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SUPPORTING INFORMATION

Development of a Ru complex-incorporated MOF photocatalyst for hydrogen production under visible-light irradiation

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Materials

Tetrapropyl orthotitanate (TPOT), tetrabutylammonium perchlorate and $RuCl_3$ were purchased from Tokyo Kasei Kogyo Co., Ltd. 2-Amino-benzenedicarboxylic acid ($H_2BDC-NH_2$), N'N-dimethylformamide (DMF), methanol, triethanolamine (TEOA), were purchased from Nacalai Tesque Inc. Hydrogen hexachloroplatinate(IV) hexahydrate ($H_2PtCl_6 \cdot 6H_2O$) was purchased from Kishida Chemicals Co., Ltd. Dichloromethane was purchased from Wako Pure Chemical Industries. Ethylenediaminetetraacetic acid disodium salt dihydrate ($EDTA-Na_2 \cdot 2H_2O$) was purchased from IBI Scientific. P25 TiO_2 was purchased from Degussa.

Catalysts preparation

Bis(4'-(4-carboxyphenyl)-terpyridine)Ru(II) complex ($Ru(tpy)_2$) as an organic linker was prepared according to the literature.[S1] Ru complex-incorporated Ti-based MOF (Ti-MOF-$Ru(tpy)_2$) was synthesized on the basis of a method for the preparation of MIL-125 (Ti-MOF) previously-reported by Dan-Hardi *et al.*,.[S2] The mixture of TPOT, $Ru(tpy)_2$, DMF and methanol was subject to react under solvothermal conditions in a Teflon-lined stainless steel autoclave for 48 h at 453 K under autogenous pressure. The precipitate was filtrated, washed repeatedly with DMF and dried at room temperature overnight. Finally, the obtained powder sample was dried under vacuum for 1 h at 423 K.

General methods

Cyclic voltammograms were obtained with Hokuto Denko HZ-5000 electrochemical measurement system at a scanning rate of 100 mV s^{-1}, equipped with a normal one-compartment cell with a Pt working electrode, a Pt counter electrode, and a nonaqueous $Ag/AgNO_3$ reference electrode. The measurements were performed in a CH_2Cl_2 solution including 0.1 M tetrabutylammonium perchlorate as a supporting electrolyte. Diffuse reflectance UV–vis spectra were obtained with a Shimadzu UV–vis recording spectrophotometer 2200A. Standard θ–2θ X-ray diffraction (XRD) data were recorded on a Shimadzu X-ray diffractmeter XRD-6100 using Cu Kα radiation (λ = 1.5406 Å). Nitrogen adsorption-desorption isotherms were collected by using a BEL-SORP mini (BEL Japan, Inc.) at 77 K. Thermogravimetric (TG) analysis was carried out using a thermal analyser (Rigaku Termoplus 8120), with a heating rate of 10 K min^{-1} in air. XAFS (XANES and EXAFS) spectra were recorded at the BL-01B1 facility of SPring-8 at the Japan Synchrotron Radiation Research Institute (JASRI). The Ru K-edge XAFS spectra were measured in the fluorescence mode, with a Si(111) double-crystal monochromator at room temperature. Curve fitting analyses of the EXAFS spectra were conducted on $k^3\chi$ (k) in k-space (k range = 3–12 Å^{-1}) using a REX2000J program (Rigaku). The photoluminescence spectra were recorded at room temperature by utilizing a SPEX Fluorolog-3 spectrofluorometer with a quartz cell directly connected to a vacuum line containing stopcocks to allow gas addition and degassing. Inductively coupled plasma mass spectrometry (ICP-MS) was performed on X Series II (Thermo Fisher Scientific Inc.) to normalise the intensity of the photoluminescence spectra on the basis of Ru amount.

Photocatalytic hydrogen production reaction

The photocatalyst (10 mg) and water containing 0.01 M TEOA and 0.05 mM H_2PtCl_6 (2 mL) were added to a Pyrex reaction vessel connected to vacuum line. The resulting mixture was evacuated at 77 K to remove dissolved oxygen. Subsequently, the sample was irradiated with the 500 W Xe lamp through a cut-off filter with stirring at room temperature. After the reaction, the resulting gas was analyzed by using a gas chromatograph (GC) of Shimadzu GC-12A with a thermal conductivity detector equipped with a packed column (MS-5A). For the investigations of sacrificial reagents dependence, water containing 0.01 M EDTA and 0.05 mM H_2PtCl_6 or water containing 10 vol% methanol and 0.05 mM H_2PtCl_6 was used as a reaction solution.

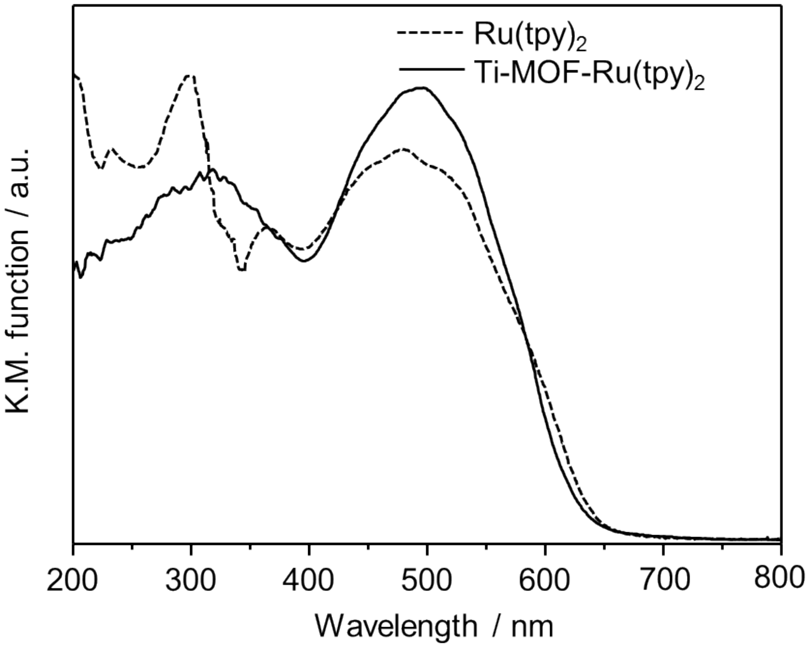

Fig. S1. Diffuse reflectance UV-vis spectra of Ti-MOF-Ru(tpy)$_2$ (solid line) and Ru(tpy)$_2$ (dotted line).

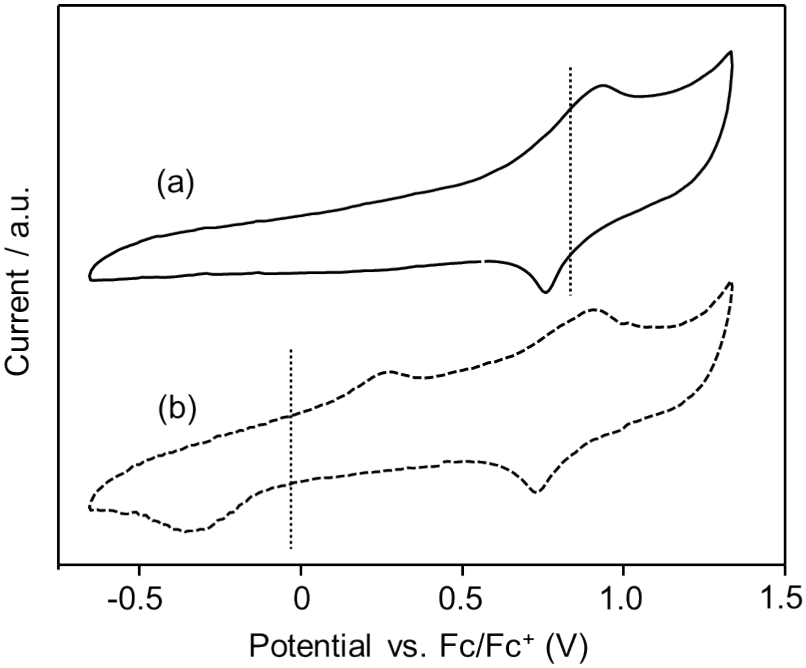

Fig. S2. Cyclic voltammograms of (a) Ru(tpy)$_2$ and (b) 2-amino-benzenedicarboxylic acid in CH_2Cl_2 with 0.1 M tetrabutylammonium perchlorate as supporting electrolytes. A Pt working electrode, a Pt counter electrode and a nonaqueous $Ag/AgNO_3$ reference electrode were used.

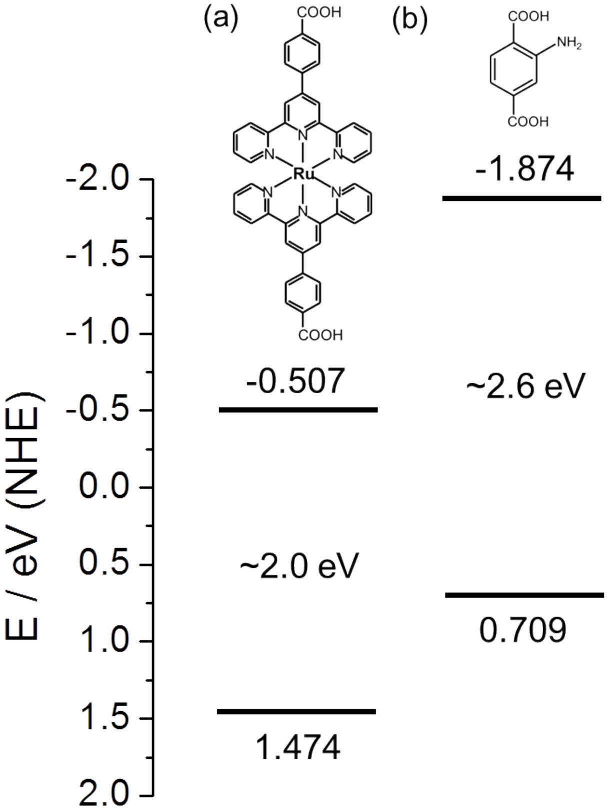

Fig. S3. Energy diagram of HOMO-LUMO levels of (a) $Ru(tpy)_2$ and (b) $H_2BDC-NH_2$. HOMO level was determined on the basis of cyclic voltammograms, and HOMO-LUMO gaps were estimated from the onset of the diffuse reflectance UV-vis spectra. For the diffuse reflectance UV-vis spectrum of $H_2BDC-NH_2$, see Ref. S3.

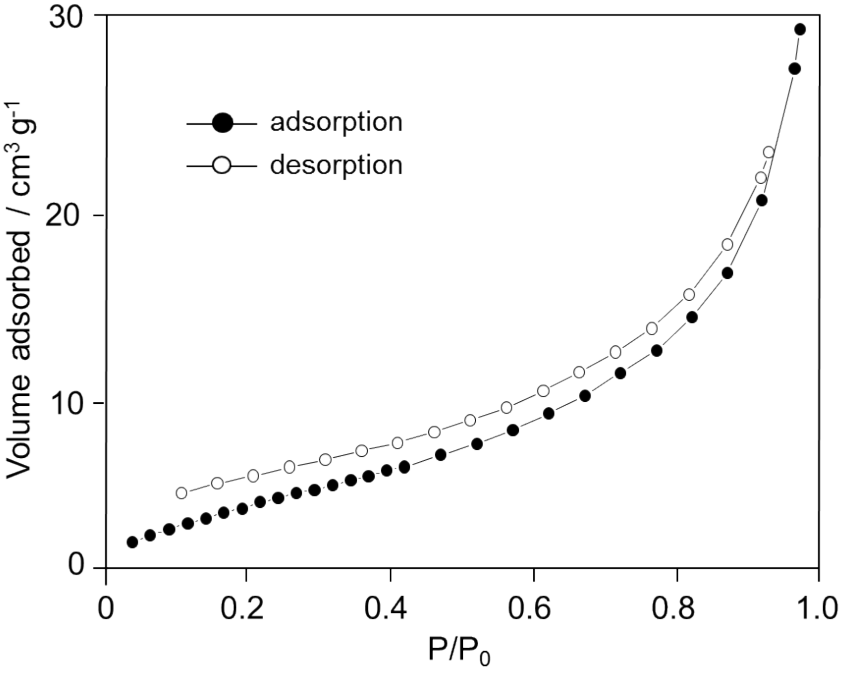

Fig. S4. N_2 adsorption-desorption isotherm of Ti-MOF-Ru(tpy)$_2$.

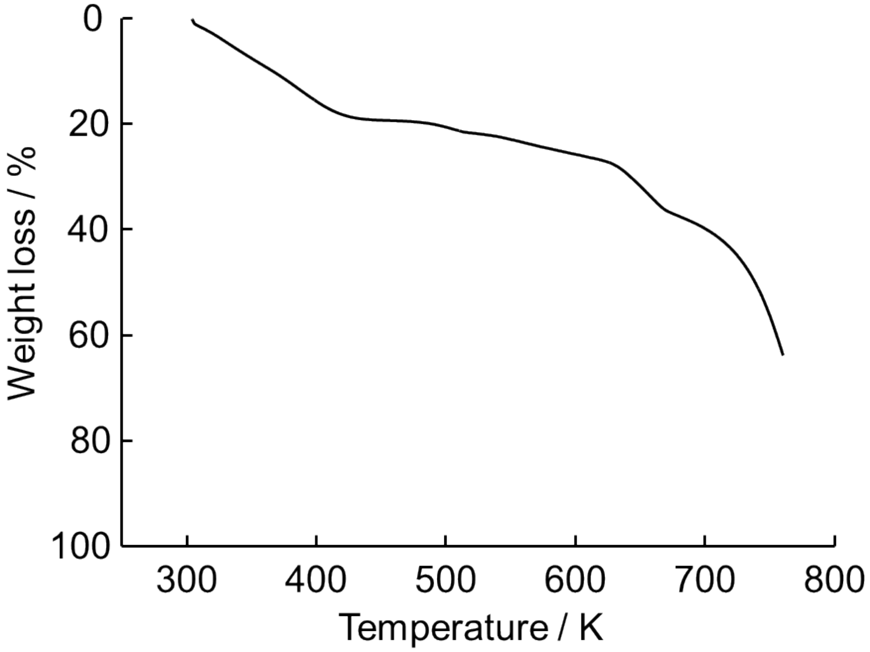

Fig. S5. TG curve of Ti-MOF-Ru(tpy)$_2$ measured with a heating rate of 10 K min^{-1} under N_2 flow.

Table S1. Control reactions of the photocatalytic H_2 production reaction for the reaction time of 6 h.

Entry	Photocatalyst	Cocatalyst	Sacrificial reagent	Light	Evolved H_2
1	Ti-MOF-Ru(tpy)$_2$	Yes	TEOA	Xe lamp ($\lambda > 420$ nm)	10.9 μmol
2	Ti-MOF-Ru(tpy)$_2$	Yes	None	Xe lamp ($\lambda > 420$ nm)	n. d.
3	Ti-MOF-Ru(tpy)$_2$	Yes	TEOA	None	n. d.
4	Ti-MOF-Ru(tpy)$_2$	No	TEOA	Xe lamp ($\lambda > 420$ nm)	2.1 μmol
5	Ru(tpy)$_2$	Yes	TEOA	Xe lamp ($\lambda > 420$ nm)	n. d.
6	Ru(tpy)$_2$/TiO$_2$	Yes	TEOA	Xe lamp ($\lambda > 450$ nm)[a]	n. d.

[a] Visible light longer than 450 nm was used for the reaction to avoid direct light absorption by TiO_2.

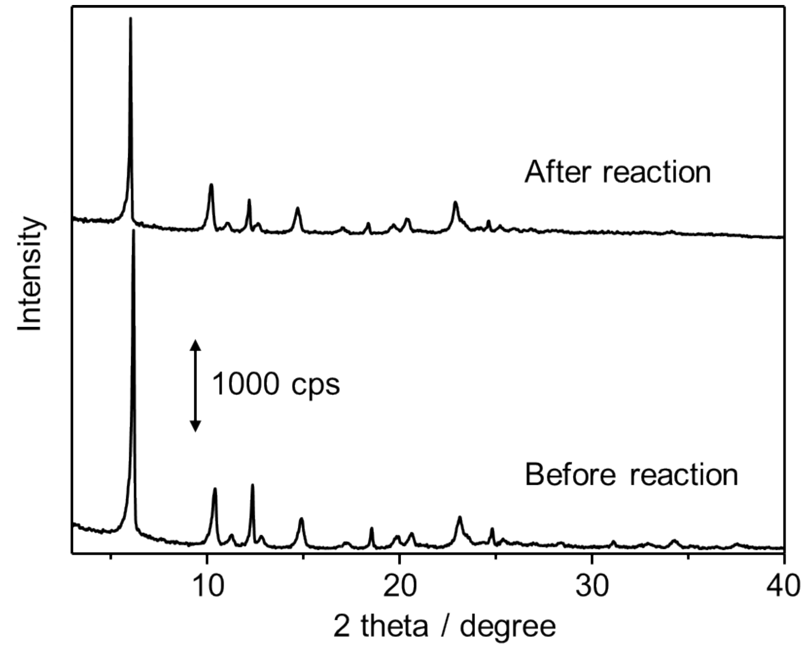

Fig. S6. XRD patterns of Ti-MOF-Ru(tpy)$_2$ before and after the photocatalytic hydrogen production from water containing 0.01 M TEOA and 0.05 mM H_2PtCl_6 for 6 h.

References

S1) E. C. Constable, E. L. Dunphy, C. E. Housecroft, M. Neuburger, S. Schaffner, F. Schaper and S. R. Batten, *Dalton Trans.*, 2007, 4323.

S2) M. Dan-Hardi, C. Serre, T. Frot, L. Rozes, G.Maurin, C. Sanchezand and G. Ferey, *J. Am. Chem. Soc.*, 2009, **131**, 10857.

S3) Y. Horiuchi, T. Toyao, M. Saito, K. Mochizuki, M. Iwata, H. Higashimura, M. Anpo and M. Matsuoka, *J. Phys. Chem. C*, 2012, **116**, 20848.