Development of a novel electron mediator based on phenylviologen for biocatalyst with CO_2 utilization

Takayuki Katagiri[1], Shusaku Ikeyama[2], Kohei Fujita[1], Yutaka Amao[1,2,*]
[1]*Graduate School of Science, Osaka City University, Osaka, Japan*
[2]*The Advanced Research Institute for Natural Science and Technology, Osaka City University, Osaka, Japan*

*E-mail: katagiri@sci.osaka-cu.ac.jp

1. Introduction

Recently, as a measure against global warming, development of the technologies for reducing greenhouse gases such as CO_2 and the renewable energy are being advanced. Under these circumstances, CO_2 utilization technologies such as artificial photosynthesis have been received much attention. As one of these technologies, molecular conversion reaction systems containing biocatalyst catalyzing a reaction producing a carbon-carbon bond used CO_2 as a feedstock were constructed.

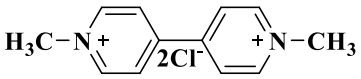
Viologen derivatives act as the electron mediator in photoredox system consisting of an electron donor, a photosensitizer and a catalysis [1]. In this system, methylviologen (MV^{2+}) is widely used as an electron mediator. For the system containing a dehydrogenase with the catalytic CO_2 addition, two-electron reduced phenylviologen (PV^{2+}) is more suitable than MV^{2+} [2]. In this study, novel water soluble viologen derivative based on PV^{2+} skeleton was designed and synthesized, and the photoreduction property of the PV^{2+} derivative was researched in the presence of the photosensitizer.

2. Experiment

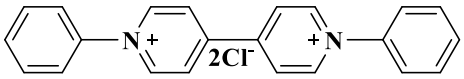
A novel viologen derivative, 1,1'-bis(p-sulfonylphenyl)-4,4'-bipyridinium dichloride (PSV^{2+}) was synthesized from 4,4'-bipyridine and the reduction potentials of PSV^{2+} were measured by cyclic voltammetry (working electrode: glassy carbon, counter electrode: platinum, reference electrode: Ag/AgCl, in 0.2 M KCl). In addition, the photoreduction properties of PSV^{2+} with photosensitization of zinc tetraphenylporphyrin tetrasulfonate (ZnTPPS) were also studied.

3. Results and discussion

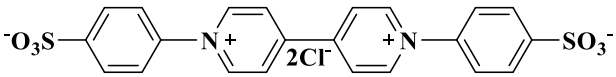
The first and second reduction potentials of PSV^{2+} are -0.38 and -0.72 V, respectively. These reduction potentials are shifted to positive potentials compared with the reduction potentials of MV^{2+} (-0.65 and -1.08 V). From the reduction potentials of PV^{2+} (-0.39 and -0.72 V), the influence of the sulfo group on the reduction potential is limited, and the phenyl group has a large influence on the reduction potential. From a result of photoreduction, the absorption maximum at 650 and 710 nm based on the two-electron reduced form of PSV^{2+} was increased with irradiation time, indicating that two-electron reduced form of PSV^{2+} was produced by photosensitization with porphyrin.



1,1'-Dimethyl-4,4'-bipyridinium dichloride (MV^{2+})



1,1'-Diphenyl-4,4'-bipyridinium dichloride (PV^{2+})



1,1'-Bis(*p*-sulfonylphenyl)-4,4'-bipyridinium dichloride (PSV^{2+})

Fig.1 Chemical structures of viologen derivatives.

Table 1. Reduction potentials of viologen derivatives. (*vs* Ag/AgCl, in 0.2 M KCl)

	E_{red1} (V)	E_{red2} (V)
MV^{2+}	-0.65	-1.08
PV^{2+}	-0.39	-0.72
PSV^{2+}	-0.38	-0.72

REFERENCES

[1] Y. Amao, *ChemCatChem*, 3(2011) 458.
[2] Y. Amao, S. Ikeyama, T. Katagiri, K. Fujita, *Farad. Discuss.*, (2017) in press