Electronic Supplementary Information

Catalytic oxidation of formic acid by dioxygen with an organoiridium complex

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Experimental Section

General Methods

All experiments were performed under an Ar or N_2 atmosphere by using standard Schlenk techniques unless otherwise noted. Purification of water (18.2 MΩ cm) was performed with a Milli-Q system (Millipore; Direct-Q 3 UV). The ^1H NMR spectra were recorded on JEOL JNM-AL300 spectrometer and Varian UNITY INOVA600. The formate was detected and analyzed by ^1H NMR measurements of the reaction solution with 3-(trimethylsilyl)propionic-2,2',3,3'-d_4 acid sodium salt (TSP, 10 mM) as an internal standard using a sealed capillary tube (i.d. = 1.5 mm) filled with D_2O for deuterium lock. The pH values were determined by a pH meter (TOA, HM-20J) equipped with a pH combination electrode (TOA, GST-5725C). The pH of the solution was adjusted by adding an aliquot of 1.00 M H_2SO_4/H_2O and 1.00-10.0 M KOH/H_2O solutions without buffer unless otherwise noted. Hydrogen and carbon dioxide gases were analyzed by a Shimadzu GC-14B gas chromatograph {N_2 carrier, active carbon with a particle size of 60–80 mesh at 353 K} equipped with a thermal conductivity detector. The experimental error in the calibration of GC was ±5%.

Chemicals.

Chemicals were purchased from commercial source and used without purification, unless otherwise noted. A water-soluble iridium complex **1** was synthesized by the following method.[1] An aqueous solution (50 mL) of $[Ir^{III}(Cp^*)(H_2O)_3](SO_4)$ (0.20 g, 0.423 mmol) and 4-(1*H*-pyrazol-1-yl)benzoic acid (0.085 g, 0.454 mmol) was stirred under reflux for 12 h. The reaction solution was filtered with a membrane filter (Toyo Roshi Kaisha, Ltd., H100A025A; pore diameter, 1 mm). The filtrate was evaporated under reduced pressure to yield a yellow powder of **1** and was dried in vacuo. ^1H and ^{13}C NMR, FTIR, ESI-MS and elementary analysis data of **1** have been previously reported.[1] Formic acid (> 99%) and ethylene glycol (> 99.5%) were purchased from Wako Pure Chemical Industries Ltd.

Oxo[5,10,15,20-tetra(4-pyridyl)porphinato]titanium(IV) ([TiO(tpyp)]) was supplied from Tokyo Chemical Industry Co., Ltd. (TCI). $Sc(NO_3)_3 \cdot 4H_2O$ (99.9%) was supplied from Mitsuwa Chemicals Co. Formic acid-*d* (DCOOH, > 99.5 %, 98 % D) and D_2O (99.9% D) were purchased from Cambridge Isotope Laboratories. Purification of water (18.2 MW cm) was performed with a Milli-Q system (Millipore; Direct-Q 3 UV).

Oxidation of formic acid (HCOOH) or formic acid-*d* (DCOOH) by dioxygen with 1 in water

An aqueous solution (5.0 μL) of HCOOH (0.4 M) or DCOOH (0.4 M) was added to 1.0 mL of water containing **1** (10 μM) and O_2 (1.4 mM in O_2-saturated solution) in a glass vial (~1 cm i.d.) sealed with a rubber septum at pH 2.8 at 298 K. In a similar manner, an anaerobic reaction was conducted in an N_2-saturated solution under otherwise the same experimental conditions. After the equilibrium is established, an aliquot (50 μL) of the gaseous headspace was sampled by means of a gastight syringe and then transferred to a gas chromatograph (Shimadzu GC-14B) for hydrogen and carbon dioxide analyses.

Oxidation of formic acid by dioxygen with 1 in a water-containing ethylene glycol

Typically, 10 μL of an aqueous solution of HCOOH (0.4 M) was added to 2.0 mL of a mixed solution (2.0 mL) of an ethylene glycol and water [40:1 (v/v)] containing **1** (2.5 μM) in a glass vial (~1 cm i.d.) sealed with a rubber septum at pH 4.3-5.9 at 298 K under O_2 atmosphere. In a similar manner, an anaerobic reaction was conducted in an N_2-saturated solution under otherwise the same experimental conditions. After the equilibrium is established, an aliquot (50 μL) of the gaseous headspace was sampled by means of a gastight syringe and then transferred to a gas chromatograph (Shimadzu GC-14B) for hydrogen and carbon dioxide analyses. The concentrations of HCOOH were changed from 2.0 mM to 0.50 M and those of **1** from 2.5 μM to 18 μM. The ratio of an ethylene glycol and water were also changed from 40:1 (v/v) to 4:1 (v/v).

Detection of hydrogen peroxide.

The amount of produced hydrogen peroxide was determined by spectroscopic titration with an acidic solution of $[\mathrm{TiO(tpypH_4)}]^{4+}$ complex (Ti-TPyP reagent).[2] The Ti-TPyP reagent was prepared by dissolving 34.03 mg of the [TiO(tpyp)] complex in 1000 mL of 50 mM hydrochloric acid. A small portion (100 mL) of the reaction solution was sampled and diluted with water. To 0.25 mL of the diluted sample, 0.25 mL of 4.8 M perchloric acid and 0.25 mL of the Ti-TPyP reagent were added. The mixed solution was then allowed to stand for 5 min at room temperature. This sample solution was diluted to 2.5 mL with water and used for the spectroscopic measurement. The absorbance at λ = 434 nm was measured by using a Hewlett Packard 8453 diode array spectrophotometer (A_S). A blank solution was prepared in a similar manner by adding distilled water instead of the sample solution in the same volume with its absorbance designated as A_B. The difference in absorbance was determined as follows: $\Delta A_{434} = A_\mathrm{B} - A_\mathrm{S}$. Based on ΔA_{434} and the volume of the solution, the amount of hydrogen peroxide was determined according to the literature.[2]

pH Adjustment.

The pH values of the solutions were determined by a pH meter (TOA, HM-20J) equipped with a pH combination electrode (TOA, GST-5725C). The pH of solution was adjusted by using 1.0 M H_2SO_4/H_2O and 1.00–10.0 M KOH/H_2O without buffer unless otherwise noted.

Reference

1. Y. Maenaka, T. Suenobu and S. Fukuzumi, *Energy Environ. Sci.*, 2012, **5**, 7360.
2. C. Matsubara, N. Kawamoto and K. Takamura, *Analyst,* 1992, **117**, 1781.

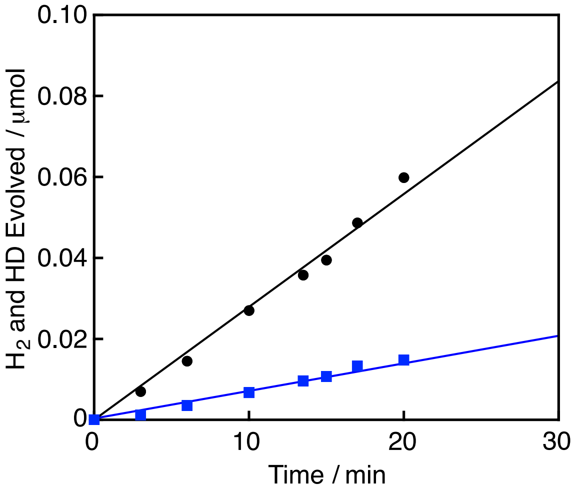

Fig. S1 Time courses of hydrogen evolution from HCOOH (2.0 mM; black circle) and DCOOH (2.0 mM; blue square) solutions (1.0 mL) in the presence of **1** (10 µM) under O_2 atmosphere at pH 2.8 at 298 K. $R^2 = 0.99$ and 0.99 for the linear correlations (black and blue, respectively).

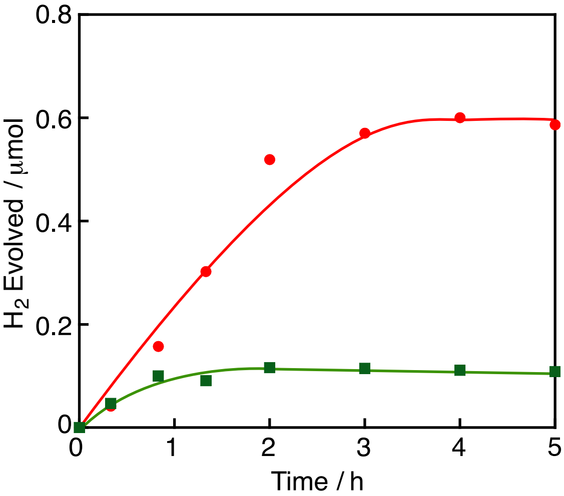

Fig. S2 Time courses of H_2 evolution from an ethylene glycol and water [9:1 (v/v)] mixed solution (2.0 mL) of formic acid (10 mM) in the presence of **1** (10 μM) under N_2 and O_2 atmosphere (red circle and green square, respectively) at pH 4.5 at 298 K.

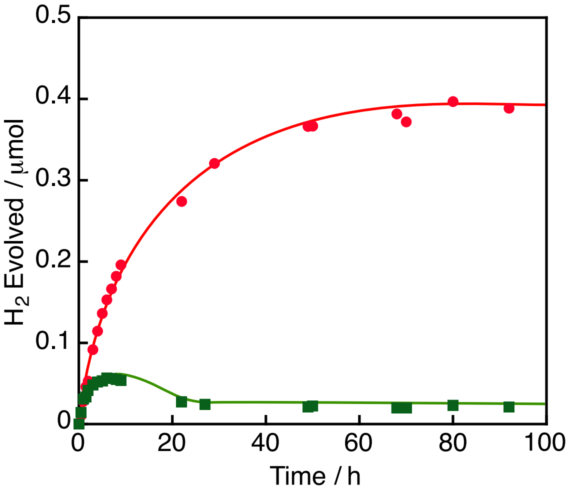

Fig. S3 Time courses of H_2 evolution from an ethylene glycol and water [40:1 (v/v)] mixed solution (2.0 mL) of formic acid (2.0 mM) in the presence of **1** (2.5 μM) under N_2 and O_2 atmosphere (red circle and green square, respectively) at pH 4.3 at 298 K.

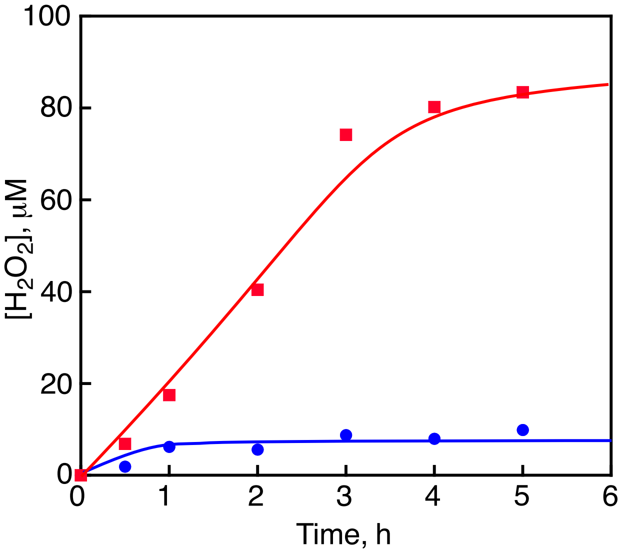

Fig. S4 Time courses of H_2O_2 formation from an ethylene glycol and water [40:1 (v/v)] mixed solution (2.0 mL) of formic acid (2.0 mM) containing **1** (2.5 μM) in the absence of FMN (blue circle) and in the presence of FMN (50 μM, red square) under O_2 atmosphere at pH 4.3 at 298 K.