

Supporting information

An effective visible-light driven fumarate production from gaseous CO₂ and pyruvate by the cationic zinc porphyrin-based photocatalytic system with dual biocatalysts

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1. Experimental setup for the isobaric system

Outline of experimental setup of the isobaric system for direct captured CO₂ gas utilization was shown in Figure S1.¹ In this system, the CO₂ gas in the balloon makes it possible to maintain a constant 1.01325×10^5 Pa pressure in the reaction system.

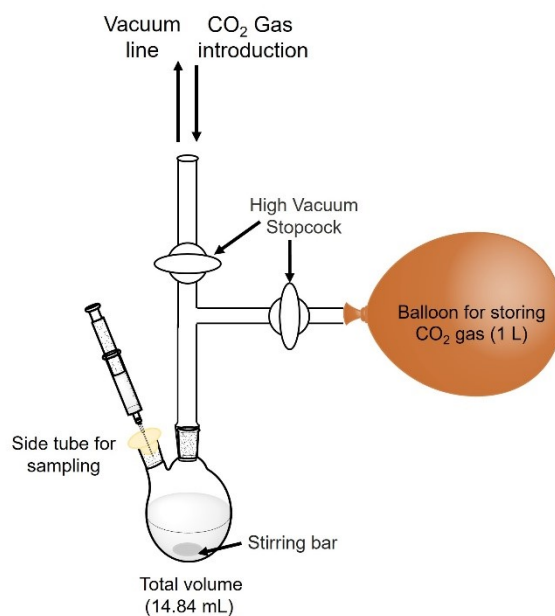


Figure S1. The experimental setup of the isobaric system for direct captured CO₂ gas utilization.

2. Determination for L-malate and fumarate concentration using ion chromatography

The concentrations of L-malate and fumarate were determined 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).¹ 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 L-malate was detected at 10.11-10.13 min. The electrical conductivity changes in the various L-malate concentrations (0 – 1000 μM) during the ion chromatograph analysis were shown in Figure S2(a). Inset of Figure S2(a) shows the relationship between the L-malate concentration and the detection peak area using ion chromatograph.

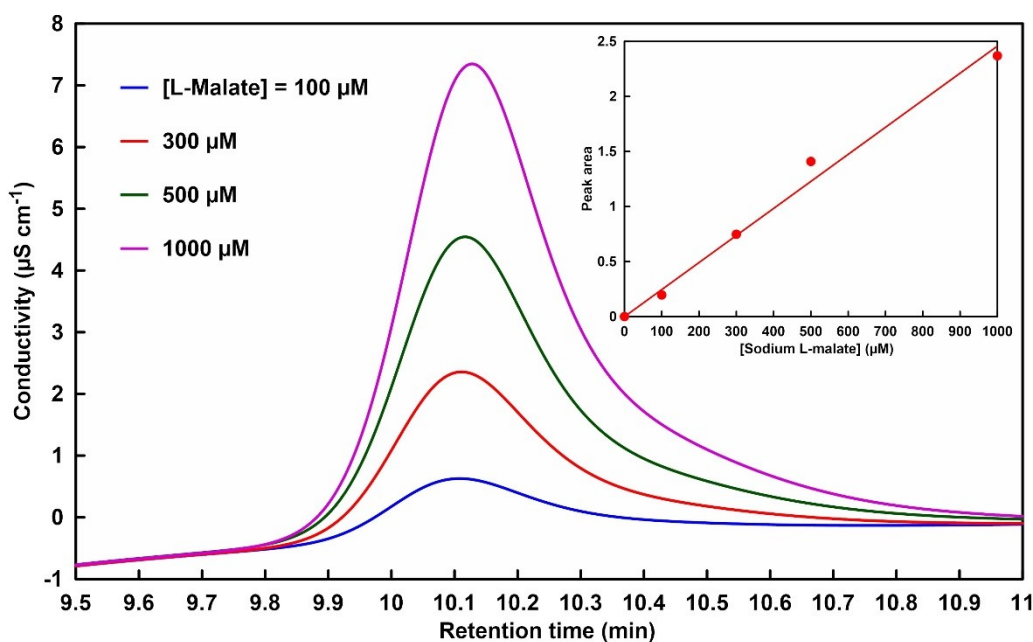
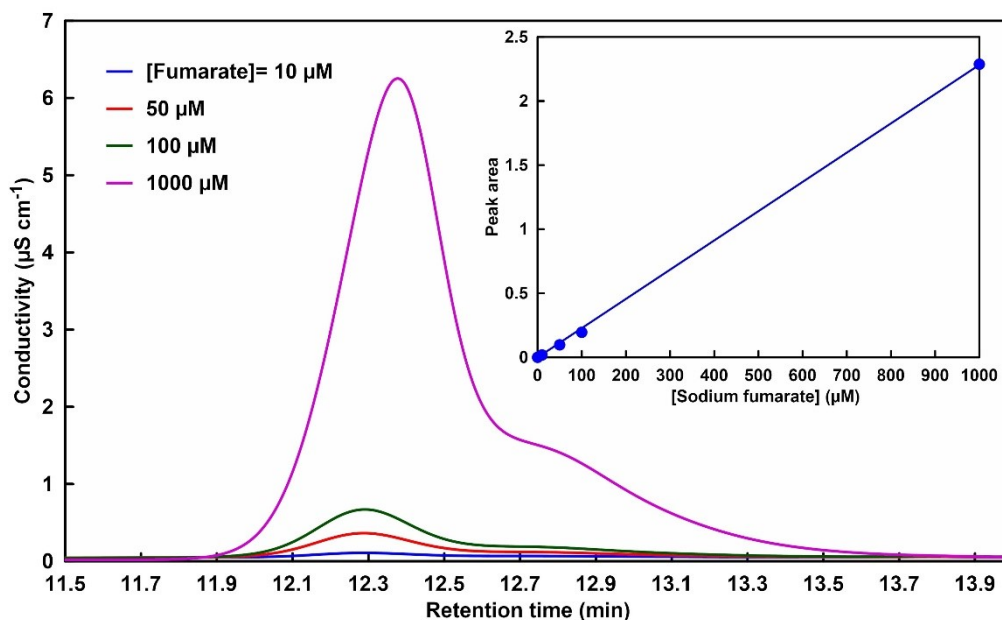


Figure S2(a). Chromatogram of sodium L-malate (0 - 1000 μM) in 50 mM-HEPES buffer (pH 7.0). Inset: Relationship between the L-malate concentration and the detection peak area.

As shown in the inset of Figure S2(a), the L-malate concentration and the detected peak area showed a good linear relationship (correlation coefficient: $r^2=0.999$) as following equation (S1).

$$\text{Peak area} = 2.46 \times 10^{-3} \times [\text{L-malate}] (\mu\text{M}) \quad (\text{S1})$$

The retention time for fumarate was detected at 12.28-12.37 min. The electrical conductivity changes in the various sodium fumarate concentrations (0 – 1000 μM) during the ion chromatograph analysis were shown in Figure S2(b). Inset of Figure S2(b) shows the relationship between the sodium fumarate concentration and the



detection peak area using ion chromatograph.

Figure S2(b). Chromatogram of sodium fumarate (0 – 1000 μM) in 50 mM-HEPES buffer (pH 7.0). Inset: Relationship between the fumarate concentration and the detection peak area.

As shown in the inset of Figure S2(b), the fumarate concentration and the detected peak area showed a good linear relationship (correlation coefficient: $r^2=0.999$) as following equation (S2).

$$\text{Peak area} = 2.28 \times 10^{-3} \times [\text{fumarate}] (\mu\text{M}) \quad (\text{S2})$$

3. Visible-light driven L-malate synthesis from pyruvate and CO₂ with the system of TEOA, zinc porphyrin, [Cp*Rh(bpy)(H₂O)]²⁺, NAD⁺ and MDH

Figure S3 shows a chart of an ion chromatogram sampled from the reaction solution of sodium pyruvate (5.0 mM), magnesium chloride (5.0 mM), TEOA (0.2 M), ZnTMAP⁴⁺ (50 μM), [Cp*Rh(bpy)(H₂O)]²⁺ (10 μM), NAD⁺(0.5 mM) and MDH (0.7 U, *ca.* 1.6 μM) in 5 mL of 500 mM HEPES-NaOH buffer (pH 7.8) after 1 and 5 h irradiation. The gas phase was filled with CO₂ gas.

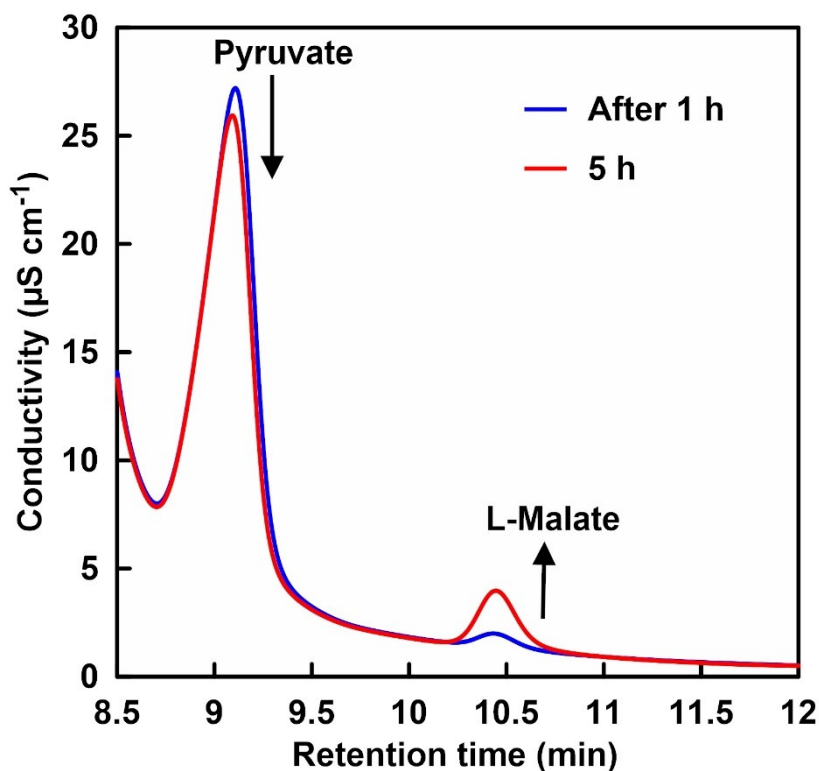


Figure S3. A chart of an ion chromatogram for pyruvate or L-malate concentration in the solution of sodium pyruvate (5.0 mM), magnesium chloride (5.0 mM), TEOA (0.2 M), ZnTMAP⁴⁺ (50 μM), [Cp*Rh(bpy)(H₂O)]²⁺ (10 μM), NAD⁺(0.5 mM) and MDH (0.7 U, *ca.* 1.6 μM) in 5 mL of 500 mM HEPES-NaOH buffer (pH 7.8) after 1 and 5 h irradiation. The gas phase was filled with CO₂ gas.

Figure S4 shows a chart of an ion chromatogram sampled from the reaction solution of sodium pyruvate (5.0 mM), magnesium chloride (5.0 mM), TEOA (0.2 M), ZnTPPS⁴⁺ (10 μM), [Cp*Rh(bpy)(H₂O)]²⁺ (10 μM), NAD⁺(0.5 mM) and MDH (0.7 U, *ca.* 1.6 μM) in 5 mL of 500 mM HEPES-NaOH buffer (pH 7.8) after 1 and 5 h irradiation. The gas phase was filled with CO₂ gas.

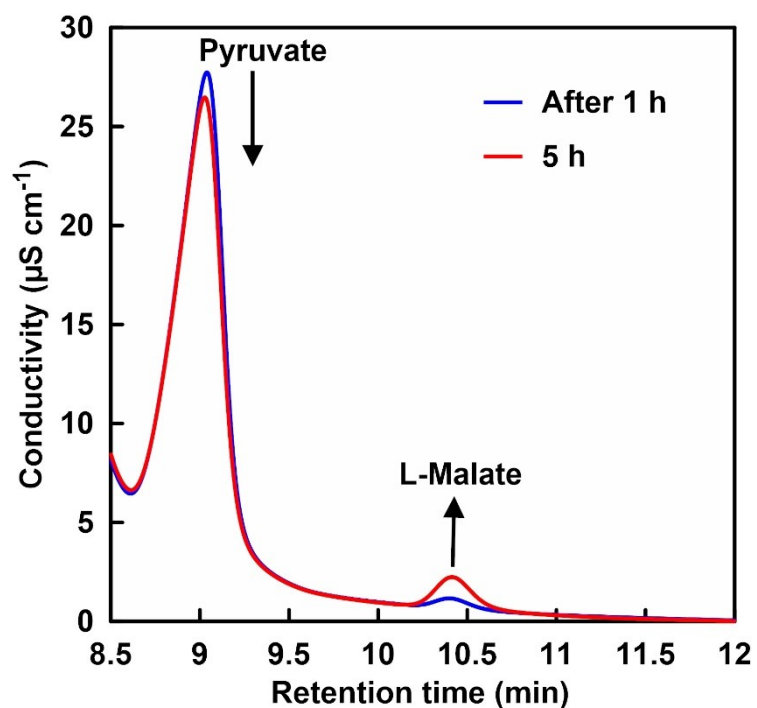
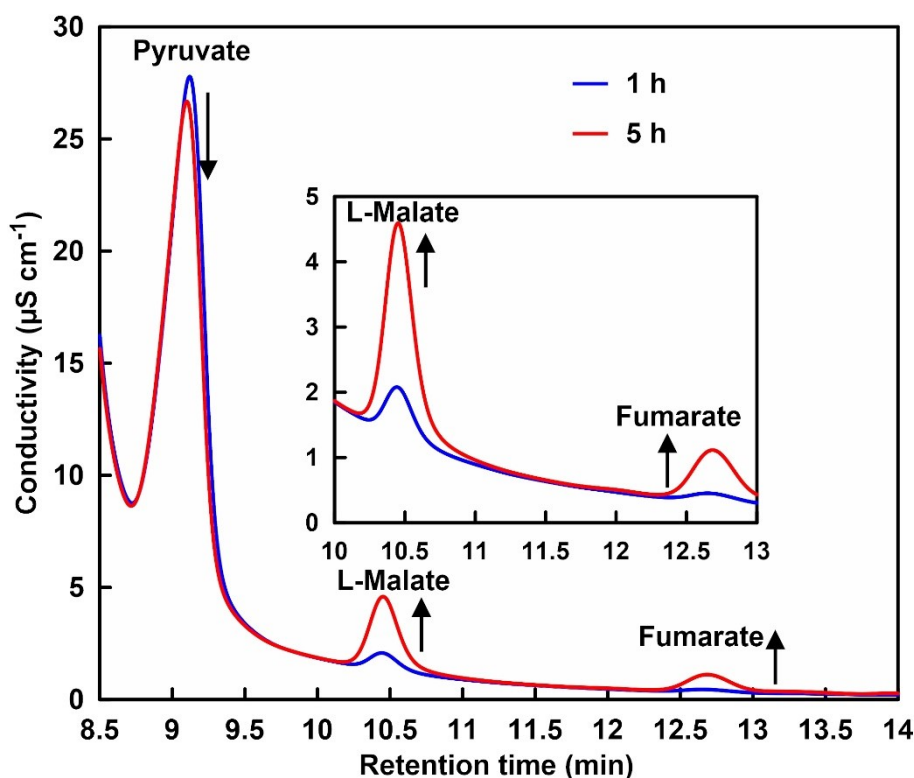


Figure S4. A chart of an ion chromatogram for pyruvate or L-malate concentration in the solution of sodium pyruvate (5.0 mM), magnesium chloride (5.0 mM), TEOA (0.2 M), ZnTPPS⁴⁻ (10 μM), [Cp*Rh(bpy)(H₂O)]²⁺ (10 μM), NAD⁺ (0.5 mM) and MDH (0.7 U, *ca.* 1.6 μM) in 5 mL of 500 mM HEPES-NaOH buffer (pH 7.8) after 1 and 5 h irradiation. The gas phase was filled with CO₂ gas.

4. Visible-light driven fumarate synthesis from pyruvate and CO₂ with the system of TEOA, zinc porphyrin, [Cp*Rh(bpy)(H₂O)]²⁺, NAD⁺, MDH and FUM

Figure S5 shows a chart of an ion chromatogram sampled from the reaction solution of sodium pyruvate (5.0 mM), magnesium chloride (5.0 mM), TEOA (0.2 M), ZnTMAP⁴⁺ (50 μM), [Cp*Rh(bpy)(H₂O)]²⁺ (10 μM), NAD⁺ (0.5 mM), MDH (0.7 U, *ca.* 1.6 μM) and FUM (0.5 U; 1.3 nM) in 5 mL of 500 mM HEPES-NaOH buffer (pH 7.8) after 1 and 5 h



irradiation. The gas phase was filled with CO₂ gas.

Figure S5. A chart of an ion chromatogram for pyruvate, L-malate or fumarate concentration in the solution of sodium pyruvate (5.0 mM), magnesium chloride (5.0 mM), TEOA (0.2 M), ZnTMAP⁴⁺ (50 μM), [Cp*Rh(bpy)(H₂O)]²⁺ (10 μM), NAD⁺ (0.5 mM), MDH (0.7 U, *ca.* 1.6 μM) and FUM (0.5 U; 1.3 nM) in 5 mL of 500 mM HEPES-NaOH buffer (pH 7.8) after 1 and 5 h irradiation. The gas phase was filled with CO₂ gas.

Figure S6 shows a chart of an ion chromatogram sampled from the reaction solution of sodium pyruvate (5.0 mM), magnesium chloride (5.0 mM), TEOA (0.2 M), ZnTPPS⁴⁺ (10 μM), [Cp*Rh(bpy)(H₂O)]²⁺ (10 μM), NAD⁺ (0.5 mM), MDH (0.7 U, *ca.* 1.6 μM) and FUM (0.5 U; 1.3 nM) in 5 mL of 500 mM HEPES-NaOH buffer (pH 7.8) after 1 and 5 h

irradiation. The gas phase was filled with CO₂ gas.

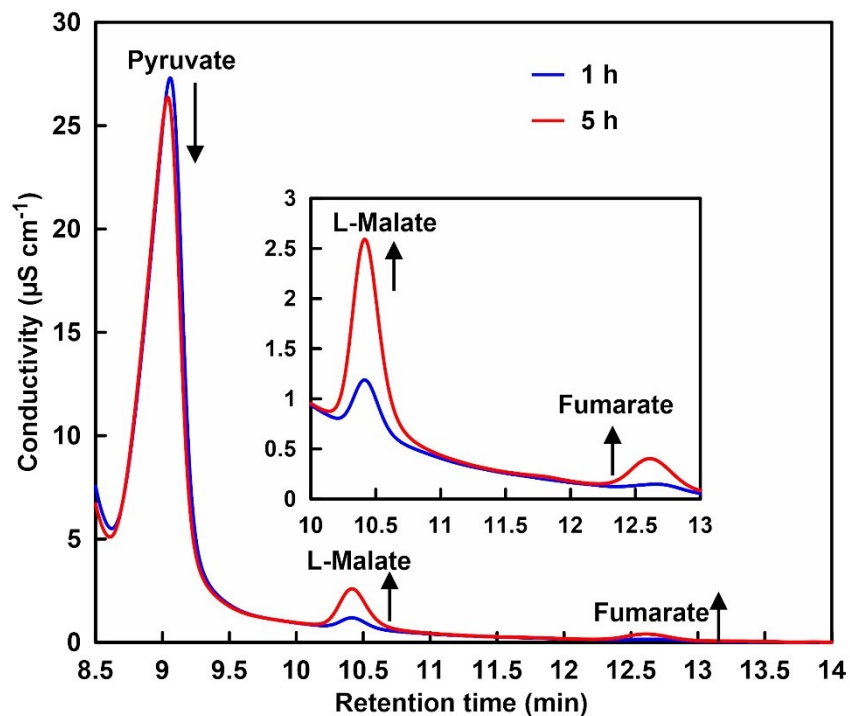


Figure S6. A chart of an ion chromatogram for pyruvate, L-malate or fumarate concentration in the solution of sodium pyruvate (5.0 mM), magnesium chloride (5.0 mM), TEOA (0.2 M), ZnTPPS⁴⁻ (10 μM), [Cp*Rh(bpy)(H₂O)]²⁺ (10 μM), NAD⁺ (0.5 mM), MDH (0.7 U, *ca.* 1.6 μM) and FUM (0.5 U; 1.3 nM) in 5 mL of 500 mM HEPES-NaOH buffer (pH 7.8) after 1 and 5 h irradiation. The gas phase was filled with CO₂ gas.

Figure S7 shows a chart of an ion chromatogram sampled from the reaction solution of sodium pyruvate (5.0 mM), magnesium chloride (5.0 mM), TEOA (0.2 M), ZnTPPS⁴⁻ (50 μM), [Cp*Rh(bpy)(H₂O)]²⁺ (10 μM), NAD⁺ (0.5 mM), MDH (0.7 U, *ca.* 1.6 μM) and FUM (0.5 U; 1.3 nM) in 5 mL of 500 mM HEPES-NaOH buffer (pH 7.8) after 1 and 5 h irradiation. The gas phase was filled with CO₂ gas.

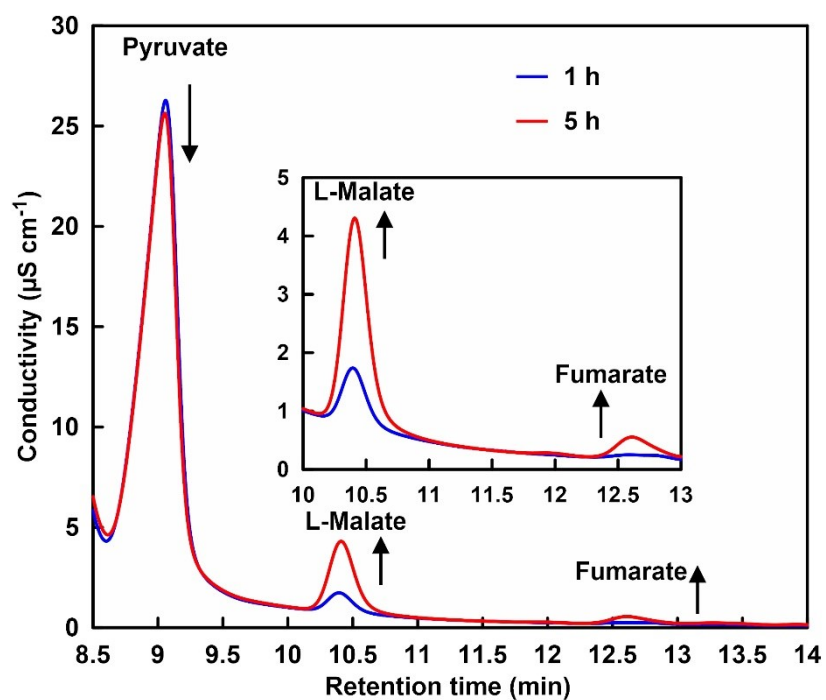


Figure S7. A chart of an ion chromatogram for pyruvate, L-malate or fumarate concentration in the solution of sodium pyruvate (5.0 mM), magnesium chloride (5.0 mM), TEOA (0.2 M), ZnTPPS⁴⁻ (50 μM), [Cp*Rh(bpy)(H₂O)]²⁺ (10 μM), NAD⁺ (0.5 mM), MDH (0.7 U, *ca.* 1.6 μM) and FUM (0.5 U; 1.3 nM) in 5 mL of 500 mM HEPES-NaOH buffer (pH 7.8) after 1 and 5 h irradiation. The gas phase was filled with CO₂ gas.