Electronic Supplementary Information

Catalytic hydrogen production from paraformaldehyde and water with an organoiridium complex

Tomoyoshi Suenobu*, Yusuke Isaka, Satoshi Shibata and Shunichi Fukuzumi*

Department of Material and Life Science, Graduate School of Engineering, Osaka University, ALCA, Japan Science and Technology Agency (JST), Suita, Osaka 565-0871, Japan

E-mail: fukuzumi@chem.eng.osaka-u.ac.jp, suenobu@chem.eng.osaka-u.ac.jp

Table of contents

Experimental section

Materials

A water-soluble iridium complex **1** was synthesised as reported previously.[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 μm). The filtrate was evaporated under reduced pressure to yield a yellow powder of **1** and was dried in vacuo. **1** was analysed by ^{1}H and ^{13}C NMR, FTIR, ESI-MS and elementary analysis as reported previously.[1] Paraformaldehyde (white powder, 1st Grade, 94.0+% as HCHO) and formalin (formaldehyde solution without stabilizer, 1st Grade, 35.0~38.0% as HCHO) were purchased from Wako Pure Chemical Industries Ltd. 3-(Trimethylsilyl)propionic-2,2′,3,3′-d_4 acid sodium salt (TSP, >98%) was purchased from Aldrich Chemicals Co. Commercially available reagents: sodium hydroxide and diluted sulphuric acid (0.5 M) (Wako Pure Chemical Industries) were the best available purity and used without further purification unless otherwise noted. Purification of water (18.2 MW cm) was performed with a Milli-Q system (Millipore; Direct-Q 3 UV).

General methods

All experiments were performed under an Ar or N_2 atmosphere by using standard Schlenk techniques unless otherwise noted. The ^{1}H NMR spectra were recorded on JEOL JNM-AL300 spectrometer and Varian UNITY INOVA600. The UV-visible absorption spectra were recorded using a Hewlett Packard 8453 diode array spectrophotometer with a quartz cuvette (light-path length = 1 cm) at 298 K. Infrared spectra of solid samples were recorded on a JASCO FT/IR-6200 instrument with 0.25 cm^{-1} resolution at ambient temperature. The solid powder samples were sandwiched with two clean and polished KBr plates and manually compressed to form a thin layer of the solid between the plates. The powder mixture of **2** and paraformaldehyde was obtained by evaporation of an aqueous solution containing both **2** and paraformaldehyde with a Smart Evaporator CEV1-GR (Bio

Chromato, Inc.) at room temperature. The electrospray ionization mass spectrometry (ESI-MS) data were obtained by a micrOTOF focus II mass spectrometer (Bruker Daltonics), equipped with an ion spray interface for positive or negative ion detection modes and N_2 was employed to assist liquid nebulization. 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 using 1.00 M H_2SO_4/H_2O and 1.00-10.0 M $NaOH/H_2O$ without buffer unless otherwise noted.

Catalytic hydrogen evolution

Typically, 0.5 mL of an aqueous solution of $[\mathbf{1}]_2\cdot SO_4$ (10 μM) was added to 0.5 mL of a paraformaldehyde aqueous solution (2.0 mg) at pH 6-11 at 298 K. The amount of evolved hydrogen gas was determined by analyzing the content of the evolved gas with gas chromatograph. H_2 and CO_2 gases were analysed 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. For the measurement of evolved gas amount, pH of the reaction solution was adjusted to 3.0 by adding 0.5 M H_2SO_4 so as to convert carbonate (CO_3^{2-}) or bicarbonate (HCO_3^-) ions dissolved in solution into CO_2 gas. The contaminated O_2 gas was detected by Shimadzu GC-17A gas chromatograph {Ar carrier, a column with molecular sieves (Agilent Technologies, 19095P-MS0) at 313 K} equipped with a thermal conductivity detector and the amount of O_2 was confirmed to be negligible. For the measurements of time course of H_2 evolution depending on pH of an aqueous paraformaldehyde solution, pH was changed from 6.0 to 10 by adding an aliquot of 0.5 M H_2SO_4 or 1.0 M NaOH. For the measurements of H_2 evolution from formalin (66.7 μmol), 0.5 mL of an aqueous solution of $[\mathbf{1}]_2\cdot SO_4$ (10 μM) was added to 0.5 mL of diluted formalin solution at pH 11 at 298 K. The rate of hydrogen evolution was determined at 298 K and 313 K.

Reference

1. Y. Maenaka, T. Suenobu and S. Fukuzumi, *Energy Environ. Sci.*, 2012, **5**, 7360.

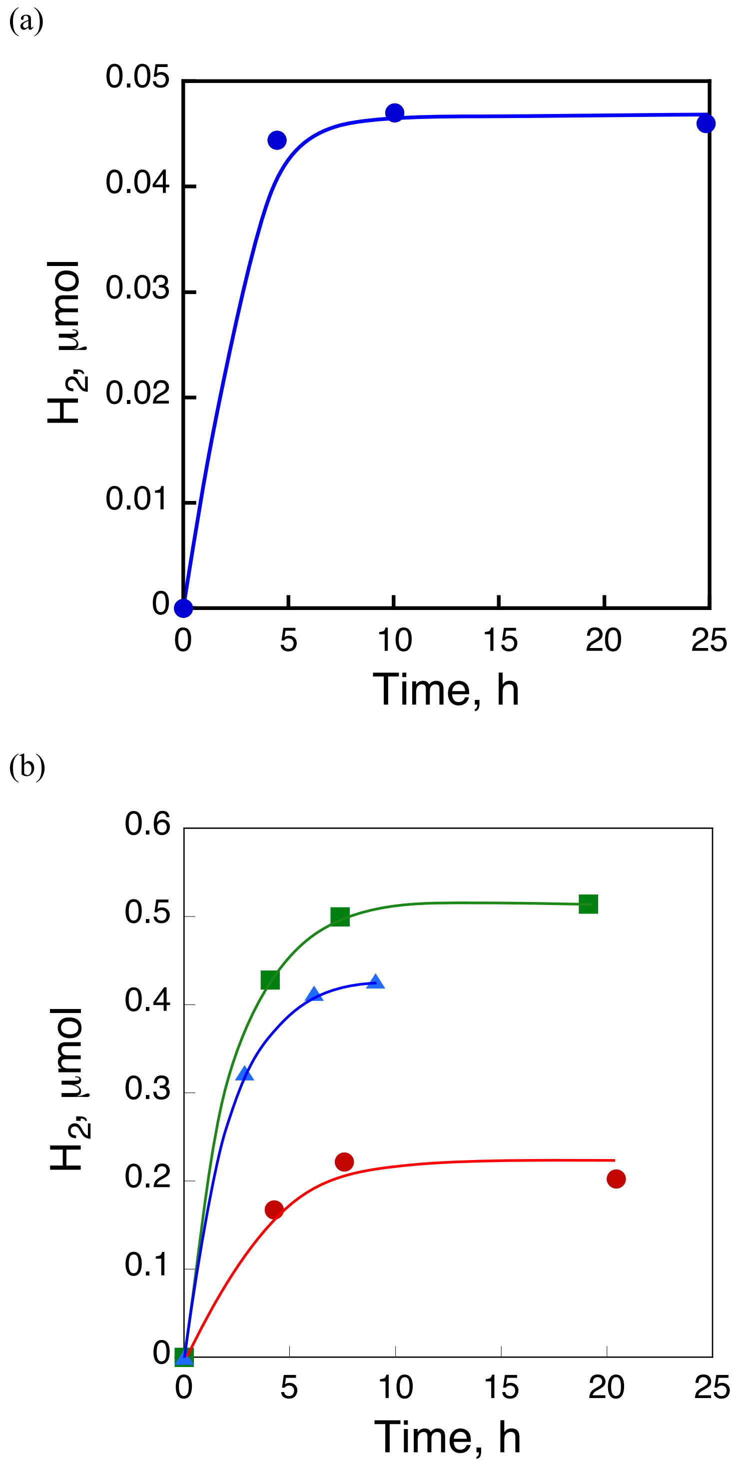

Fig. S1 Time course of H_2 evolution from deaerated aqueous solution of paraformaldehyde (66.7 µmol) in the presence of (a) **3** (1.0 µM, 1.0 mL) at 298 K at pH 11 and (b) **3** (5.0 µM, 1.0 mL) at 313 K (blue triangle), 333 K (green square) and 353 K (red circle) at pH 11.

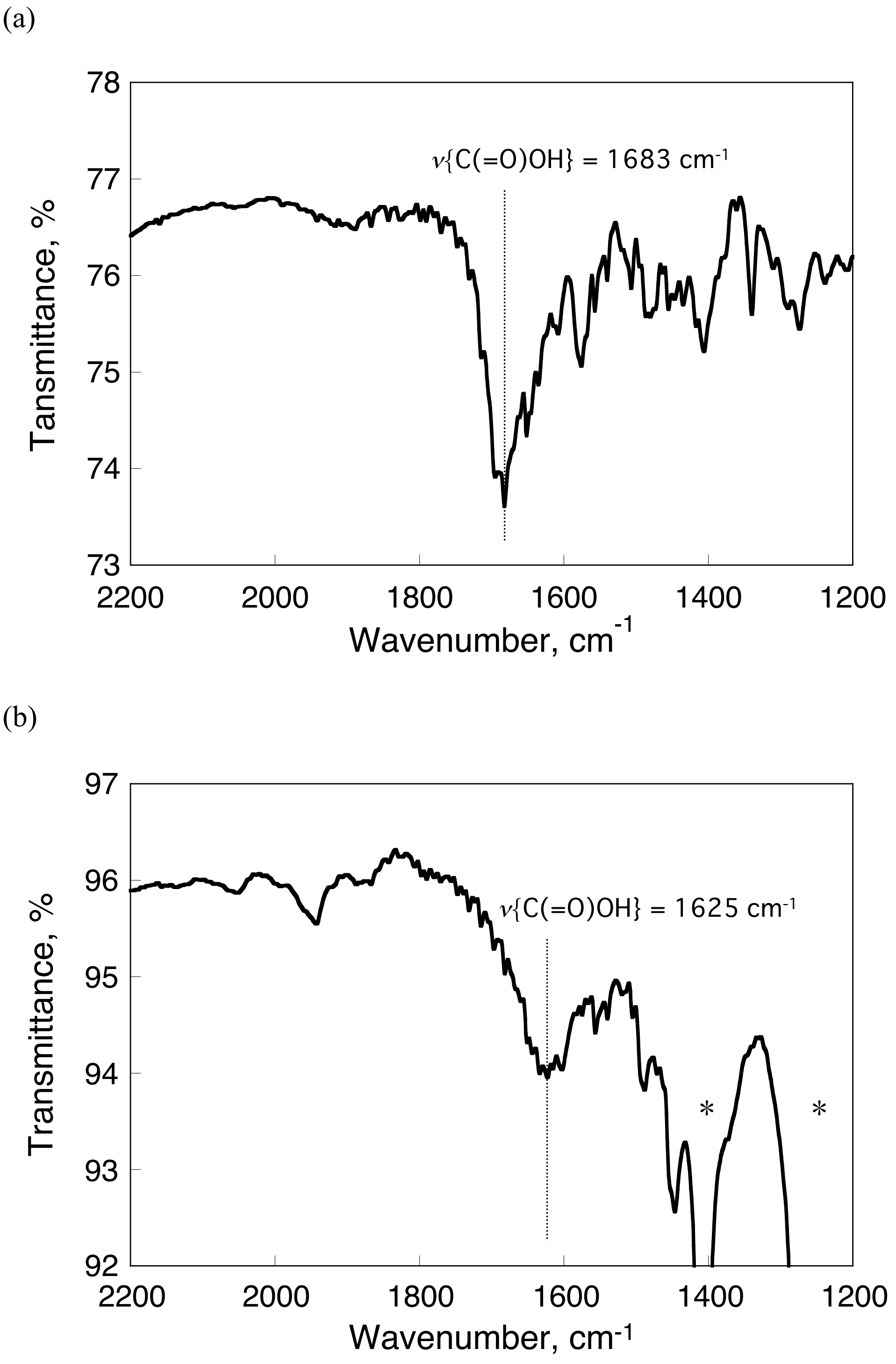

Fig. S2 IR spectra of (a) a solid powder of **2** and (b) that of the mixture of **2** and paraformaldehyde. The mixture was prepared by evaporating a mixed solution (2.0 mL) of **2** (25 μM) and paraformaldehyde (31 μM) that was stirred for 1 h in advance at pH 7 at room temperature. The astarisk mark (*) denotes the strong absorption due to paraformaldehyde.

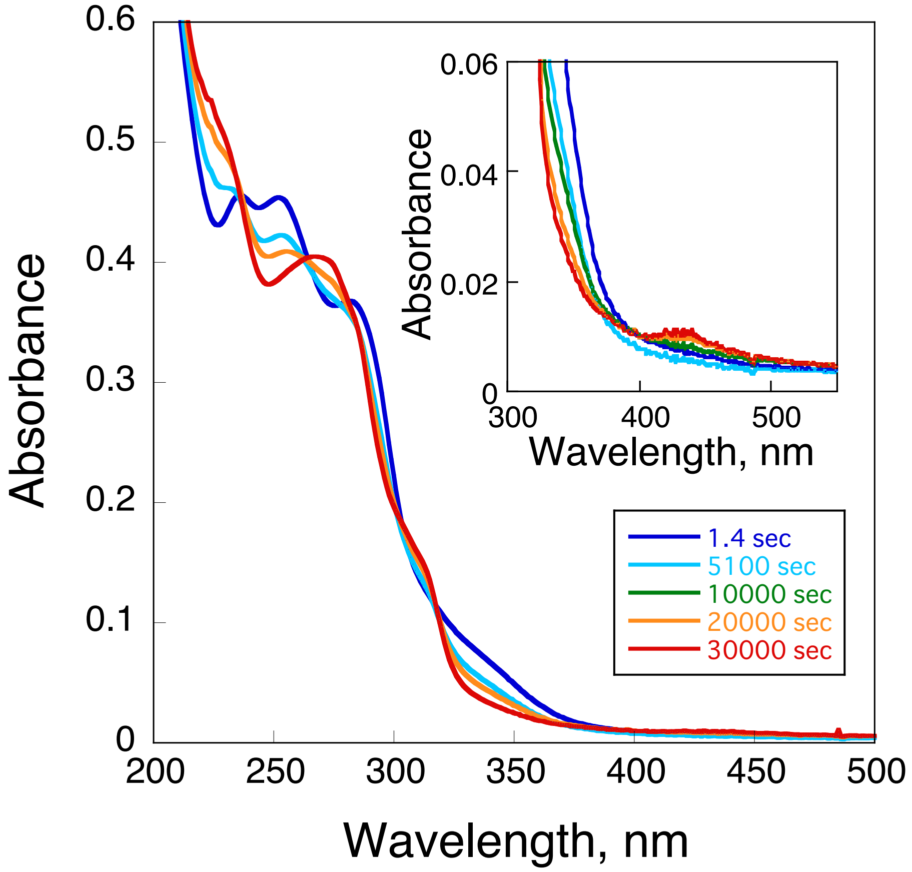

Fig. S3 Time-based UV-visible absorption spectral changes of a deaerated aqueous solution of **2** (25 µM, 2.0 mL) after addition of formalin (66.7 µmol) at pH 7. Inset: Magnified view of the wavelength region $\lambda > 300$ nm.

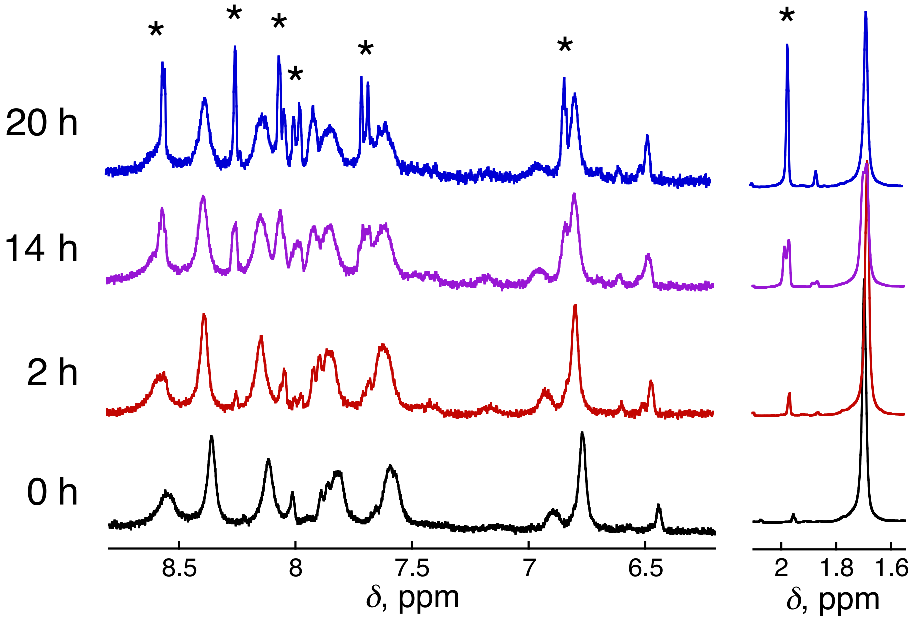

Fig. S4 Time-based changes of ^{1}H-NMR spectrum of **3** (3.3 mM, t = 0 h) in a D_2O solution upon addition of paraformaldehyde (9.6 mM) at 298 K containing TSP as an internal standard using a sealed capillary tube (i.d. = 1.5 mm) filled with D_2O. The peaks with asterisk marks (*) could be assigned to the ligands of the formate complex, [**Ir**-OC(=O)H]$^-$. The values of chemical shift are listed below. The slightly down-field shift ($\Delta\delta \sim +0.1$ ppm) of the peaks at $8.6 > \delta > 6.7$ as well as the up-field shift ($\Delta\delta \sim -0.02$ ppm) of a peak at $\delta = 1.7$ (η^5-$C_5(C\underline{H}_3)_5$) from t = 0 h to t = 2 h might correspond to the formation of the methanediol adduct [**Ir**-OCH_2OH]$^-$ (or **Ir**-$HOCH_2OH$) that remains until t = 20 h. Peaks assignable to the C-H proton of free and coordinated methanediol as well as formate do not appear because of fast H-D exchange of C-H proton in methanediol in basic D_2O. The line broadnig might be due to fast exchange of the ligands, e.g., $HOCH_2O^-$ (or $HOCH_2OH$) as well as the hydrogen bonding with the solvent D_2O.

[**Ir**-OC(=O)H]$^-$: ^{1}H NMR (300 MHz, in D_2O, reference to TSP, 298 K, pD 11): δ (ppm) 1.98 (s, η^5-$C_5(C\underline{H}_3)_5$, 15H), 6.83 (d, J = 3 Hz, 1H), 7.69 (d, J = 8 Hz, 1H), 7.98 (d, J = 8 Hz, 1H), 8.04 (d, J = 5 Hz, 1H), 8.24 (s, 1H), 8.55 (d, J = 3 Hz, 1H)

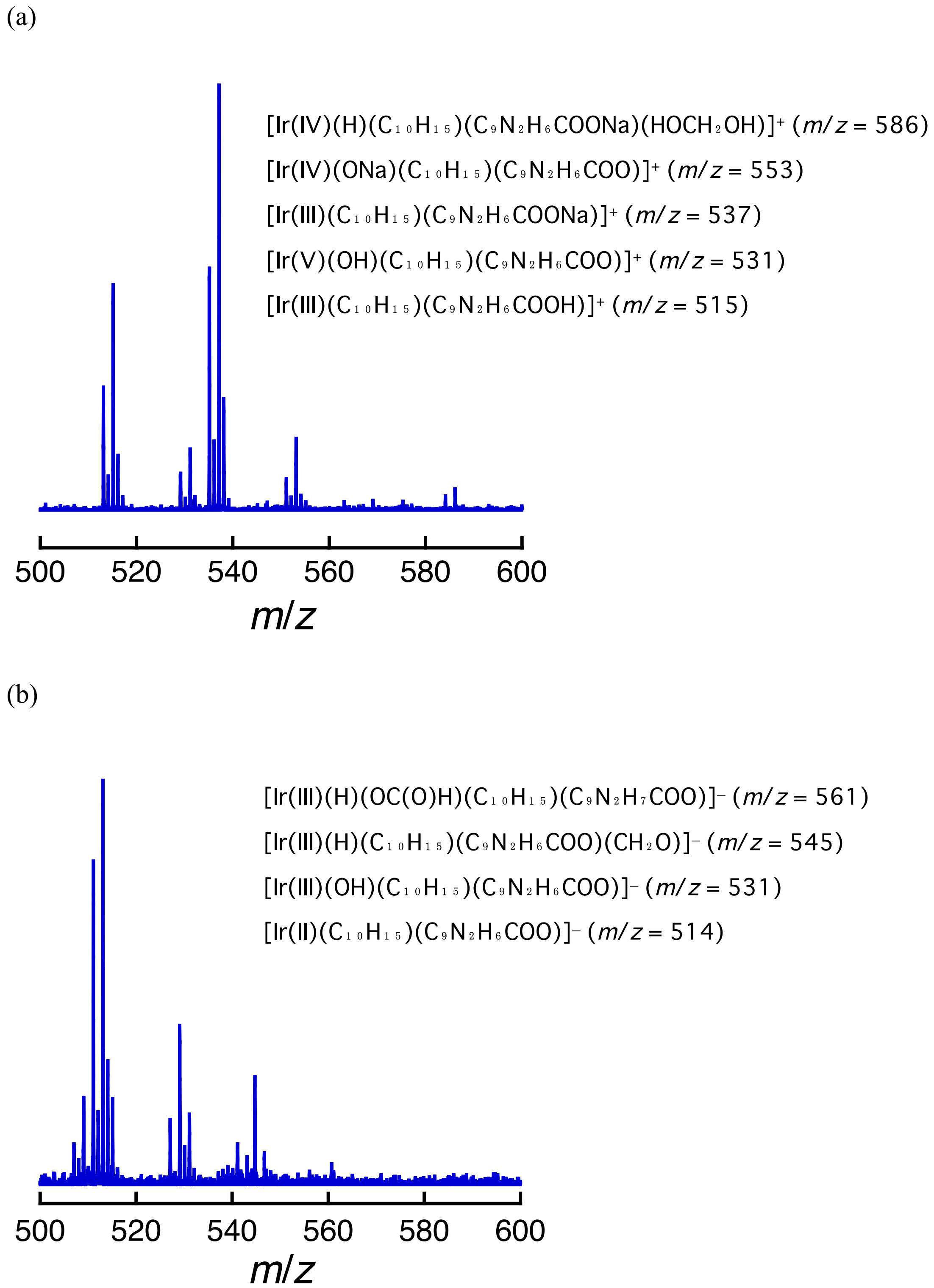

Fig. S5 ESI-MS spectra observed under (a) the positive-ion mode for a deaerated aqueous solution of **3** (3.3 mM) in the presence of paraformaldehyde (9.6 mM) for 14 h at 298 K at pH 11 and (b) the negative-ion mode. The solution was diluted by 100 times with deaerated H_2O and supplied for the measurement.