Supplementary Information

Stability of Pt(II)-based H_2-evolving catalysts against H_2 in aqueous solution

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Experimental Section

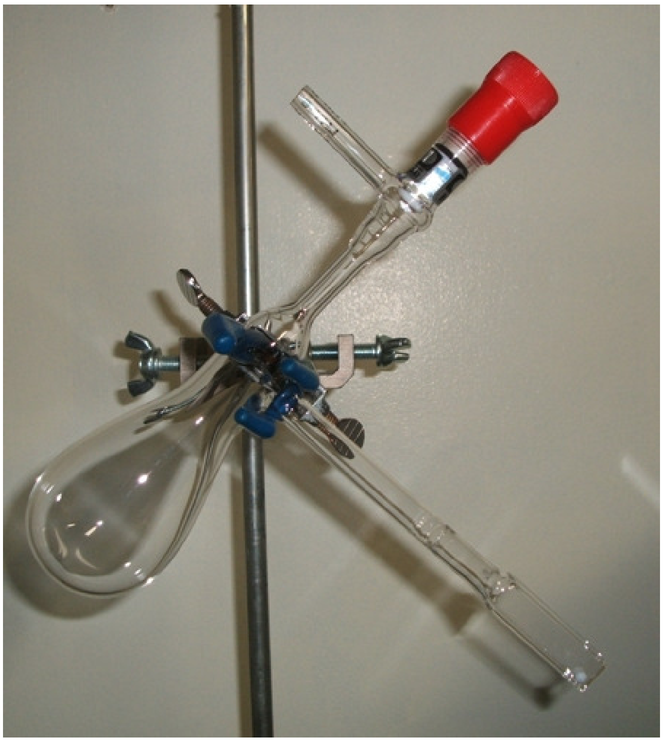
Chemicals.

cis-$PtCl_2(NH_3)_2$ and K_2PtCl_4 (Tanaka Kikinzoku Kogyo) were used as received. $PtCl_2$(dcbpy) (dcbpy = 4,4'-dicarboxy-2,2'-bipyridine),[1] [PtCl(terpy)]Cl·$2H_2O$ (terpy = 2,2';6',2"-terpyridine),[2] and $PtCl_2$(en) (en = ethylenediamine)[3] were synthesized as previously described.

Measurements.

The time-course UV-vis absorption spectroscopy of Pt(II) complex under 1 atm of H_2 gas.

The time-course of UV-vis absorption spectra of each Pt(II) complex under 1 atm of H_2 gas were recorded using Shimadzu UV-2450SIM and UV-2550 spectrophotometers. The solution of each Pt(II) complex was first degassed by three cycles of freeze-pump-thaw treatment using the custom-made cell (see below). Next, the gas phase in the cell was filled with 1 atm of H_2 gas by using a balloon having a volume of at least 1 L. During each experiment, the solution was continuously stirred with a magnetic stirrer bar. The cell was thoroughly washed with aqua regia prior to each experiment to avoid the factor arising from the presence of colloidal platinum, which might be depositted over the inner surface of the cell.



A custom-made cell used for the experiments in Figs. 1, 2, S9, S10 and S11.

Energy dispersive X-ray spectroscopy (EDX).

The energy dispersive X-ray spectrum of the solid deposited was measured on a Shimadzu EDX-720 spectrometer using a Rh target. The measurement was carried out in helium atmosphere in order to avoid X-ray emissions being absorbed by air. The quantitative analysis of the elements involved in the bulk samples were determined by use of the fundamental parameter (FP) method implemented in this setup, without preparing any standard materials. The FP method is considered as a powerful method in giving somewhat reliable results.

X-ray photoelectron spectroscopy (XPS).

An X-ray photoelectron spectrum was measured on a Shimadzu ESCA-3400 at a vacuum pressure less than 1×10^{-5} Pa in the analysis chamber. A standard Mg Kα excitation source (1253.6 eV) was used in the measurement. The sample was placed on a carbon tape. Deconvolution was carried out using CasaXPS[4] in which a Shirley type background was employed.

References.

[1] H, Ozawa, M. Haga, K. Sakai, *J. Am. Chem. Soc.* 2006, **128**, 4926-4927.

[2] M. Howe-Grant, S. J. Lippard, *Inorg. Synth.* 1980, **20**, 101-105.

[3] F. Basolo, J. C. Bailar, B. R. Tarr, *J. Am. Chem. Soc.* 1950, **72**, 2433-2438.

[4] CasaXPS Version 2.3.15, Casa Software Ltd., Teignmouth TQ14 8DE, United Kingdom.

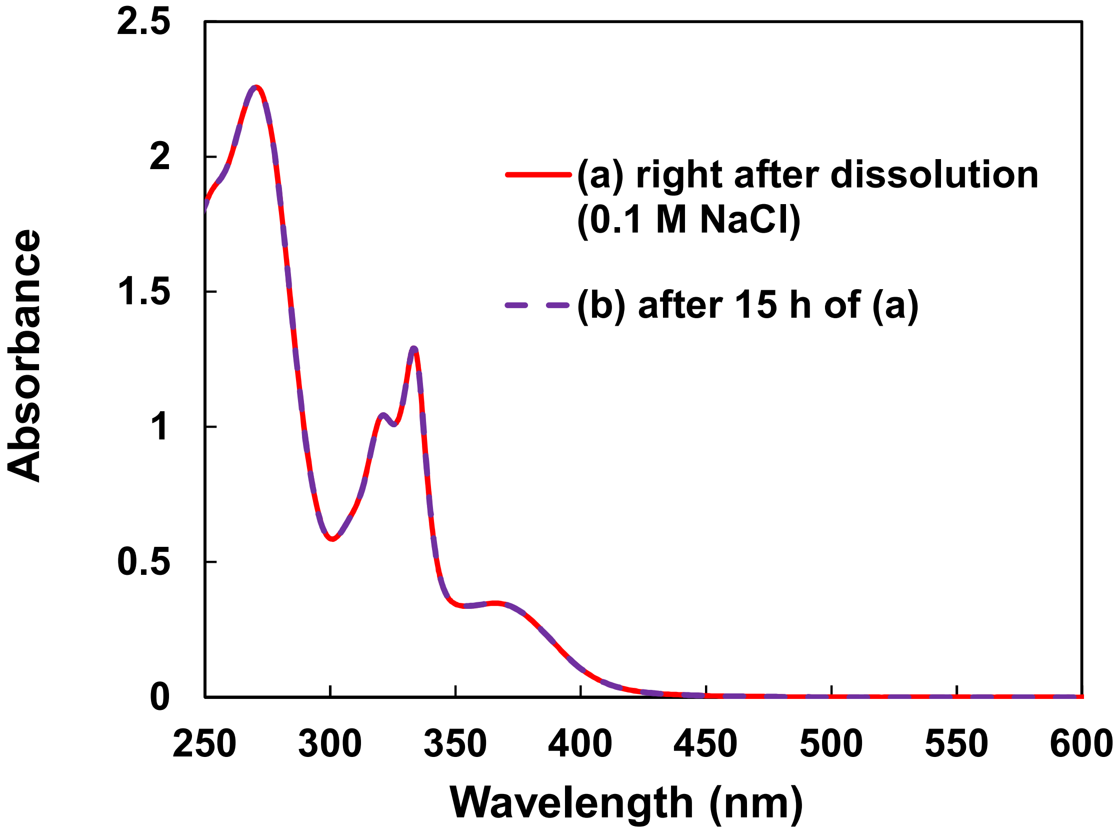


Fig. S1 (a) UV-vis absorption spectrum of 0.1 mM $PtCl_2$(dcbpy) (**1**) in an aqueous acetate buffer solution (0.03 M CH_3COOH, 0.07 M CH_3COONa; pH 5.0) containing *0.1 M NaCl* at 20 °C. The time spent for the dissolution of the complex was *ca.* 30 min. (b) UV-vis absorption spectrum of the solution after standing the solution (b) over 15 h at 20 °C.

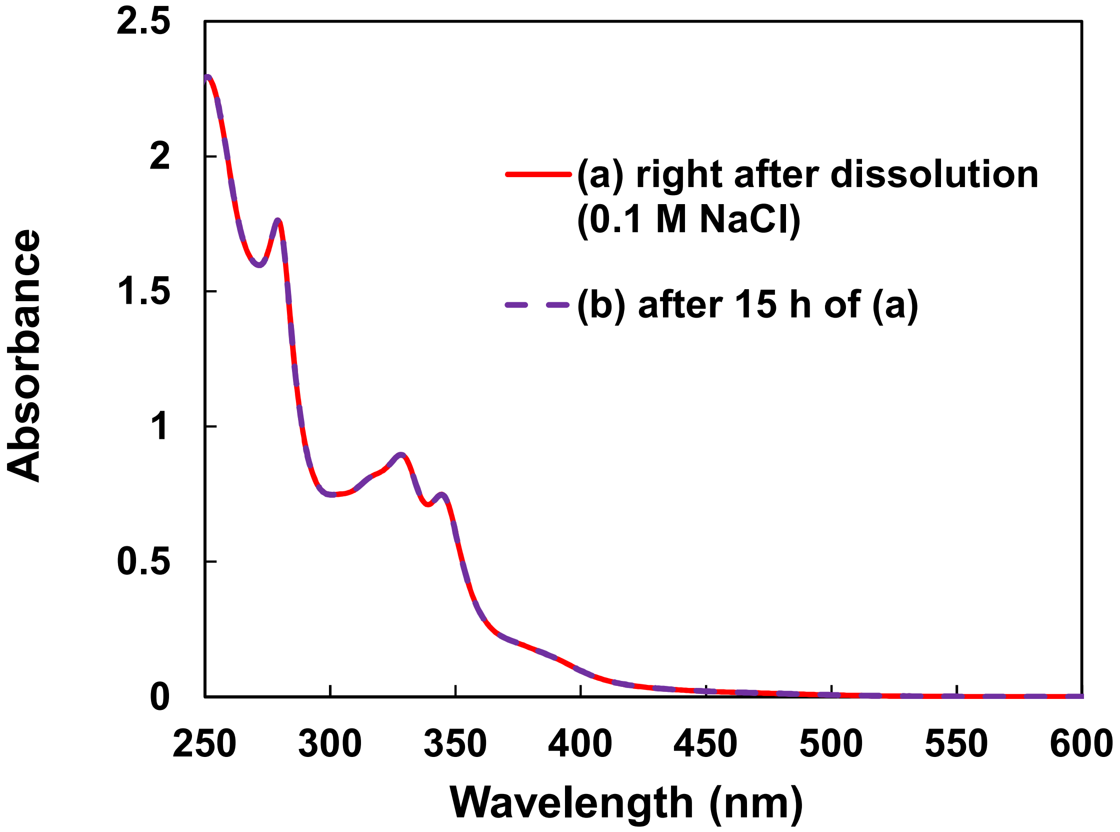


Fig. S2 (a) UV-vis absorption spectrum of 0.1 mM [PtCl(terpy)]Cl·2H_2O (**2**) in an aqueous acetate buffer solution (0.03 M CH_3COOH, 0.07 M CH_3COONa; pH 5.0) containing *0.1 M NaCl* at 20 °C. The time spent for the dissolution of the complex was *ca.* 15 min. (b) UV-vis absorption spectrum of the solution after standing the solution (b) over 15 h at 20 °C.

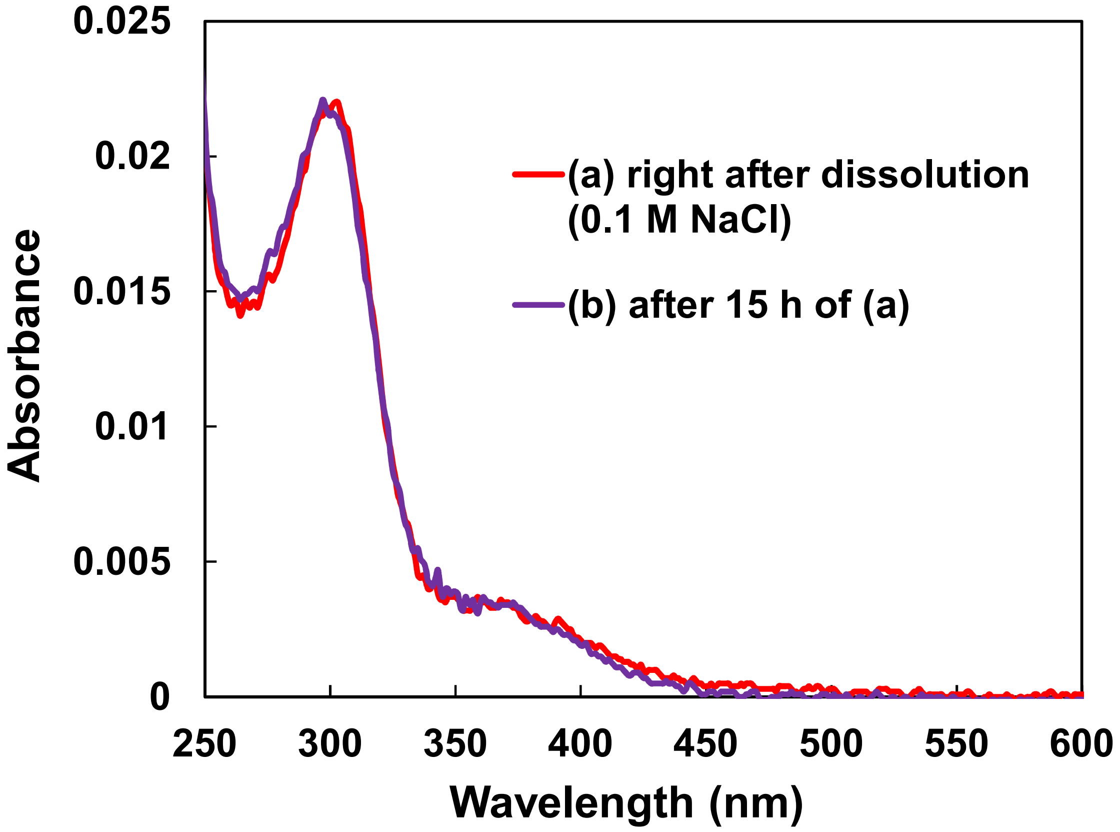


Fig. S3 (a) UV-vis absorption spectrum of 0.1 mM *cis*-$PtCl_2$(en) (**3**) in an aqueous acetate buffer solution (0.03 M CH_3COOH, 0.07 M CH_3COONa; pH 5.0) containing *0.1 M NaCl* at 20 °C. (b) UV-vis absorption spectrum of the solution after standing the solution (b) over 15 h at 20 °C.

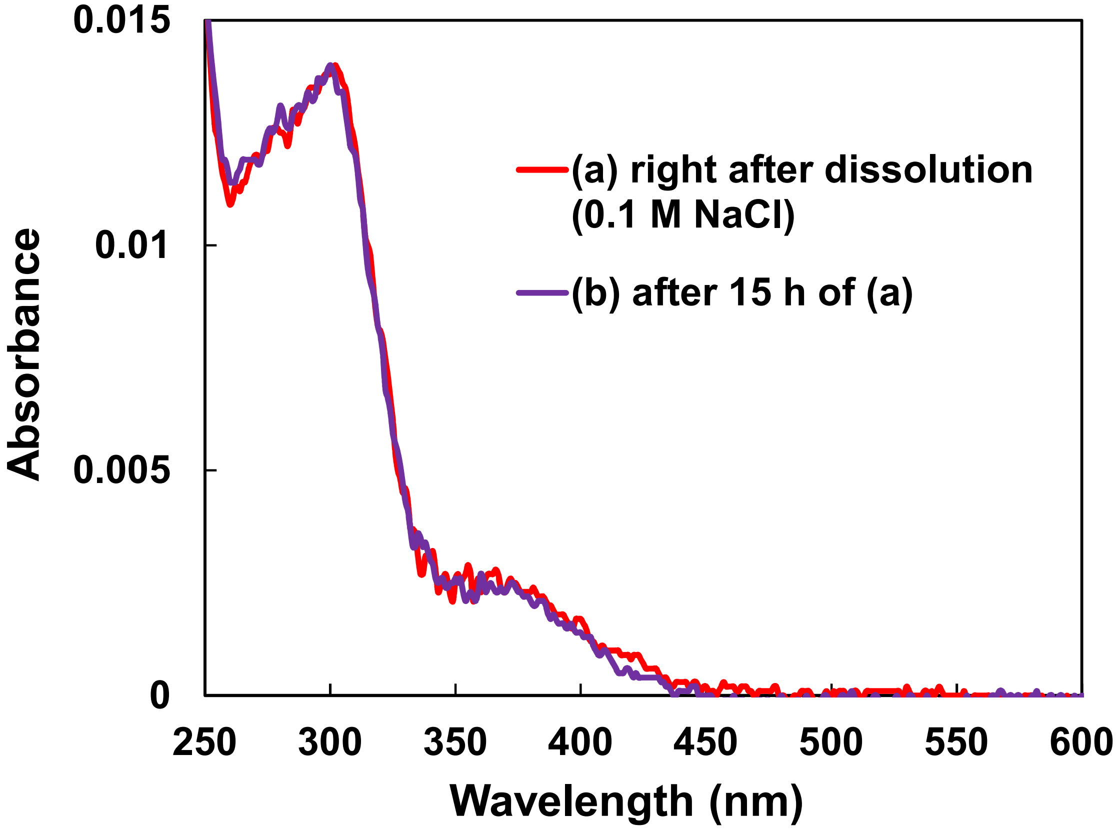


Fig. S4 (a) UV-vis absorption spectrum of 0.1 mM *cis*-$PtCl_2(NH_3)_2$ (**4**) in an aqueous acetate buffer solution (0.03 M CH_3COOH, 0.07 M CH_3COONa; pH 5.0) *containing 0.1 M NaCl* at 20 °C. (b) UV-vis absorption spectrum of the solution after standing the solution (a) over 15 h at 20 °C.

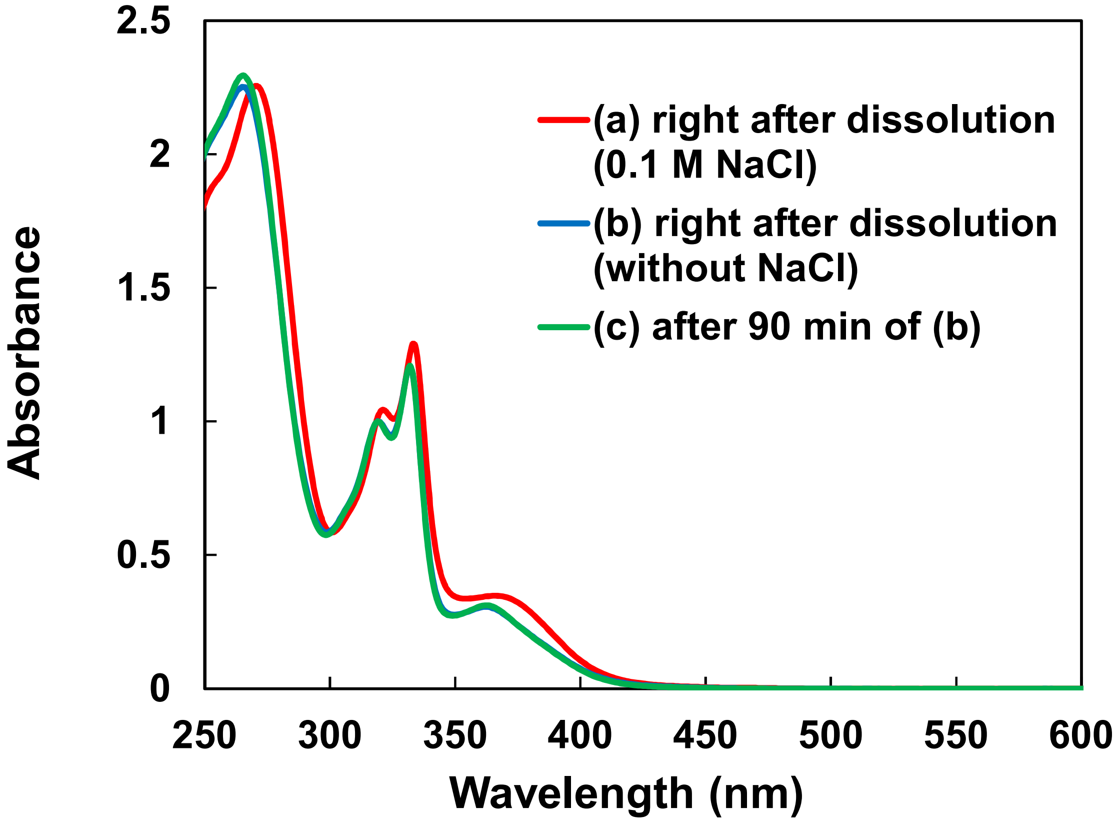


Fig. S5 (a) UV-vis absorption spectrum of 0.1 mM $PtCl_2$(dcbpy) (**1**) in an aqueous acetate buffer solution (0.03 M CH_3COOH, 0.07 M CH_3COONa; pH 5.0) containing *0.1 M NaCl* at 20 °C. The time spent for the dissolution of the complex was *ca.* 30 min. (b) UV-vis absorption spectrum of 0.1 mM $PtCl_2$(dcbpy) (**1**) in an aqueous acetate buffer solution (0.03 M CH_3COOH, 0.07 M CH_3COONa; pH 5.0) at 20 °C. The time spent for the dissolution of the complex was *ca.* 30 min. (c) UV-vis absorption spectrum of the solution after standing the solution (b) over 90 min at 20 °C.

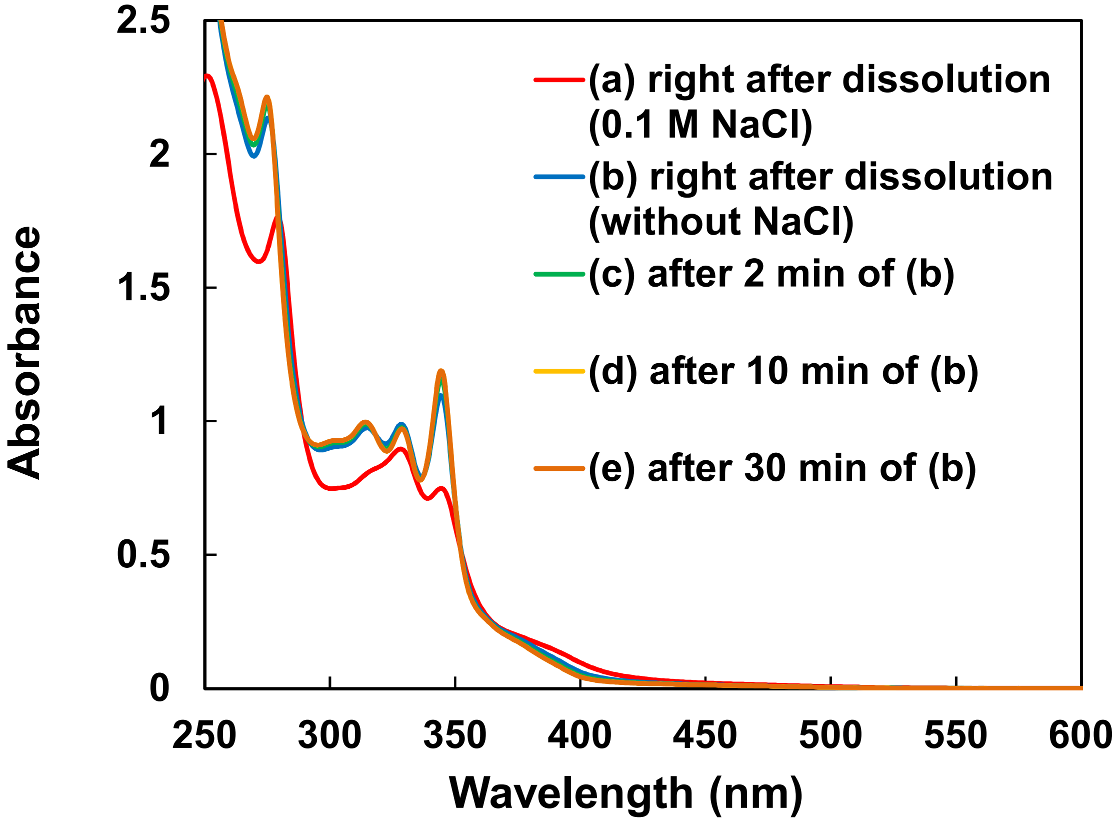


Fig. S6 (a) UV-vis absorption spectrum of 0.1 mM [PtCl(terpy)]Cl·2H_2O (**2**) in an aqueous acetate buffer solution (0.03 M CH_3COOH, 0.07 M CH_3COONa; pH 5.0) containing *0.1 M NaCl* at 20 °C. The time spent for the dissolution of the complex was *ca.* 15 min. (b) UV-vis absorption spectrum of 0.1 mM [PtCl(terpy)]Cl·2H_2O (**2**) in an aqueous acetate buffer solution (0.03 M CH_3COOH, 0.07 M CH_3COONa; pH 5.0) at 20 °C. (c)-(e) UV-vis absorption spectra of the solution after standing the solution (b) over 2 min for (c), 10 min for (d), and 30 min for (e) at 20 °C.

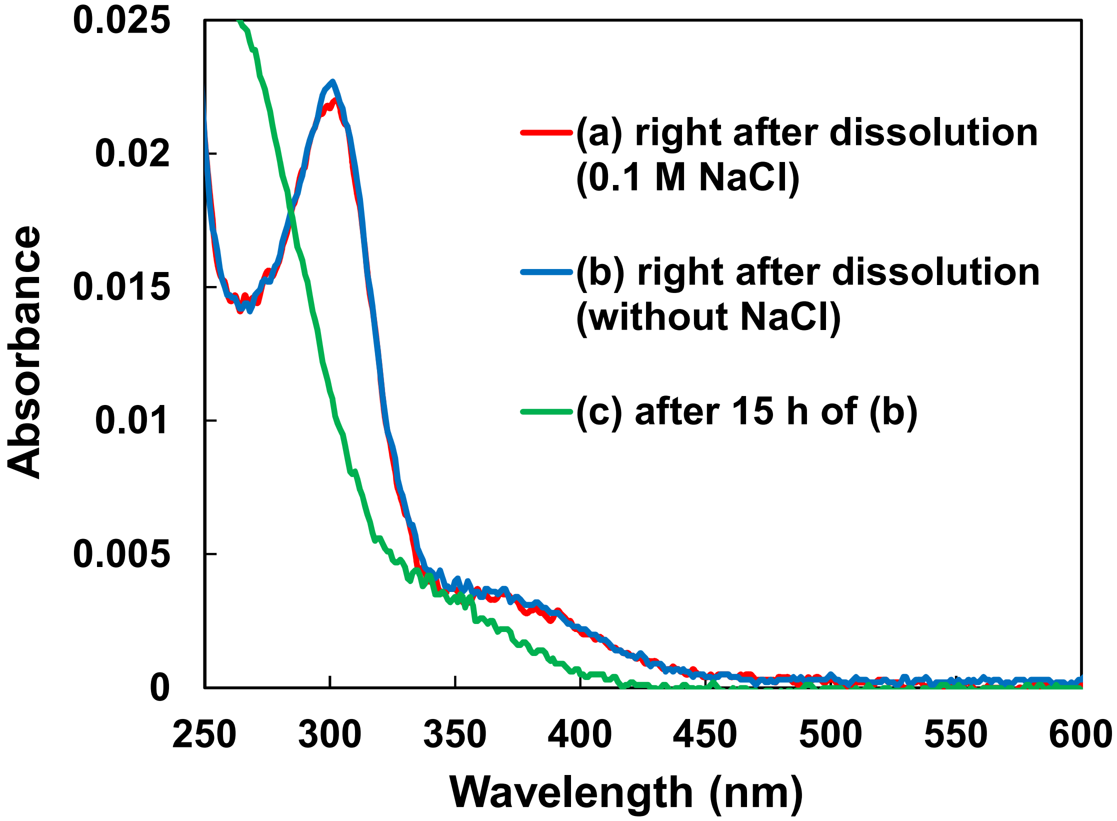


Fig. S7 (a) UV-vis absorption spectrum of 0.1 mM *cis*-PtCl$_2$(en) (**3**) in an aqueous acetate buffer solution (0.03 M CH_3COOH, 0.07 M CH_3COONa; pH 5.0) containing *0.1 M NaCl* at 20 °C. (b) UV-vis absorption spectrum of 0.1 mM *cis*-PtCl$_2$(en) (**3**) in an aqueous acetate buffer solution (0.03 M CH_3COOH, 0.07 M CH_3COONa; pH 5.0) at 20 °C. (c) UV-vis absorption spectrum of the solution after standing the solution (b) over 15 h at 20 °C.

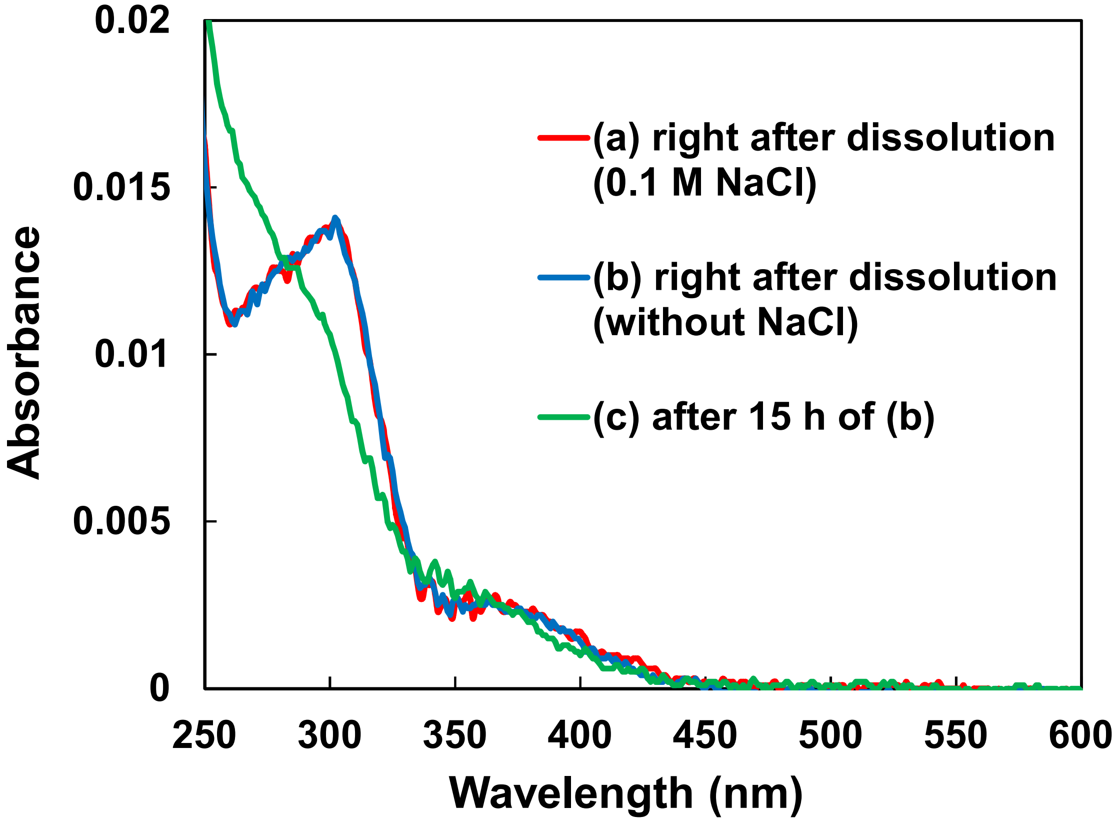


Fig. S8 (a) UV-vis absorption spectrum of 0.1 mM *cis*-$PtCl_2(NH_3)_2$ (**4**) in an aqueous acetate buffer solution (0.03 M CH_3COOH, 0.07 M CH_3COONa; pH 5.0) containing *0.1 M NaCl* at 20 °C. (b) UV-vis absorption spectrum of 0.1 mM *cis*-$PtCl_2(NH_3)_2$ (**4**) in an aqueous acetate buffer solution (0.03 M CH_3COOH, 0.07 M CH_3COONa; pH 5.0) at 20 °C. (c) UV-vis absorption spectrum of the solution after standing the solution (b) over 15 h at 20 °C.

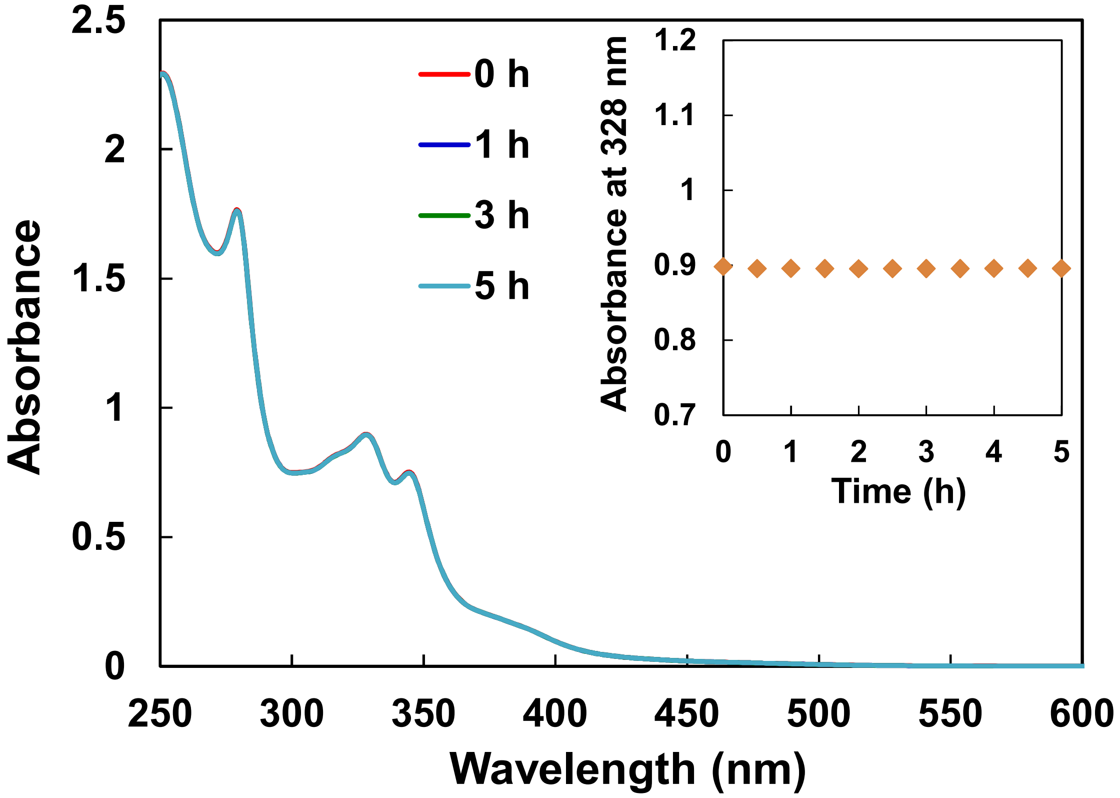


Fig. S9 The time-course of UV-vis absorption spectra of 0.1 mM [PtCl(terpy)]Cl·2H_2O (**2**) under 1 atm of H_2 gas in an aqueous acetate buffer solution (0.03 M CH_3COOH, 0.07 M CH_3COONa; pH 5.0) containing 0.1 M NaCl at 20 °C. The inset shows the change in absorbance at 328 nm. The solution was first degassed by three cycles of freeze-pump-thaw treatment.

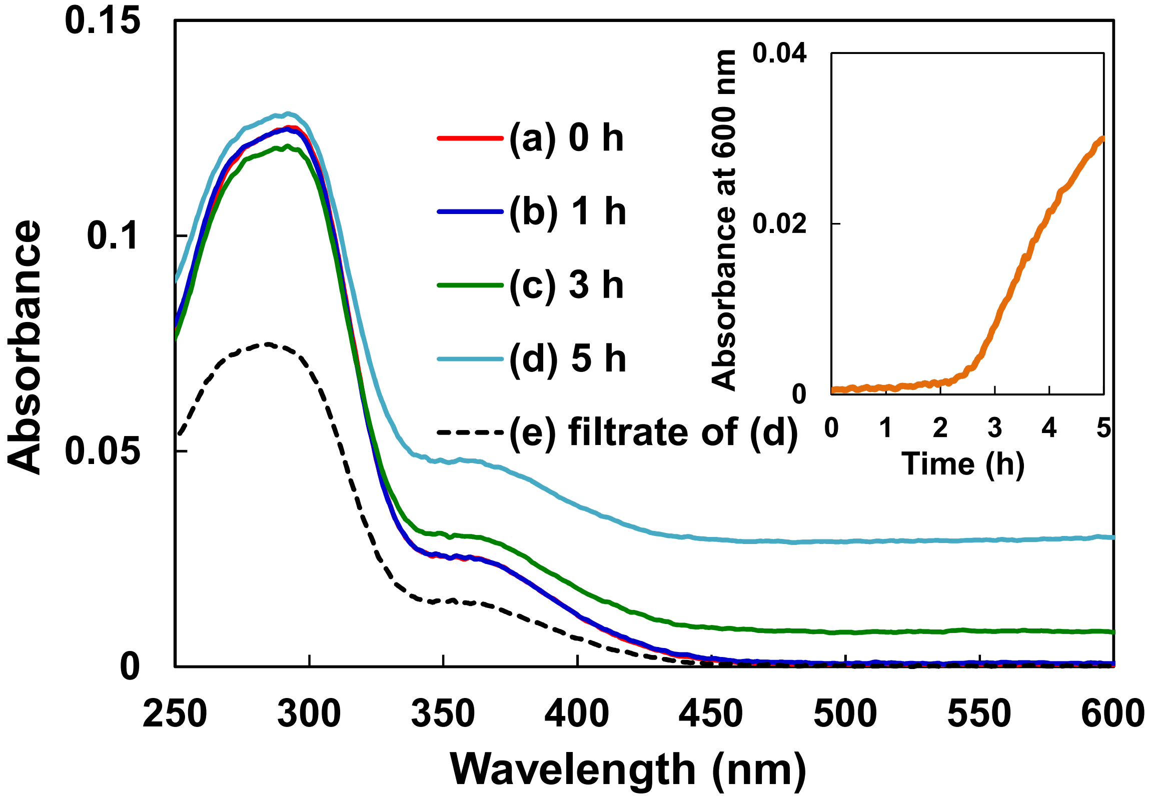


Fig. S10 (a)-(d) The time-course of UV-vis absorption spectra of 1.0 mM *cis*-$PtCl_2(NH_3)_2$ (**4**) under 1 atm of H_2 gas in an aqueous acetate buffer solution (0.03 M CH_3COOH, 0.07 M CH_3COONa; pH 5.0) containing 0.1 M NaCl at 20 °C. (e) The UV-vis absorption spectrum of the filtrate of the solution used for (d), where the solution was filtered by a syringe filter with a pore diameter of 0.45 μm. The inset shows the change in absorbance at 600 nm. The solution was first degassed by three cycles of freeze-pump-thaw treatment.

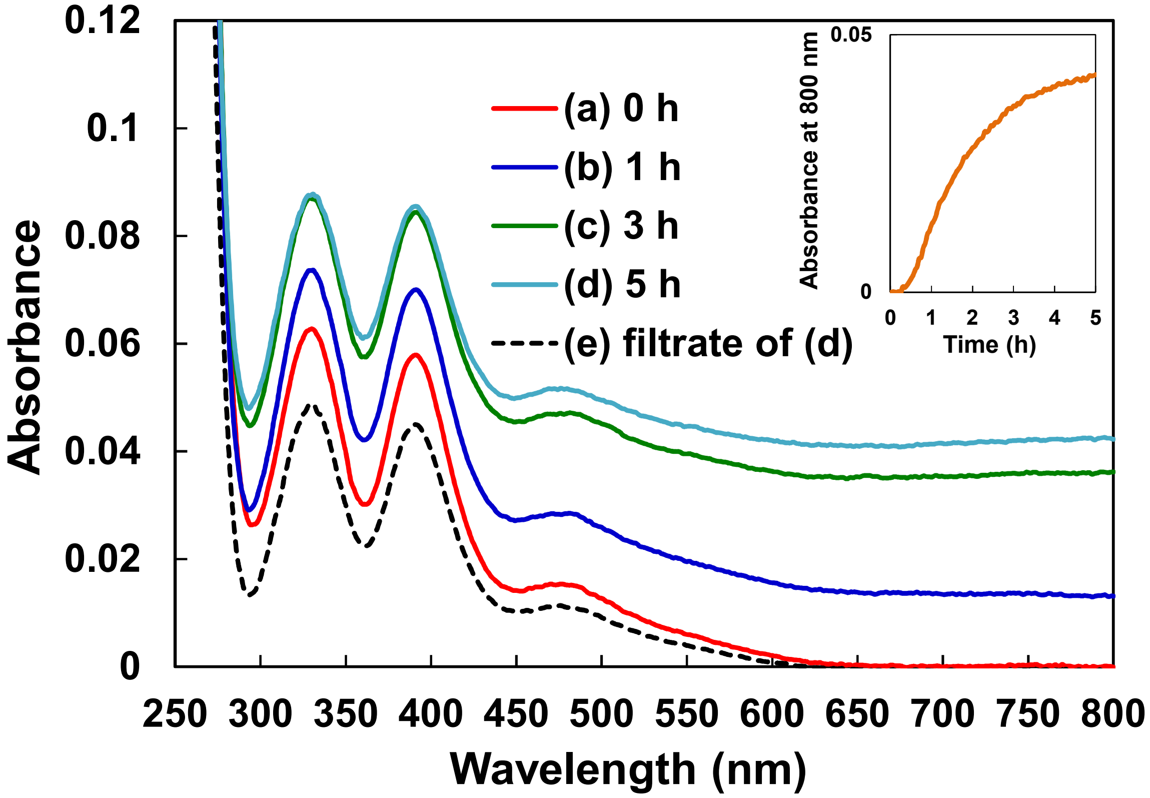


Fig. S11 (a)-(d) The time-course of UV-vis absorption spectra of 1.0 mM K_2PtCl_4 under 1 atm of H_2 gas in an aqueous acetate buffer solution (0.03 M CH_3COOH, 0.07 M CH_3COONa; pH 5.0) containing 0.1 M NaCl at 20 °C. (e) The UV-vis absorption spectrum of the filtrate of the solution used for (d), where the solution was filtered by a syringe filter with a pore diameter of 0.45 µm. The inset shows the change in absorbance at 800 nm.

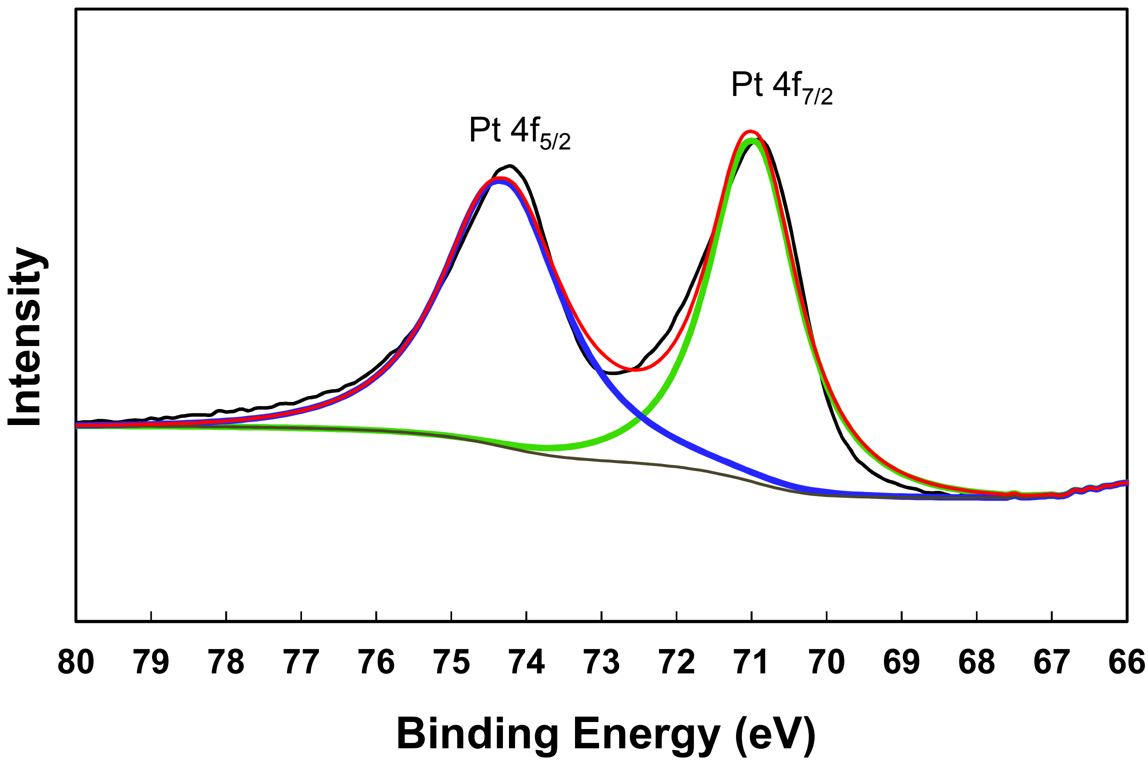


Fig. S12 X-ray photoelectron spectrum for the Pt species in the solid particles produced in the experiment for *cis*-$PtCl_2(NH_3)_2$ (**4**). The Pt $4f_{7/2}$ and $4f_{5/2}$ binding energies are respectively determined as 71.0 and 74.3 eV, where those for Pt metal were reported to be 71.2 and 74.5 eV (C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder, G. E. Muilenberg, Eds.; *Handbook of X-ray Photoelectron Spectroscopy*, Perkin-Elmer Corp.: Eden Prairie, MN, 1979.).

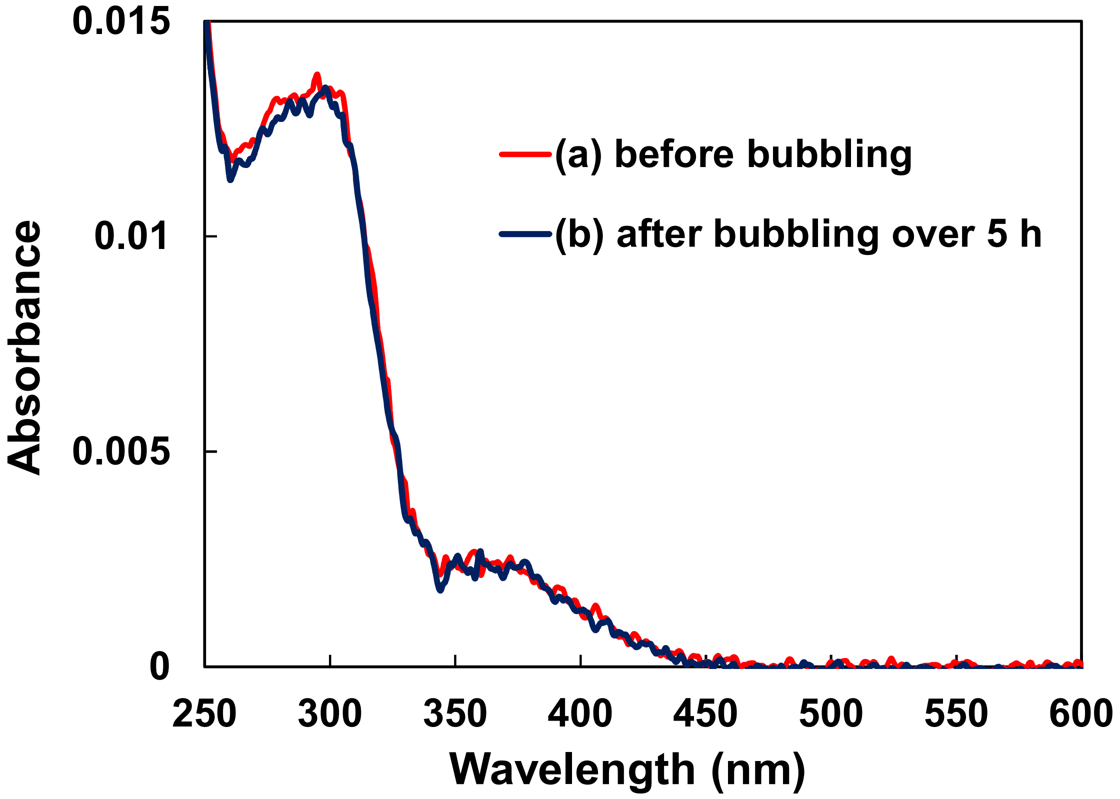


Fig. S13 (a) UV-vis absorption spectrum of 0.1 mM *cis*-$PtCl_2(NH_3)_2$ (**4**) in an aqueous acetate buffer solution (0.03 M CH_3COOH, 0.07 M CH_3COONa; pH 5.0) containing 0.1 M NaCl at 20 °C. (b) UV-vis absorption spectrum of the solution after continuously bubbling the solution (a) with 504 ppm of H_2 gas (10 mL/min) over 5 h at 20 °C.