**Supporting information**

**Preparation of zinc tetraphenylporphyrin tetrasulfonate (ZnTPPS)**

A 100 mg of tetraphenylporphyrin tetrasulfonate (H\(_2\)TPPS; 83.0 µmol) was dissolved in 150 mL of methanol and then was heated with stirring at 50 °C for 30 min. After that, a 5-fold equivalent of zinc acetate dihydrate (91.0 mg, 410 µmol) was added to the solution and was reflexed at 60 °C for 3 h. The synthesis of ZnTPPS was confirmed by the change of UV-vis absorption spectrum with the spectrophotometer (SHIMADZU, MaltiSpec-1500). During the synthesis of ZnTPPS from H\(_2\)TPPS, the Soret band of H\(_2\)TPPS at 414 nm shifted to 421 nm, four Q bands (516, 552, 580 and 632 nm) disappeared and two new absorption bands at 557 and 595 nm appeared as shown in Figure S1.

![Figure S1. UV-vis absorption spectra of ZnTPPS and H\(_2\)TPPS in the methanol solution.](image-url)
Detection for pyruvate and lactate using an ion chromatography

For the measurement of lactate production in the visible-light driven pyruvate reduction with the system of TEOA, ZnTPPS, MV and Pt-PVP, the lactate or pyruvate was detected using ion chromatography system (Dionex ICS-1100; electrical conductivity detector) with an ion exclusion column (Thermo ICE AS1; column length: 9 x 150 mm; composed of a 7.5 μm cross-linked styrene/divinylbenzene resin with functionalized sulfonate groups). The 1.0 mM octane sulfonic acid and 5.0 mM tetrabutylammonium hydroxide were used as an eluent and a regenerant, respectively. The retention time for lactate was detected at 7.45 min as shown Figure S2.

Figure S2. Chromatogram of lactate (0.80 mM) in 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) buffer (pH 7.0).

Figure S3 shows the relationship between the lactate concentration and the detection peak area at 7.45 min of retention time using an ion chromatograph.

Figure S3. Relationship between the lactate concentration and the detection peak area at 7.45 min of retention time.
As shown in Figure S3, the lactate concentration and the detected peak area showed a good linear relationship (correlation coefficient: \( r^2 = 0.999 \)) as following equation (1).

\[
\text{Peak area} = 1.41 \times [\text{Lactate}] \text{ (mM)} \quad (1)
\]
The amount of lactate was detected using ion chromatography system (Metrohm, Eco IC; electrical conductivity detector) with an ion exclusion column (Metrosep Organic Acids 250/7.8 Metrohm; column size: 7.8 x 250 mm; composed of 9 µm polystyrene-divinylbenzene copolymer with sulfonic acid groups). The 1.0 mM perchloric acid and 50 mM lithium chloride in aqueous solution were used as an eluent and a regenerant, respectively. Flow rate of eluent solution was adjusted to be 0.5 mL min\(^{-1}\).

The retention time for lactate was detected at 12.9 min as shown Figure S5.

Figure S4. Chromatogram of lactate (0.80 mM) in diluted water.

Figure S5 shows the relationship between the lactate concentration and the detection peak area at 12.9 min of retention time using an ion chromatograph.

Figure S5. Relationship between the lactate concentration and the detection peak area at 12.9 min of retention time.

As shown in Figure S5, the lactate concentration and the detected peak area showed a good linear relationship (correlation coefficient: \(r^2=0.999\)) as following equation (2).

\[
\text{Peak area} = 1.43 \times \text{[Lactate] (mM)} \quad (2)
\]
Detection for hydrogen using a gas chromatography

The amount of hydrogen was detected using gas chromatography system (GC-2014, SHIMADZU Corporation) with a thermal conductivity detector (TCD). Activated charcoal column (column length: 3 mm I.D. × 2 m) was equipped for detecting hydrogen gas. The temperature of injection, column and detector were 100.0, 70.0 and 100.0 °C respectively. Argon gas was used by carrier gas and the flow rate was adjusted to be 30.0 mL min⁻¹. The retention time for hydrogen gas was detected around 1.0 min. Figure S6 shows the relationship between the amount of hydrogen and the detection peak area around 1.0 min of retention time using a gas chromatography.

![Figure S6](image)

**Figure S6.** Relationship between the amount of hydrogen and the detection peak area around 1.0 min of retention time.

As shown in Figure S6, the amount of hydrogen and the detected peak area showed a good linear relationship (correlation coefficient: $r^2=0.999$) as following equation (3).

\[
\text{Peak area} = 13112 \times \text{[amount of hydrogen]} \text{ (µmol)} \quad (3)
\]
Chromatogram of electrical conductivity changes in the system of sodium pyruvate and hydrogen gas

Figure S7 shows the electrical conductivity measured using ion chromatography system (Dionex ICS-1100) in the system of sodium pyruvate (2.0 mM) and hydrogen gas (22.3 μmol) in 5.0 ml of 50 mM HEPES buffer (pH 7.0) after 1 h incubation.

![Chromatogram of electrical conductivity changes in the system of sodium pyruvate and hydrogen gas](image)

**Figure S7.** Chromatogram of electrical conductivity changes in the system of sodium pyruvate and hydrogen gas in HEPES buffer (pH 7.0) after 1 h incubation.

Chromatogram of electrical conductivity changes in the system of sodium pyruvate and hydrogen gas in the presence of Pt-PVP

Figure S8 shows the electrical conductivity measured using ion chromatography system (Dionex ICS-1100) in the system of sodium pyruvate (2.0 mM), hydrogen gas (22.3 μmol) and Pt-PVP (164 μM) in 5.0 ml of 50 mM HEPES buffer (pH 7.0) after 1 h incubation.

![Chromatogram of electrical conductivity changes in the system of sodium pyruvate and hydrogen gas in the presence of Pt-PVP](image)

**Figure S8.** Chromatogram of electrical conductivity changes in the system of sodium pyruvate, hydrogen gas and Pt-PVP in HEPES buffer (pH 7.0) after 1 h incubation.
Chromatogram of electrical conductivity changes in the system of consisting of ZnTPPS, MV, Pt-PVP and sodium pyruvate in HEPES buffer (without TEOA)

Figure S9 shows the time dependence of electrical conductivity changes in the system of ZnTPPS (17 µM), MV (1.0 mM), Pt-PVP (160 µM) and sodium pyruvate (2.0 mM) in 5.0 ml of 50 mM HEPES buffer (pH 7.0) under continuous irradiation.

![Chromatogram of electrical conductivity changes in the system of ZnTPPS, MV, Pt-PVP and sodium pyruvate in HEPES buffer (without TEOA)](image)

**Figure S9.** Chromatogram of electrical conductivity changes in the system of ZnTPPS, MV, Pt-PVP and sodium pyruvate in HEPES buffer (pH 7.0) before and after 60 min irradiation.

Chromatogram of electrical conductivity changes in the system of consisting of TEOA, ZnTPPS, MV and sodium pyruvate in HEPES buffer (without Pt-PVP)

Figure S10 shows the time dependence of electrical conductivity changes in the system of TEOA (0.2 M), ZnTPPS (17 µM), MV (1.0 mM) and sodium pyruvate (2.0 mM) in 5.0 ml of 50 mM HEPES buffer (pH 7.0) under continuous irradiation.

![Chromatogram of electrical conductivity changes in the system of TEOA, ZnTPPS, MV and sodium pyruvate in HEPES buffer (without Pt-PVP)](image)

**Figure S10.** Chromatogram of electrical conductivity changes in the system of TEOA, ZnTPPS, MV and sodium pyruvate in HEPES buffer (pH 7.0) before and after 60 min irradiation.
Chromatogram of electrical conductivity changes in the system of TEOA, MV and sodium pyruvate in HEPES buffer (without ZnTPPS)

Figure S11 shows the time dependence of electrical conductivity changes in the system of TEOA (0.2 M), MV (1.0 mM), Pt-PVP (160 µM) and sodium pyruvate (2.0 mM) in the presence of zinc acetate (0.2 mM) in 5.0 ml of 50 mM HEPES buffer (pH 7.0) under continuous irradiation.

**Figure S11.** Chromatogram of electrical conductivity changes in the system of TEOA, MV, Pt-PVP and sodium pyruvate in the presence of zinc acetate in HEPES buffer (pH 7.0) before and after 60 min irradiation.
Table S1. Summary of the various control reactions for visible-light driven pyruvate reduction to lactate.

<table>
<thead>
<tr>
<th>Reaction system</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lactate</td>
</tr>
<tr>
<td>TEOA/ZnTPPS/MV/Pt-PVP containing pyruvate under visible-light</td>
<td>○</td>
</tr>
<tr>
<td>irradiation</td>
<td></td>
</tr>
<tr>
<td>TEOA/ZnTPPS/MV/Pt-PVP containing pyruvate under dark condition</td>
<td>×</td>
</tr>
<tr>
<td>TEOA/ZnTMPyP/MV/Pt-PVP containing pyruvate under visible-light</td>
<td>○</td>
</tr>
<tr>
<td>irradiation</td>
<td></td>
</tr>
<tr>
<td>ZnTPPS/MV/Pt-PVP containing pyruvate under visible-light</td>
<td>×</td>
</tr>
<tr>
<td>irradiation</td>
<td></td>
</tr>
<tr>
<td>TEOA/ZnTPPS/MV containing pyruvate under visible-light</td>
<td>×</td>
</tr>
<tr>
<td>irradiation</td>
<td></td>
</tr>
<tr>
<td>Pyruvate + hydrogen gas</td>
<td>×</td>
</tr>
<tr>
<td>Pyruvate + Pt-PVP+ hydrogen gas</td>
<td>×</td>
</tr>
<tr>
<td>TEOA/ MV/Pt-PVP containing pyruvate and zinc acetate under</td>
<td>×</td>
</tr>
<tr>
<td>visible-light irradiation</td>
<td></td>
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