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Electronic Supplementary Information (ESI)

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Concerto catalysis — harmonising [NiFe]hydrogenase and NiRu model catalysts

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Experimental

Materials and methods

All experiments were carried out under a N_2 atmosphere by using standard Schlenk techniques and a glovebox. $[Ni^{II}LRu^{II}(\eta^6\text{-}C_6Me_6)(H_2O)](NO_3)_2$,[1] [NiFe]$H_2$ase (from *Desulfovibrio vulgaris* Miyazaki F)[2] and buffer solutions[3] at pH 2–12 for D_2/H_2O exchange reactions were prepared by the methods described in the literature. A phosphate buffer solution at pH 6.8 was prepared by Na_2HPO_4 and KH_2PO_4. Distilled water was purchased from Wako Pure Chemical Industries, Ltd, which was used as received. H_2 gas (99.9999%) was purchased from Taiyo Toyo Sanso Co., Ltd., D_2 gas (99.5%) was purchased from Sumitomo Seika Chemicals Co., Ltd., and HD gas (HD 97%, H_2 1.8%, D_2 1.2%) was purchased from Isotec Inc.; these were used without further purification.

H_2, HD and D_2 gases were determined by Shimadzu GC-8A (He carrier) with a $MnCl_2$-alumina column (model: Shinwa OGO-SP) at –196 ˚C (liquid N_2) and equipped with a thermal conductivity detector. In a pH range of 2–12, the pH of the solution was determined by a pH meter (TOA; HM-5A) equipped with a glass electrode (TOA; GS-5015C). Electrospray ionisation mass spectrometry (ESI-MS) data were obtained by an API 365 triple-quadrupole mass spectrometer (PE-Sciex) in the positive detection mode, equipped with an ion spray interface. The sprayer was held at a potential of + 5.0 kV, and compressed N_2 was employed to assist liquid nebulisation. IR spectra were recorded on a Thermo Nicolet NEXUS 8700 FT-IR instrument from 650 to 4000 cm^{-1} using 2 cm^{-1} standard resolution at ambient temperature. UV-visible spectra were recorded on a JASCO V-670 UV-Visible-NIR Spectrophotometer.

Synthesis and Characterisation of $[Ni^{II}L(H_2O)(\mu\text{-}H)Ru^{II}(\eta^6\text{-}C_6Me_6)](NO_3)$ {[1](NO$_3$), L = *N*,*N*'-dimethyl-*N*,*N*'-bis(2-mercaptoethyl)-1,3-propanediamine}

The aqua complex $[Ni^{II}LRu^{II}(\eta^6\text{-}C_6Me_6)(H_2O)](NO_3)_2$ (130 mg, 0.20 mmol) was

added to phosphate buffer solution (5.0 mL) of pH 6.8. H_2 (0.10 MPa) was bubbled through the solution at 25 °C to gradually precipitate dark-red crystals of [**1**](NO_3). After 3 h of the H_2 bubbling, the crystals were isolated by filtration {34% isolated yield based on $[Ni^{II}LRu^{II}(\eta^6\text{-}C_6Me_6)(H_2O)](NO_3)_2$}. ESI-MS analysis of the filtrate has shown a prominent signal at *m*/*z* 543.2 {relative intensity (*I*) = 100% in the range of *m*/*z* 200–1000}, that corresponds to $[\mathbf{1} - H_2O]^+$. ESI-MS (in H_2O), *m*/*z* 543.2 ($[\mathbf{1} - H_2O]^+$; *I* = 100% in the range of *m*/*z* 100–2000). IR (cm^{-1}, KBr disk) 1740 (Ni-H-Ru). Anal. Calcd for [**1**](NO_3)·H_2O: $C_{21}H_{43}N_3NiO_5RuS_2$: C, 39.32; H, 6.76; N, 6.55. Found: C, 39.54; H, 6.62; N, 6.54.

Typical procedure for hydrogen isotope exchange reaction between gaseous isotopes and medium isotopes catalysed by [1](NO_3).

Complex [**1**](NO_3) (1.0 μmol) was dissolved in H_2O buffer solutions (1.0 mL) at pH 2–12, respectively, under a N_2 atmosphere. D_2 gas (2.3 mL, 0.10 MPa) was injected in the resulting solution. The solution was shaken (100 rpm, Asone shaking incubator, Model PIC-100S) at 37 °C for 1 h. The gas present in the vial was sampled by a gas-tight syringe and analysed for H_2, HD and D_2 gases by GC. Isotope ratios for each of the identical runs were averaged. The maximum value of generation of H_2 (3.1 μmol) at pH 3.5 was normalised as 100% in Fig. 2.

Typical procedure for hydrogen isotope exchange reaction between gaseous isotopes and medium isotopes catalysed by [NiFe]H_2ase.

[NiFe]H_2ase (0.10 nmol) and methyl viologen ($[MV]^{2+}$) (1.0 μmol) were dissolved in H_2O buffer solutions (1.0 mL) at pH 2–12, respectively, under a N_2 atmosphere. D_2 gas (2.3 mL, 0.10 MPa) was injected in the resulting solution. The solution was shaken (100 rpm, Asone shaking incubator, Model PIC-100S) at 37 °C for 1 h. The gas present in the vial was sampled by a gas-tight syringe and analysed for H_2, HD and D_2 gases by GC. Isotope ratios for each of the identical runs were averaged. The maximum

value of generation of H_2 (18 μmol) at pH 7.1 was normalised as 100% in Fig. 3.

Typical procedure for hydrogen isotope exchange reaction between gaseous isotopes and medium isotopes catalysed by [1](NO$_3$) and [NiFe]H$_2$ase.

Complex [**1**](NO$_3$) (1.0 μmol), [NiFe]H$_2$ase (0.10 nmol) and $[MV]^{2+}$ (1.0 μmol) were dissolved in H_2O buffer solutions (1.0 mL) at pH 2–12, respectively, under a N_2 atmosphere. D_2 gas (2.3 mL, 0.10 MPa) was injected in the resulting solution. The solution was shaken (100 rpm, Asone shaking incubator Model, PIC-100S) at 37 °C for 1 h. The gas present in the vial was sampled by a gas-tight syringe and analysed for H_2, HD and D_2 gases by GC. Isotope ratios for each of the identical runs were averaged. The maximum value of generation of H_2 (17 μmol) at pH 4.2 was normalised as 100% in Fig. 4.

Reaction of $[MV]^{2+}$ with H_2 catalysed by [1](NO$_3$).

Complex [**1**](NO$_3$) (3.0 μmol) and $[MV]^{2+}$ (0.75 μmol) were dissolved in H_2O buffer solutions (3.0 mL) at pH 7 under a N_2 atmosphere. H_2 gas was injected in the resulting solution. The solution was shaken (100 rpm, Asone shaking incubator Model, PIC-100S) at 37 °C for 1 h. The reaction was followed by UV-vis spectroscopy in Fig S1a.

Reaction of $[MV]^{2+}$ with H_2 catalysed by [NiFe]H$_2$ase.

[NiFe]H$_2$ase (0.30 nmol) and $[MV]^{2+}$ (0.75 μmol) were dissolved in H_2O buffer solutions (3.0 mL) at pH 7 under a N_2 atmosphere. H_2 gas was injected in the resulting solution. The solution was shaken (100 rpm, Asone shaking incubator Model, PIC-100S) at 37 °C for 1 h. The reaction was followed by UV-vis spectroscopy in Fig S1b. The UV-vis spectra showed the appearance of the absorption around 600 nm derived from reduced methyl viologen ($[MV]^+$).

Reaction of $[MV]^{2+}$ with H_2 catalysed by 1•H$_2$ase {[1](NO$_3$) and [NiFe]H$_2$ase}.

Complex [**1**](NO_3) (3.0 μmol), [NiFe]H_2ase (0.30 nmol) and $[MV]^{2+}$ (0.75 μmol) were dissolved in H_2O buffer solutions (3.0 mL) at pH 7 under a N_2 atmosphere. H_2 gas was injected in the resulting solution. The solution was shaken (100 rpm, Asone shaking incubator Model, PIC-100S) at 37 °C for 1 h. The reaction was followed by UV-vis spectroscopy in Fig S1c. The UV-vis spectra showed the appearance of the absorption around 600 nm derived from $[MV]^{+}$.

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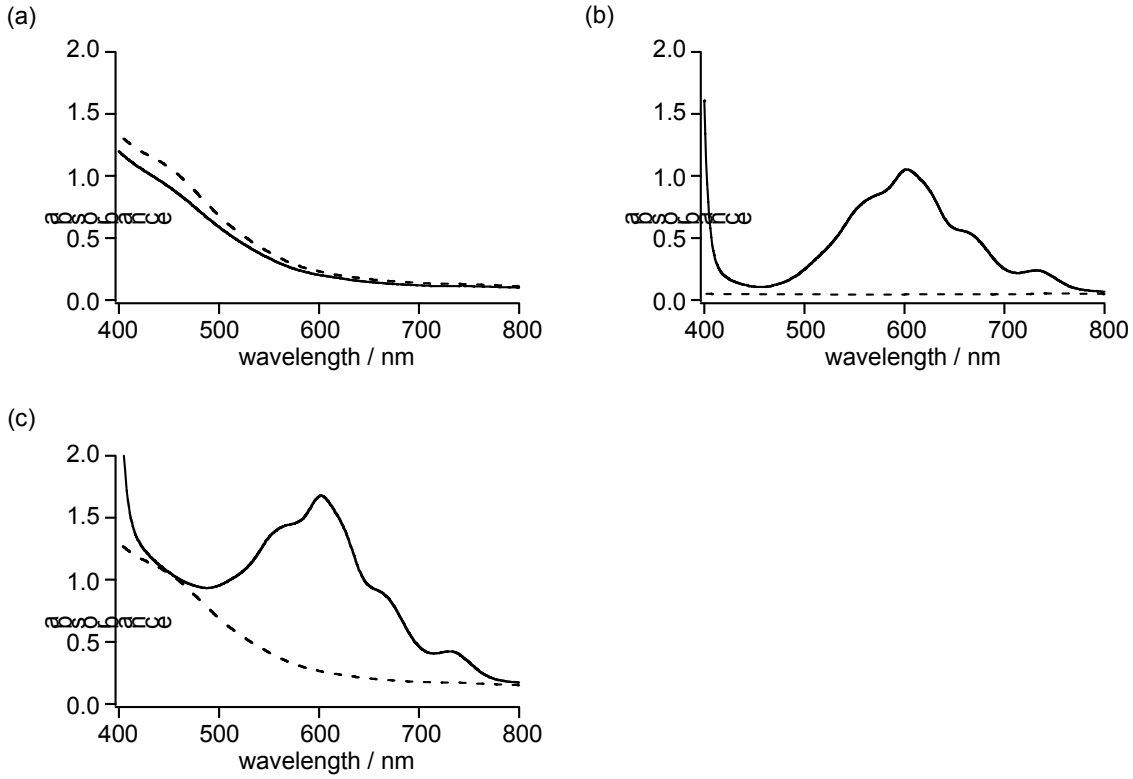

Fig. S1 UV-vis spectra of the reaction of $[MV]^{2+}$ with H_2 catalysed by (a) [**1**](NO_3), (b) [NiFe]H_2ase and (c) **1**•H_2ase {[**1**](NO_3) and [NiFe]H_2ase} in H_2O buffer solution at pH 7 at 37 °C for 1 h. The dotted line and solid line show the spectra before and after the reaction with H_2, respectively. The absorbance around 600 nm (solid line) in spectra (b) and (c) is derived from reduced $[MV]^{+}$.