

## Ru(II)-Re(I) Binuclear Photocatalysts Connected by $-\text{CH}_2\text{XCH}_2-$ ( $\text{X} = \text{O}, \text{S}, \text{CH}_2$ ) for $\text{CO}_2$ Reduction

Eishiro Kato,<sup>a</sup> Hiroyuki Takeda,<sup>a,b</sup> Kazuhide Koike,<sup>b,c</sup> Kei Ohkubo,<sup>a</sup> and Osamu Ishitani<sup>a,b\*</sup>

### Supporting Information

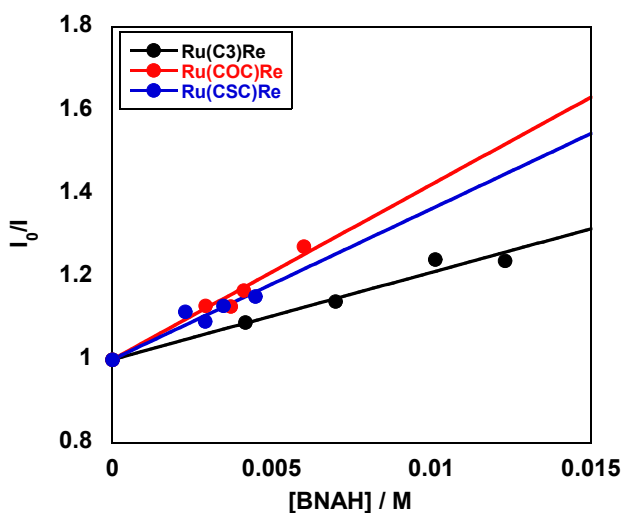


Figure S1. The Stern-Volmer plot of the diads.

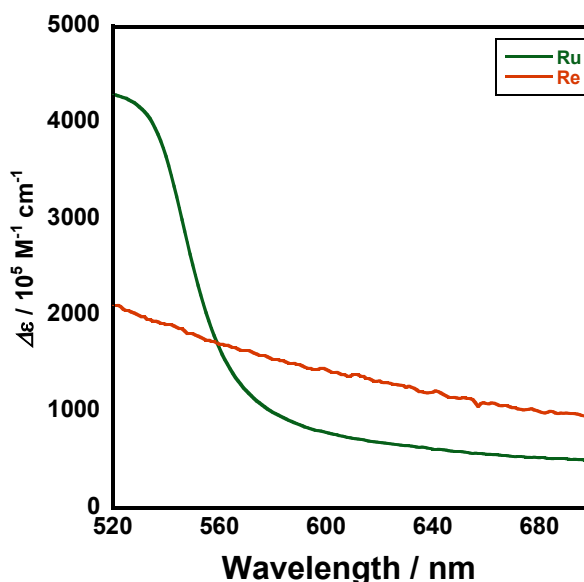
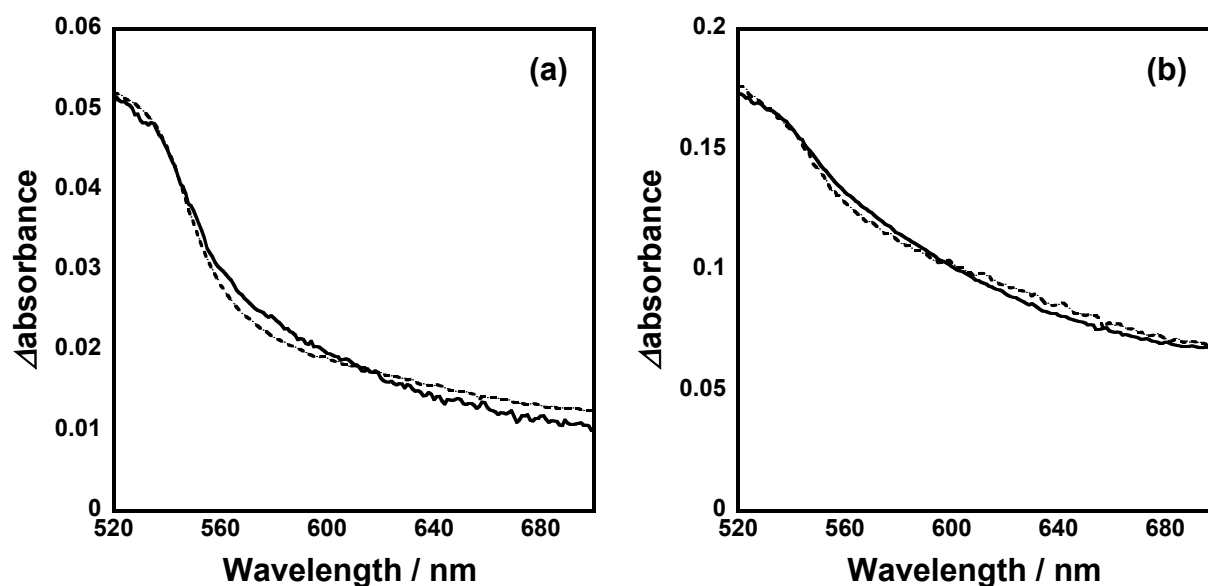
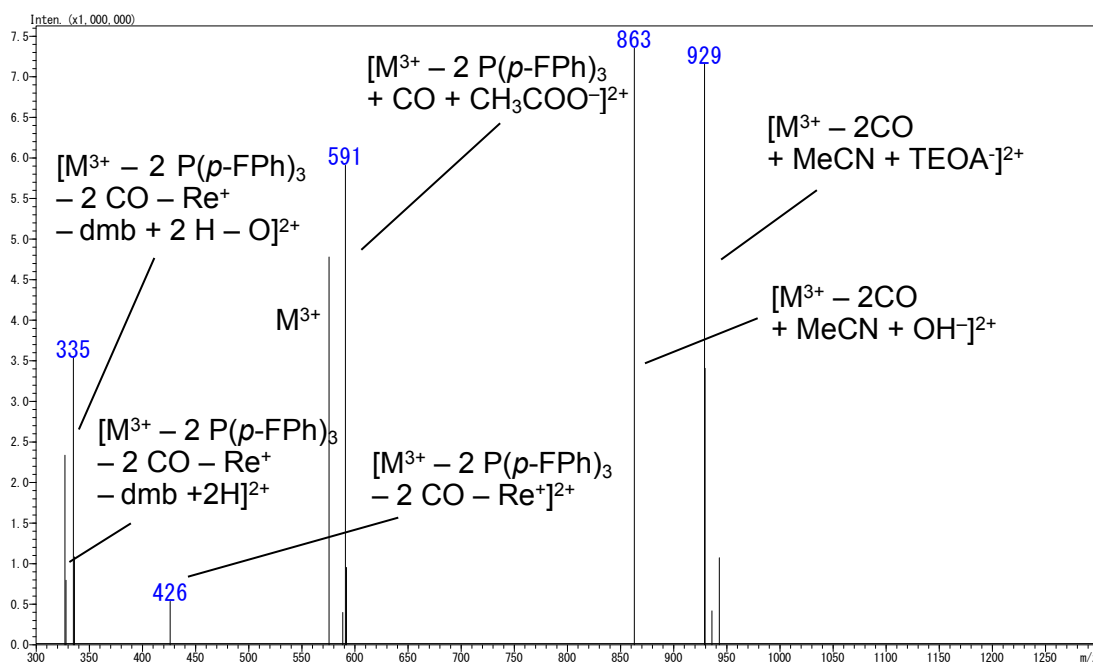


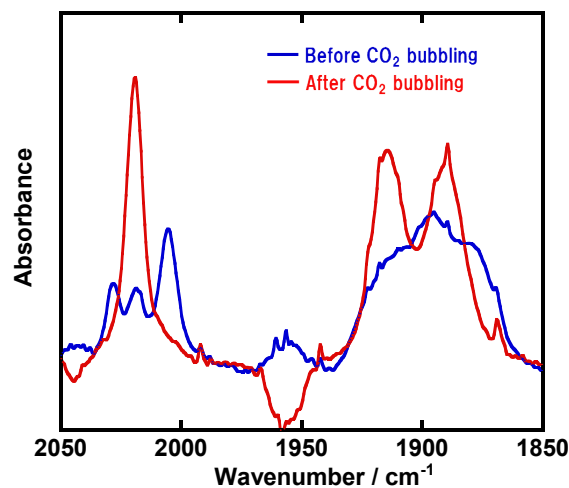
Figure S2. UV-vis absorption spectra of OER species in an Ar-saturated  $\text{CH}_3\text{CN}$  solution containing 0.1 M  $\text{Et}_4\text{NBF}_4$  at room temperature obtained by flow electrolysis method: **Ru** (green line) and **Re** (orange line).<sup>S1</sup>



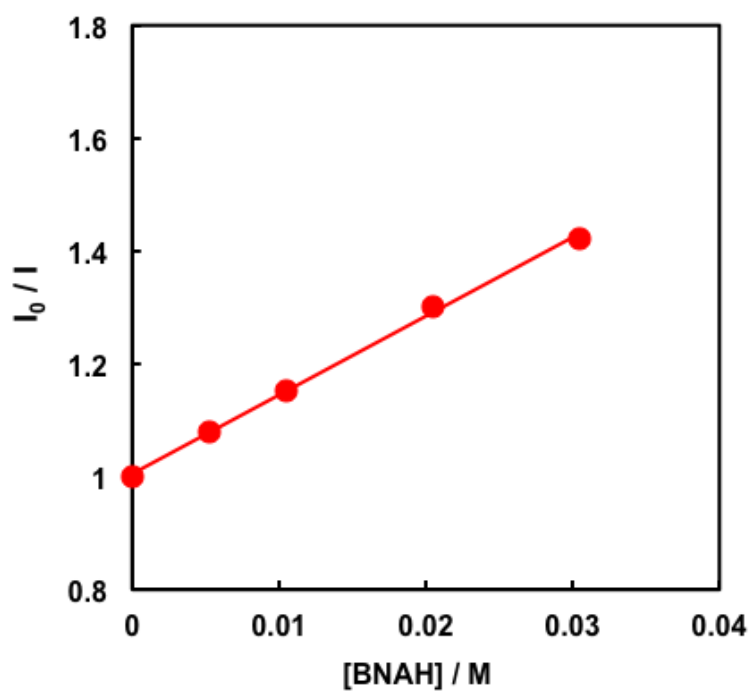
**Figure S3.** Differential UV-vis absorption spectrum of the photocatalytic reaction solution using (a):  $\text{Ru}(\text{CH}_2\text{CH}_2\text{CH}_2)\text{Re}$  before and after irradiation for 1080 s (solid line); (b):  $\text{Ru}(\text{CH}_2\text{OCH}_2)\text{Re}$  before and after irradiation for 2610 s (solid line) and the simulated spectrum using the spectra of the OER species of  $\text{Ru}$  and  $\text{Re}$  (broken line).



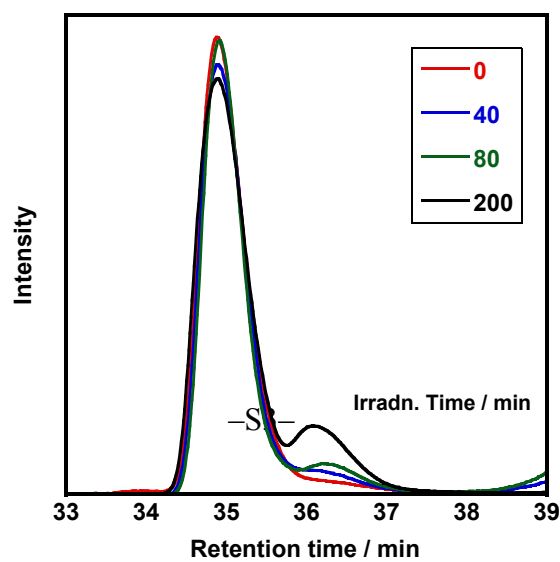
**Figure S4.** ESI-MS spectrum of the eluate at 36.1 min of retention time separated from the reaction solution after the photocatalytic reaction (120 min photoirradiation) of  $\text{Ru}(\text{CH}_2\text{OCH}_2)\text{Re}$  ( $\text{M}^{3+}$ ) by SEC using an MeCN-MeOH (1:1 v/v) mixed eluent containing 0.05 M  $\text{NH}_4^+\text{CH}_3\text{COO}^-$  with a shodex PROTEIN KW402.5 columns and a KW-LG guard-column under the following conditions: flow rate, 0.2 ml  $\text{min}^{-1}$ ; column temperature, 40 °C.



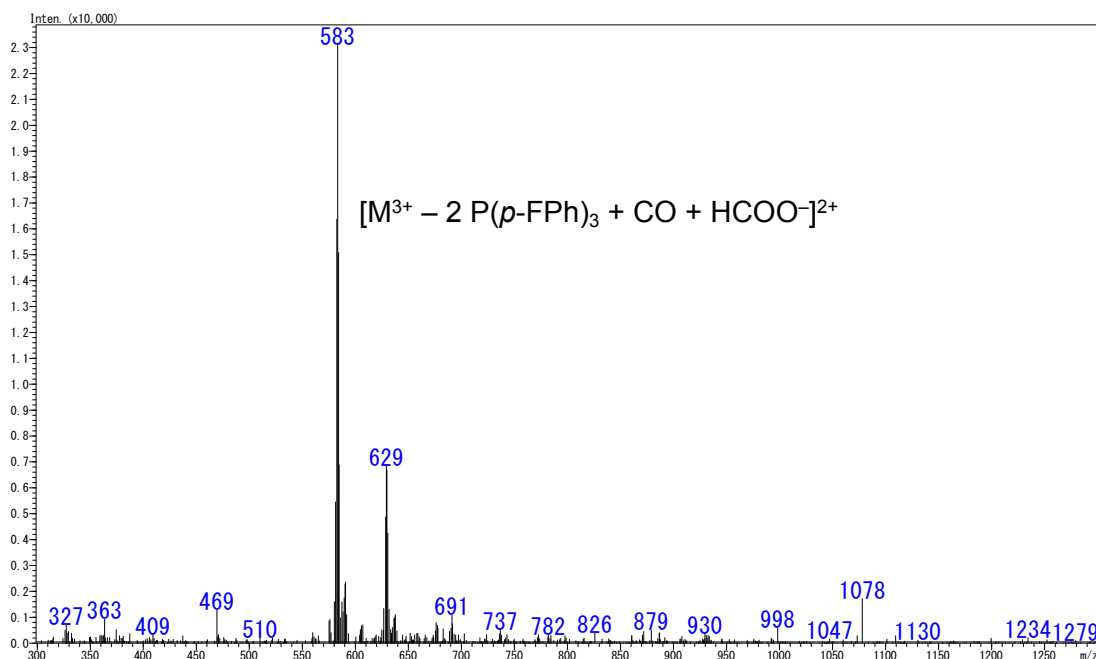
**Figure S5.** IR spectra of a DMF-TEOA (5:1 v/v) mixed solution containing  $\text{Ru}(\text{CH}_2\text{OCH}_2)\text{Re}(\text{X})$  ( $\text{X} = \text{DMF}$  or  $\text{TEOA}$ ) before and after  $\text{CO}_2$  bubbling for 15 min.



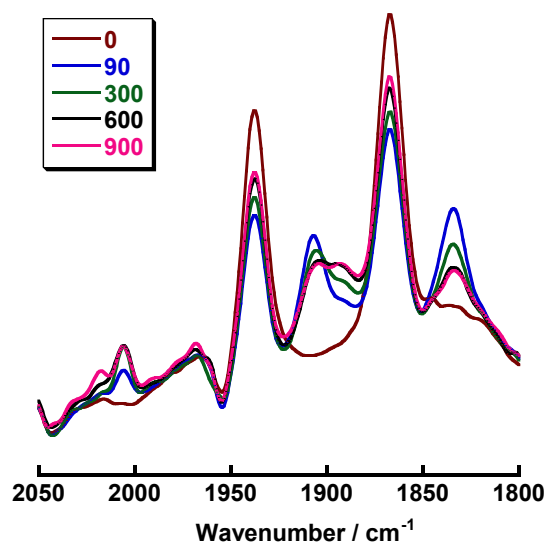
**Figure S6.** The Stern-Volmer plot of  $\text{Ru}(\text{CH}_2\text{OCH}_2)\text{Re}(\text{CO})_3(\text{X})$  ( $\text{X} = -\text{OC}(\text{O})\text{OC}_2\text{H}_4\text{N}(\text{C}_2\text{H}_4\text{OH})_2$ ).



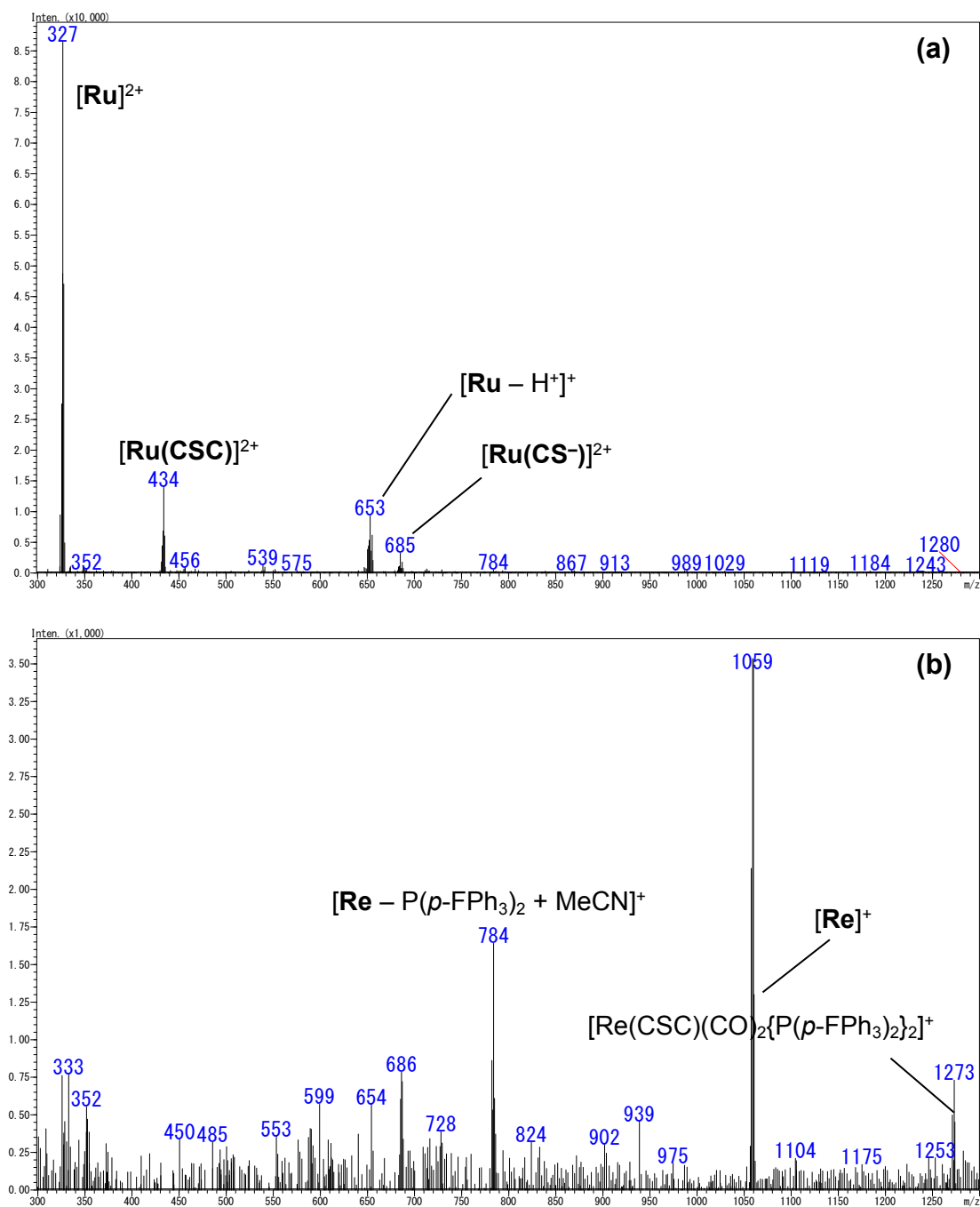
**Figure S7.** Analytical-SEC chromatograms of the solution after the photocatalytic reaction (irradiation time: 0, 40, 80 and 200 min) with a shodex PROTEIN KW402.5 columns and a KW-LG guard-column using an MeCN-MeOH (1:1 v/v) mixed eluent containing 0.5 M  $\text{NH}_4^+\text{CH}_3\text{COO}^-$  under the following conditions: flow rate, 0.2 ml  $\text{min}^{-1}$ ; column temperature, 40 °C; detection wavelength, 390 nm. In the photocatalytic reaction,  $\text{CO}_2$  saturated DMF-TEOA solutions containing BNAH (0.1 M) and  $\text{Ru}(\text{CH}_2\text{CH}_2\text{CH}_2)\text{Re}$  (0.3 mM) were irradiated at 480 nm using the lamp house apparatus with light intensity of  $3.2 \times 10^{-9}$  einstein  $\text{s}^{-1}$ .



**Figure S8.** ESI-MS spectrum of the eluate at 36.1 min of retention time separated from the reaction solution after the photocatalytic reaction (120 min photoirradiation) of  $\text{Ru}(\text{CH}_2\text{CH}_2\text{CH}_2)\text{Re}$  ( $\text{M}^{3+}$ ) by SEC using an MeCN-MeOH (1:1 v/v) mixed eluent containing 0.05 M  $\text{NH}_4^+\text{CH}_3\text{COO}^-$  with a shodex PROTEIN KW402.5 columns and a KW-LG guard-column under the following conditions: flow rate, 0.2 ml  $\text{min}^{-1}$ ; column temperature, 40 °C.



**Figure S9.** *In-situ* IR spectra of a DMF-TEOA (5:1 v/v) solutions containing **Ru(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)Re** (1 mM) and BNAH (0.1 M) during photoirradiation using 480-nm light under a CO<sub>2</sub> atmosphere.



**Figure S10.** ESI-MS spectrum of the eluates at 36.5 min (a) and 37.8 min (b) of retention time separated from the reaction solution after the photocatalytic reaction (120 min photoirradiation) of  $\text{Ru}(\text{CH}_2\text{SCH}_2)\text{Re}$  ( $\text{M}^{3+}$ ) by SEC using an MeCN-MeOH (1:1 v/v) mixed eluent containing 0.05 M  $\text{NH}_4^+\text{CH}_3\text{COO}^-$  with a shodex PROTEIN KW402.5 columns and a KW-LG guard-column under the following conditions: flow rate,  $0.2 \text{ ml min}^{-1}$ ; column temperature,  $40 \text{ }^\circ\text{C}$ .

## Reference

- S1. H. Tsubaki, A. Sugawara, H. Takeda, B. Gholamkhash, K. Koike and O. Ishitani, *Res. Chem. Intermed.*, 2007, **33**, 37.