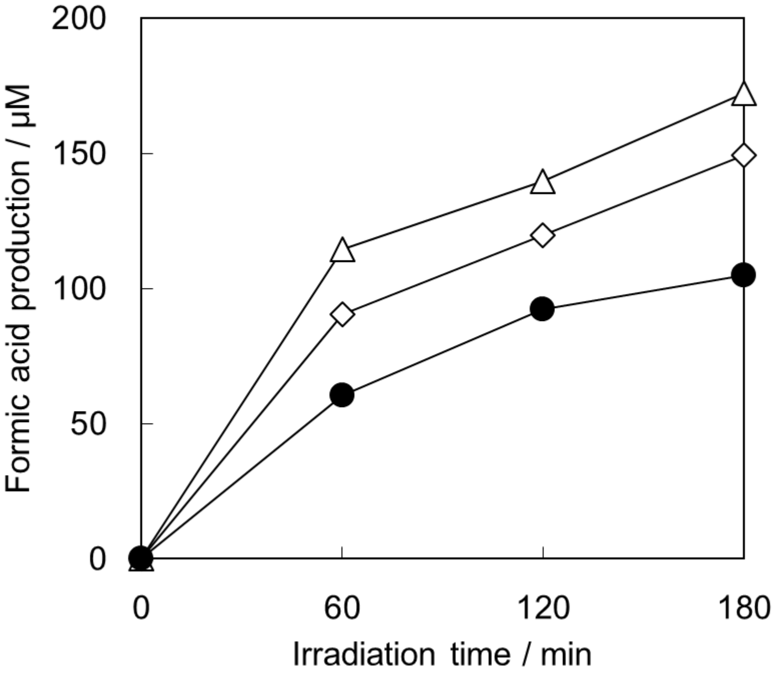
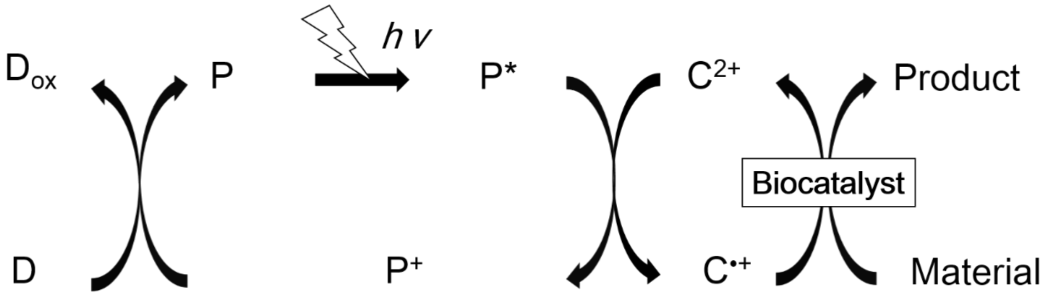


Fig. 5



Scheme 1

Table 1. Reduction potential and dihedral angle of BP.

BP	Reduction potential / V		Dihedral angle / °
	E_{red1}	E_{red2}	
CV	- 0.50	- 0.91	43.9
CMV	- 0.59	-0.93	43.4
MV	- 0.67	-0.98	43.4

Table 2. Conproportion constant and abundance ratio of one electron reduced form of BP.

BP	Conproportion constant	% one electron reduced form
CV	8.7×10^{6}	99.9
CMV	5.7×10^{5}	99.7
MV	1.8×10^{5}	99.5

Table 3. Stern-Volmer Quenching constant K_{sv} of ZnTPPS in the presence of BP.

BP	K_{sv} / μM^{-1}
CV	0.115
CMV	0.141
MV	0.195