Electronic Supplementary Information for Development of a framework catalyst for photocatalytic hydrogen evolution

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1. Experimental section

Materials

3-Aminopropinoic acid, 1,8-naphthalic anhydride and benzoic acid were purchased from Tokyo Chemical Industry (TCI). Ethylenediaminetetraacetic disodium salt (EDTA-2Na, \geq 99.0%) was purchased from Sigma-Aldrich. All solvents and reagents are of the highest quality available and used as received. HNIP, Na₄[Rh₂(CO₃)₄], Rh₂(Bnz)₄ and CM-1 were prepared by the literature methods.^{S1,S2,S3,S4} All syntheses were performed under an atmosphere of dry nitrogen or dry argon unless otherwise indicated.

Measurement apparatus

¹H NMR spectra were acquired on a JEOL JNM-LA400 spectrometer, where chemical shifts in DMF- d_Z or CDCl₃ were referenced to internal tetramethylsilane. Elemental analyses were carried out on a J-SCIENCE LAB MICRO CORDER JM10 elemental analyser. UV-Vis absorption spectra and UV-Vis diffuse reflectance spectra were recorded on a Shimadzu UV-3600 UV-Vis-NIR spectrophotometer. A white standard of BaSO₄ was used as reference for diffuse reflectance spectroscopic measurement. The photocatalytic studies were performed by using a xenon lamp (λ > 320 nm, 300 W) equipped CM-2 cold mirror. Gas analysis for H₂ was performed using a Shimadzu GC-2014 gas chromatograph equipped with a thermal conductivity detector (TCD) and fitted with a molecular sieve 5A column (Ar carrier gas), calibrated with standard H_2 (0.5% of H_2 in argon). FT-IR spectroscopy data were collected using a PerkinElmer Spectrum 100 FT-IR spectrometer. ESI-TOF-MS spectra were recorded on a JEOL JMS-T100LP mass spectrometer. Scanning electron microscopy (SEM) images were obtained on JEOL CarryScope JCM-5700. All the ESI-TOF mass spectrometric measurements were recorded in the positive ion mode at a cone voltage of 20 V. Cyclic voltammograms were measured at room temperature on a BAS ALS Model 650DKMP electrochemical analyser in DMF (sample = 0.5 mM; 0.1 M tetra-nbutylammonium perchlorate (TBAP)) unless otherwise indicated. A glassy carbon, platinum wire, and Ag/Ag^+ electrode (Ag/0.01 M AgNO₃) were used as the working, auxiliary, and reference electrodes, respectively. The redox potentials were calibrated against the redox potential for the ferrocene/ferrocenium (Fc/Fc⁺) couple. Dynamic light scattering (DLS) measurements were performed using particle size analyzer (Photal Otsuka Electronic ELSZ-1000).

X-ray Crystallography

Crystals of **FC-1** were mounted in a loop. Diffraction data at 123 K were measured on a RAXIS-RAPID Imaging Plate diffractometer equipped with confocal monochromated Mo-K α radiation and data was processed using RAPID-AUTO (Rigaku). The structure was solved by direct method using *SIR-92*⁵⁵ and refined by the full-matrix least squares techniques on F^2 (*SHELXL-97*).⁵⁶ All non-hydrogen atoms were refined anisotropically. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC 1494945 for **FC-1**. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

2. Synthesis of CM-1



Scheme S1. Synthesis of CM-1

3-(1,8-Naphthalimido)propanoic acid (HNIP) was synthesized as previously reported.⁵¹ Synthesis of CM-1 was performed by following a published procedure.⁵⁴ A round bottom Schlenk flask was charged with Na₄[Rh₂(CO₃)₄] (90 mg, 0.15 mmol), HNIP (323 mg, 1.20 mmol) and 30 mL of water. The mixture was refluxed for 2 h. The resulting green precipitate was obtained by filtration, washed with water and MeOH. The green solid was stirred in the mixture of MeOH (150 mL) and acetone (150 mL) to remove the unreacted ligand. The green solid was collected by filtration and washed by diethyl ether. After drying under air, CM-1 was obtained as green powder. Yield: 76 mg (0.06 mmol), 40%. ¹H-NMR (400 MHz, DMF-*d*₇): 8.54 (d, *J* = 7.4 Hz, 2H, naphth) 8.39 (d, *J* = 8.2 Hz, 2H, naphth) 7.87 (t, *J* = 7.8 Hz, 2H, naphth) 4.18 (t, *J* = 7.6 Hz, 2H, N-CH₂) 2.48 (t, *J* = 7.6 Hz, 2H, CH₂-COO) ppm. ESI-TOF MS (DMF): *m/z* 1522.41 [1314.08 + 1-methyl-4,4'-bipyridinium + DMF – 2H₂O] (Note that 1-methyl-4,4'-bipyridinium iodide was used as an additive for mass spectroscopy measurement). Elemental analysis for CM-1·7.5H₂O: Found: C, 49.3; H, 4.3; N 3.7. Calc. for C₆₀H₄₀N₄O₁₆Rh₂: C, 49.7; H, 4.1; N, 3.8%. Single crystal X-ray quality crystals of **FC-1** were grown by vapor diffusion technique from DMSO/CHCl₃ solution.

3. X-ray crystallographic data

Formula	$C_{68}H_{64}N_4O_{20}Rh_2S_4$
Fw	1591.29
crystal color, habit	orange, block
crystal size, mm ³	0.23 × 0.17 × 0.09
crystal system	monoclinic
space group	P 21/n
<i>a,</i> Å	9.8868(4)
<i>b,</i> Å	27.3918(12)
<i>c,</i> Å	12.3432(5)
eta, deg	102.369(7)
<i>V</i> , Å ³	3265.2(2)
Ζ	2
F(000)	1628
d_{calc} , g/cm ³	1.619
μ(MoKα), mm⁻¹	0.714
<i>Т,</i> К	123(2)
R_1	0.0611
wR ₂	0.1639
GOF	1.135

 Table S1. Summary of the crystallographic data for FC-1.



Figure S1. (a) An ORTEP drawing of **FC-1** (50% probability ellipsoids). Hydrogen atoms and crystal solvent molecules are omitted for clarity. (b) Crystal packing of **FC-1** along the *a* axis. Intracolumnar and intercolumnar π – π stacking interactions are shown in pale blue and pale red lines, respectively. Hydrogen atoms, DMSO molecules at the axial positions except for the coordinated sulfur atoms and crystal solvent molecules observed in the channels are omitted for clarity. O = red, C = grey, N = blue, S = yellow, Rh = sea green. (c) Intermolecular interactions observed in **FC-1**. The mean interplanar separation between two NIP moieties was calculated as follows. First, the mean plane of the **NIP** moiety containing N2 atom (plane 1: N2 and C19-30) was defined. Next, the distances between plane 1 and atoms constituting the neighboring **NIP** moiety was measured. The average of the obtained distances corresponds to the distance of π - π interactions. Distances of intracolumnar and interacolumnar π - π interactions operation: 3, 3, 0, 2) and C9-15 (symmetry operation: 2, 2, 0, 1), respectively.

4. Photophysical properties



Figure S2. Solution UV-Vis absorption spectra in DMF of free ligand HNIP (blue) and CM-1 (red line). For HNIP, the band corresponds to $\pi - \pi^*$ transition appears at 334 nm. In the case of CM-1, the bands correspond to $\pi - \pi^*$ transition (NIP moieties) and $\pi^* \rightarrow \sigma^*$ transition (Rh(II) centre) were observed at 334 and 585 nm, respectively.



Scheme S2. Schematic illustration of MO diagram of $Rh(II)_2$ centre having d^7-d^7 configuration.



Figure S3. Diffuse reflectance UV-Vis spectra of the solid samples of free ligand HNIP (blue line) and FC-1 (red line). For HNIP, the band corresponds to $\pi - \pi^*$ transition appears at 335 nm. In the case of FC-1, the bands correspond to $\pi - \pi^*$ transition (NIP moieties) and $\pi^* \rightarrow \sigma^*$ transition (Rh(II) centre) were observed at 335 and 515 nm, respectively.



Figure S4. Solution fluorescence emission spectra in DMF solution at 0.04 mM of free ligand H**NIP** (blue) and **CM-1** (red line) at ambient temperature, the excitation wavelength was 334 nm. For H**NIP**, the emission band appears at 393 nm. For **CM-1**, a very weak emission band (less than 1 a.u.) was observed at 379 nm.



Figure S5. Solid state fluorescence emission spectra free ligand HNIP (blue) and **FC-1** (red line). The excitation wavelengths were 373 nm and 353 nm for HNIP and **FC-1**, respectively. The emission band of HNIP appears at 462 nm, while no emission band was not observed in **FC-1**.

5. Electrochemical and spectroelectrochemical studies

All experimental procedures were conducted at ambient temperature, 20 °c, under argon. A standard three-electrode configuration was employed in conjunction with a CH Instruments potentiostat interfaced to a computer with CH Instruments 650 DKMP software. A platinum auxiliary electrode and Ag/Ag⁺ reference electrode were used for all measurement in solution. Cyclic voltammetry was performed using a GC disk working electrode (diameter 3 mm, from BAS Inc.). The working electrode was treated between scans by means of polishing with 0.05 μ m alumina paste (from BAS Inc.) and washing with purified water. Ferrocene was used as an internal standard, and all potentials reported within this work are referenced to the NHE at 0.551 V.

UV-Vis spectral measurements were recorded using SHIMADZU UV-2550 UV-VIS spectrophotometer with a conventional quartz cuvette (path length, I = 1 cm). Spectroelectrolysis was performed using a BAS Inc. spectroelectrochemical quartz cell (I = 1 mm) containing a Pt gauze (working electrode), Pt wire (auxiliary electrode) and Ag/Ag⁺ (reference electrode) in conjunction with the CH Instruments potentiostat.



Figure S6. Cyclic voltammograms of 0.5 mM of **CM-1** (red line) and H**NIP** (blue line) in DMF containing 0.1 M TBAP at room temperature under Ar atmosphere (WE: GC, AE: Pt wire, RE: Ag/Ag⁺), at scan rate of 15 mV/s.



Figure S7. (a) Spectroelectrochemical changes of **CM-1** (0.2 mM) in a DMF solution containing 0.1 M TBAP upon apply potential from the resting potential (0.24 V vs. NHE, red line) to -1.5 V (blue line). (b) UV-vis absorption spectra of **CM-1** at the resting potential (red line), at -1.5 V (blue line), at the resting potential (0.24 V) recorded after the reduction (grey dotted line). All measurements were performed at room temperature under Ar atmosphere (WE: Pt gauze, AE: Pt wire, RE: Ag/Ag⁺).



Figure S8. Spectroelectrochemical changes of H**NIP** (0.8 mM) in DMF containing 0.1 M TBAP upon apply potential from the resting potential (0.23 V vs. NHE, red line) to -1.4 V (blue line) at room temperature under Ar atmosphere (WE: Pt gauze, AE: Pt wire, RE: Ag/Ag⁺).



Figure S9. Cyclic voltammogram of **CM-1** (0.5 mM) upon addition of acetic acid (2.90 M) containing 0.1 M TBAP in DMF at room temperature under Ar atmosphere (WE: GC, AE: Pt wire, RE: Ag/Ag⁺), at scan rate of 15 mV/s.



Figure S10. Cyclic voltammogram of **CM-1** (0.5 mM) in the excess amount of water containing 0.1 M TBAP in DMF at room temperature under Ar atmosphere (WE: GC, AE: Pt wire, RE: Ag/Ag⁺), at scan rate of 15 mV/s.

6. Solid-state cyclic voltammogram measurement

To investigate redox behavior of **FC-1**, cyclic voltammograms (CVs) of **FC-1** deposited on a glassy carbon (GC) working electrode were measured. The procedure to deposit **FC-1** on the GC electrodes are as follows. First, 5 mg of as synthesized **FC-1** was suspended in methanol. The obtained suspension was further ultra-sonicated for 15 min. Subsequently, 20 μ L of the suspension was dropped onto the surface of a freshly polished GC electrode and dried under air for 1 h, yielding a GC electrode modified by thin **FC-1** layer (Scheme S3). By utilizing the modified electrode, CVs were measured using a standard three-electrode cell incorporating a GC working electrode, a platinum wire auxiliary electrode and Ag/Ag⁺ reference electrode. The measurements were performed at room temperature under Ar atmosphere. Initially, CVs of **FC-1** were measured in dichloromethane containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) as an electrolyte. As shown in Fig. S11, the CVs of **FC-1** in dichloromethane were observed at 1.20 V and -0.95 V (vs. NHE), which correspond to the Rh^{III}Rh^{II}/Rh^{III}Rh^{III} redox couple and the reduction of **NIP** moiety, respectively.

For the investigation of the electrocatalytic H_2 evolution of **FC-1**, the cyclic voltammograms of was measured in in 1.0 M acetate buffer as an electrolyte at pH 5. In this measurement, saturated calomel reference electrode (SCE) was employed as a reference electrode. As shown in Fig. S12, the large irreversible current was observed with the onset potential of -0.71 V vs. NHE, indicating the electrocatalytic H_2 evolution.



Scheme S3. Schematic illustration of the procedure to modify a GC electrode with FC-1.



Figure S11. Cyclic voltammograms of **FC-1** deposited on a GC electrode (green line) and a blank solution (green dots) in dichloromethane containing 0.1 M TBAP and **CM-1** (red line) in a DMF solution containing 0.1 M TBAP. All measurements were performed under Ar atmosphere (WE: GC, CE: Pt wire, RE: Ag/Ag⁺), at scan rate of 100 mV/s.



Figure S12. Cyclic voltammograms of **FC-1** deposited on a GC electrode (green line) and a blank solution (grey line) in 1.0 M acetate buffer pH 5 at room temperature under Ar atmosphere (WE: GC, CE: Pt wire, RE: SCE), at scan rate of 100 mV/s.



Figure S13. Cyclic voltammograms of **FC-1** deposited on a GC electrode (solid line) and various buffer blank solution at pH 5 (dash line) under Ar atmosphere (WE: GC, CE: Pt wire, RE: SCE), at scan rate of 100 mV/s.

7. Photocatalytic H₂ production studies

All photocatalytic experiments were conducted at 20 °C using a custom-made photoreactor with coolant to control the temperature of sample during photoreaction (Scheme S4). A cylindrical UV cuvette with 4.0 mL of gas head space was used for all experiments. In a typical run, 3.5 mg of catalyst was suspended in 4.0 mL of acetate buffer containing EDTA-2Na as a sacrificial electron donor. Prior the reaction, the suspension was ultra-sonicated for 15 min and then the system was purged by Ar gas bubbling for 30 min. The photocatalytic reactions were executed by using a xenon lamp (λ > 320 nm, 300 W) equipped CM-2 cold mirror. The evolved H₂ in the gas phase was analyzed by a gas chromatography (GC-2014, molecular sieve 5A column, Ar carrier gas) equipped with a thermal conductivity detector (TCD).

For the study of the influence of particle size on the photocatalytic activity, the particle sizes of **FC-1** were controlled by changing the period of sonication (5, 10 and 15 min) prior to the photoreaction (Ultrasonic cleaner Aiwa AU-16C (28 kHz, 75 W)). The size of **FC-1** particles were determined by dynamic light scattering (DLS) technique.

The reusability experiments of **FC-1** for photocatalytic H₂ production were performed using the system containing 3.5 mg of **FC-1**, and 4.0 mL of acetate buffer (1.0 M) with EDTA-2Na (0.2 M) at pH 5. After 3 h of the photocatalytic reaction, the catalyst was filtered through membrane filter, washed several time with water then dried overnight under vacuum. Resulting powder was further used in the next photocatalytic experiment. Other experimental conditions are same as mentioned above.



Scheme S4. (a) A photograph of the photocatalytic H₂ production reactor; (b) schematic illustration of the custom-made photoreactor.



Figure S14. Photocatalytic H₂ production from a reaction mixture containing 3.5 mg of **FC-1** (green line) and 4.0 mL of acetate buffer (1.0 M) with 0.2 M EDTA-2Na at pH 5. Control experiments were carried out in the absence of light (blue line), **FC-1** (red line), and EDTA-2Na (brown line).

Mercury test of FC-1

The photocatalytic activity of **FC-1** was examined in the presence of mercury. **FC-1** (3.5 mg) was suspended in 4.0 mL of acetate buffer (1.0 M) containing EDTA-2Na (0.2 M) as a sacrificial electron donor and the pH of the solution was adjusted to 5.0. Prior to the reaction, the suspension was ultrasonicated for 15 min and then 1 drop of mercury was added. As shown in Figure S15, the addition of mercury did not affect the photocatalytic activity, which indicates no formation of Rh-based nanoparticles during the catalysis.



Figure S15. Photocatalytic H₂ production of **FC-1** in the presence (blue line) and absence (red line) of mercury. The reaction mixture contains 3.5 mg of **FC-1** and 4.0 mL of acetate buffer (1.0 M) with 0.2 M EDTA-2Na at pH 5.



Figure S16 Photographs of the reaction mixture before (left) and after 3h (right) of photocatalytic reaction.



Figure S17. Photocatalytic H₂ production of **FC-1** (3.5 mg) at various pH. The pH values of the reaction media were adjusted by using 1.0 M acetate buffer solution. 0.2 M of EDTA-2Na (4.0 mL) was used as a sacrificial electron donor.



Figure S18. Dependence of buffer solution on photocatalytic H_2 production of **FC-1** (3.5 mg) at pH 5. In all experiments, the concentration of the buffer was 1.0 M. 0.2 M EDTA-2Na (4.0 mL) was used as a sacrificial electron donor.



Figure S19. The influence of the capping ligand on photocatalytic H_2 production of **FC-1** (3.5 mg). The reaction was performed in 4.0 mL mixture of $CH_3CN/1.0$ M buffer solution containing 0.2 M EDTA-2Na as a sacrificial electron donor.

Influence of the particle size on photocatalytic H_2 evolution

The particles of **FC-1** with various were obtained by changing the period of sonication prior to the photocatalytic hydrogen production. The size of **FC-1** particles were determined by using the DLS measurements (Tables S2). As shown in Fig. S20, the catalytic activity of **FC-1** was not affected by the size of the particles.

Table S2. Various particle size of FC-1 upon sonication period at 5, 10 and 15 min.

Sonication time (min)	Average particle size (μm)
5	80.7
10	62.2
15	41.9



Figure S20. The influence of the average particle size on photocatalytic H₂ production of **FC-1** (3.5 mg). The reaction was performed in 1.0 M acetate buffer solution (pH 5) containing 0.2 M EDTA-2Na as a sacrificial electron donor.

8. Stability of the catalyst



Figure S21. Photocatalytic H_2 production of **FC-1** with prolonged reaction time. Conditions: **FC-1** (3.5 mg), 0.2 M EDTA-2Na in 4.0 mL acetate buffer (1.0 M) at pH 5.



Figure S22. ESI-TOF-MS spectra of **FC-1** (a) before and (b) after photocatalytic reaction 75 h. In this experiment, **FC-1** was dissolved in DMF and 1-methyl-4,4'-bipyridinium, which can coordinate to the axial sites of the Rh₂ centre, was added to the resulting solution to ionize the neutral Rh complex. Major peaks at m/z values of 1450.33 and 1522.41 are assigned to molecular compositions as follows: (i) **FC-1** + 1-methyl-4,4'-bipyridinium + DMF – $2H_2O$ and (ii) **FC-1** + 1-methyl-4,4'-bipyridinium + DMF – $2H_2O$.



Figure S23 (a) Time course plots of hydrogen evolution of **FC-1** over three consecutive reuse experiments from the system containing 3.5 mg of **FC-1** and 0.2 M EDTA-2Na in 4.0 mL of water at pH 5 (controlled by 1.0 M acetate buffer solution). (b) FT-IR spectra of **FC-1** before and after 75 h of the photoreaction. *Inset*: SEM images of **FC-1** before (left) and after the photoreaction (right).

9. Mechanistic insight



Scheme S5. Two possible pathways to generate a key intermediate, $Rh^{II}Rh^{I}-H$, from **FC-1** in this lightdriven H₂ production system. a) Path 1: the intermolecular reductive quenching of **NIP**^{*} by sacrificial electron donor (EDTA-2Na) and b) Path 2: the intramolecular oxidative quenching of **NIP**^{*} by Rh₂ centre.



Figure S24. Fluorescence spectra of H**NIP** (40 μ M) in EtOH/water (4/6, v/v) in the presence of EDTA-2Na (0 – 500 eq.), excitation wavelength at 342.0 nm.



Figure S25. Fluorescence spectra of HNIP (50 μ M) in DMF in the presence of **CM-1** (0 – 2 eq.), excitation wavelength at 334.0 nm.

Based on the results of spectroscopic and electrochemical measurements, the Gibbs free energy (ΔG°) of photo induced electron transfer process was estimated by using the Rehm-Weller equation (Eq.1).^{S7}

$$\Delta G^{\circ} = E_{ox}(D) - E_{red}(A) - E_{00} - C \text{ (Eq. 1)}$$

Where E_{00} is the excited-state energy of photosensitizer; $E_{ox}(D)$ and $E_{red}(A)$ represent the oxidation potential of donor and the reduction potential of acceptor, respectively; *C* is the columbic term. In our system, E_{ox} corresponds to the oxidation potential of the **NIP** moiety (2.14 V vs. NHE in DMF) and E_{red} corresponds to the reduction potential of the Rh centre (-0.71 V vs. NHE in acetate buffer). The lowest excited-state energy of photosensitizer (**NIP***) moiety (E_{00}) was roughly estimated to be 3.44 eV from the cross point of absorption and emission spectra of H**NIP** in DMF at room temperature (Fig. S26). Due to the large dielectric constant of water at 20 °C (80.103)^{S8}, the columbic term can be negligible^{S7} and a negative ΔG° of -0.59 eV was obtained. These exergonic value confirm that the photoinduced intramolecular electron transfer process is thermodynamically favorable in our system.



Figure S26. Normalized absorption (blue line) and emission spectra (red line) of H**NIP** in DMF upon excitation wavelength at 320 nm.

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