Supporting Information

Synthesis of Os(II)-Re(I)-Ru(II) Hetero-Trinuclear Complexes and Their Photophysical Properties and Photocatalytic Abilities

Yasuomi Yamazaki and Osamu Ishitani*

Department of Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1-NE-1, Ookayama, Meguro-ku, Tokyo, 152-8550, Japan

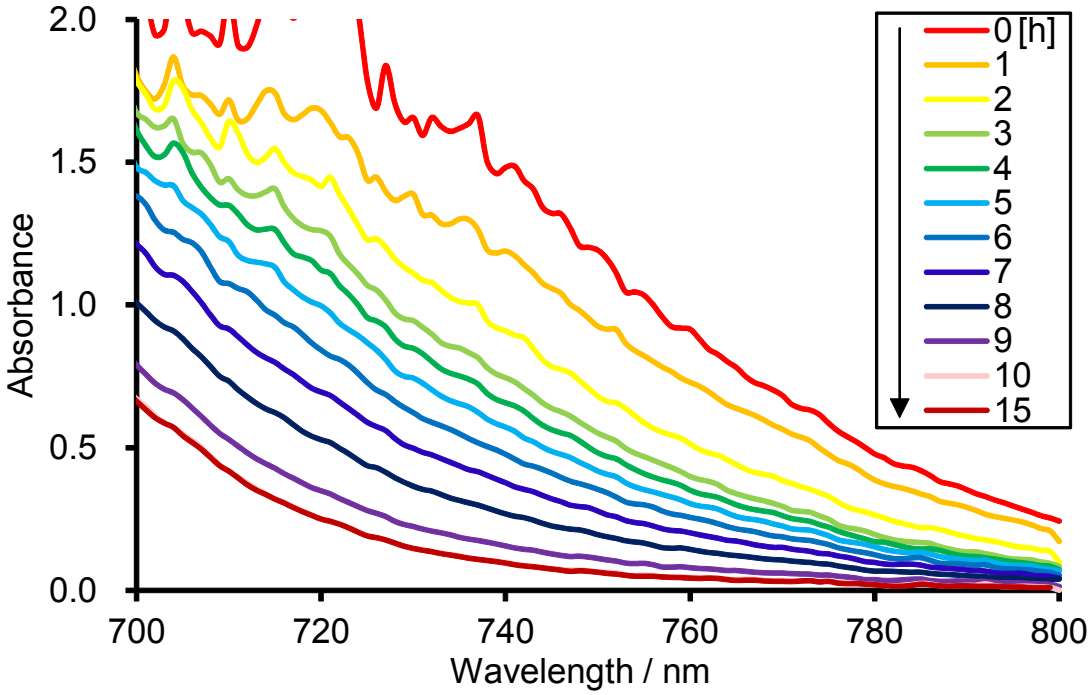

Figure S1. Absorption spectra change during photochemical hydrogenation of **Os=(5-Re)=Ru**.

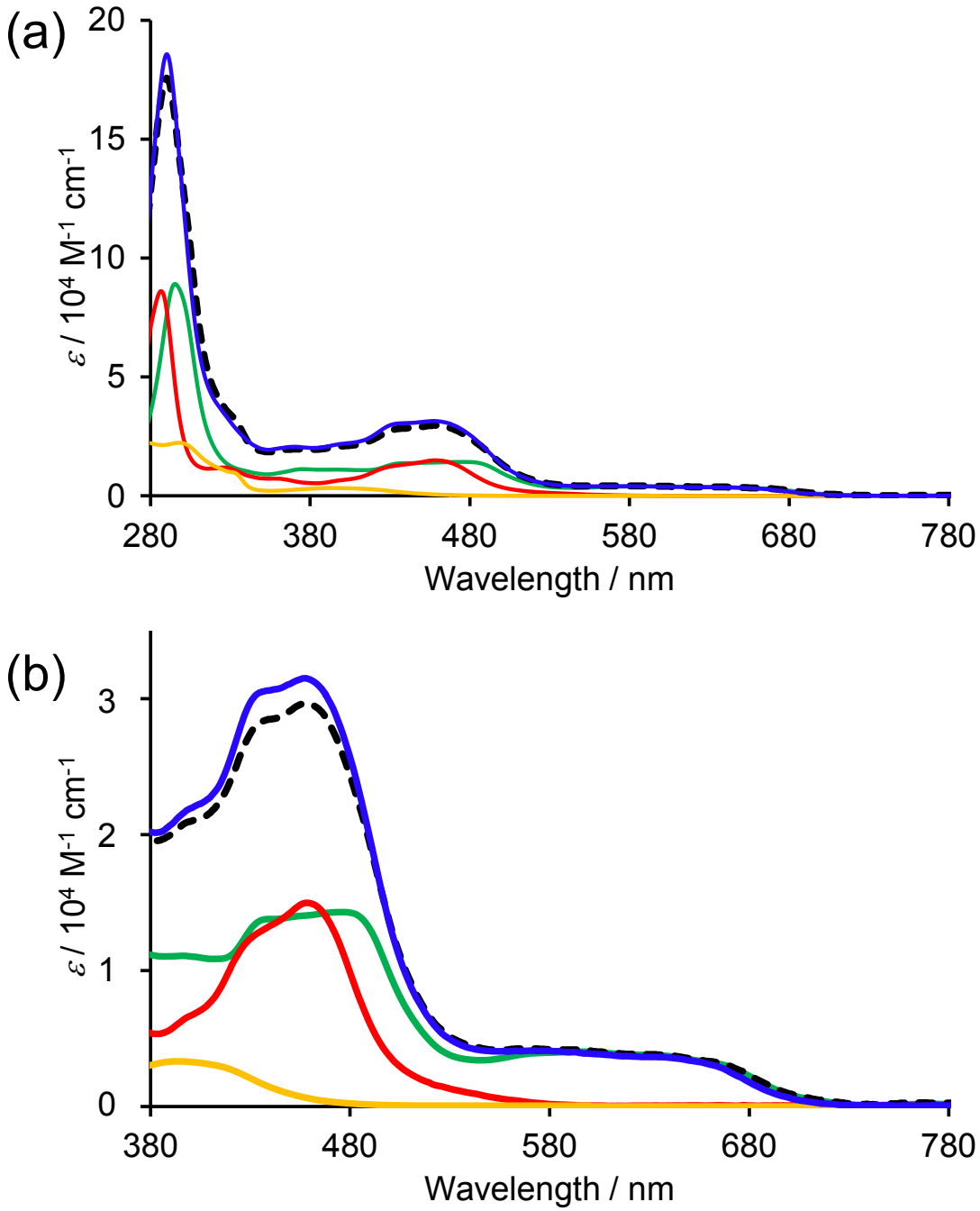

Figure S2. UV-Vis absorption spectra of the obtained trinuclear complex (a) **Os-(5-Re)-Ru** (blue) and corresponding mononuclear complexes, i.e., **Os(Me)** (green), **5-Re(Me)** (yellow) and **Ru(Me)** (red). The 1:1:1 summation spectrum of **Os(Me)**, **Re(Me)** and **Ru(Me)** are illustrated as a dotted line. The solvent was MeCN. The enlarged figures of (a) (380-780 nm) are shown in (b).

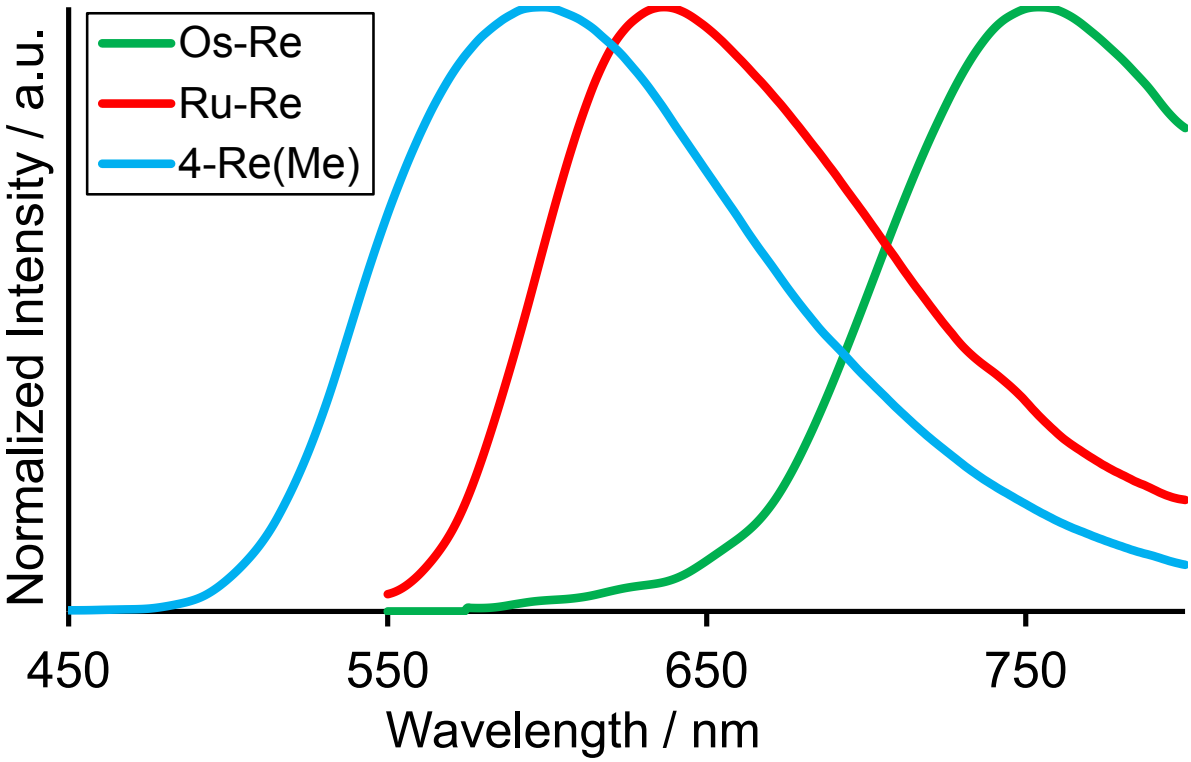

Fig. S3. Emission spectra of **Os-Re** (green), **Ru-Re** (red) and **4-Re(Me)** (blue).

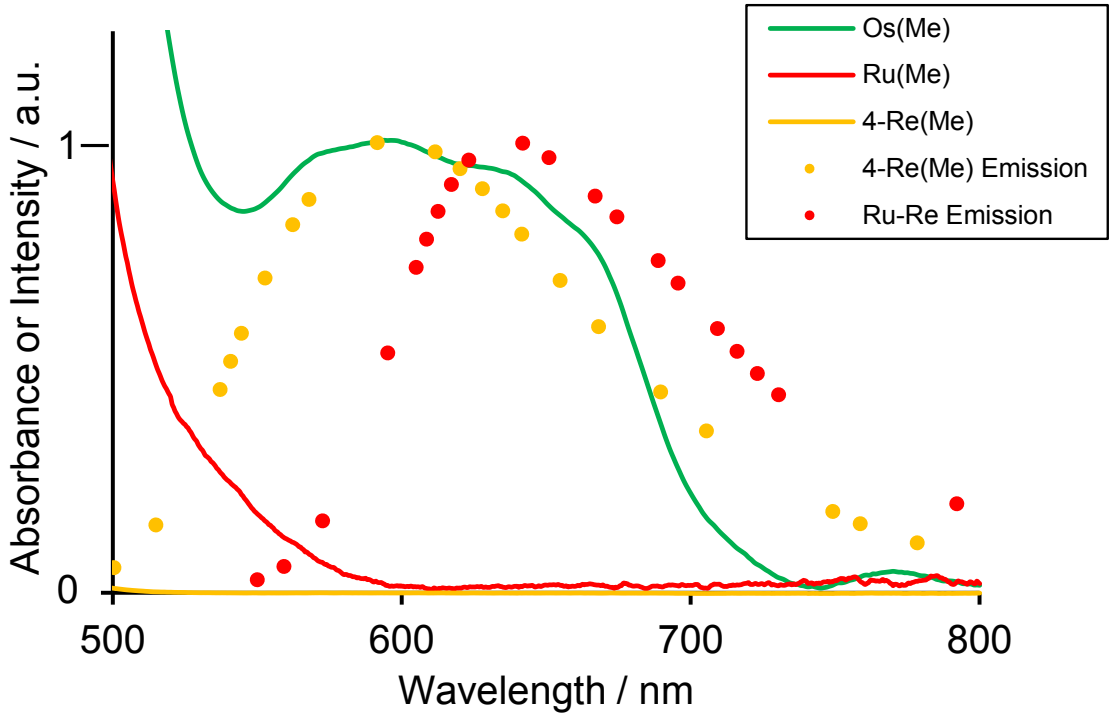

Figure S4. Absorption spectra of **Ru(Me)** (red solid line) and **Os(Me)** (green solid line) and emission spectra of **4-Re(Me)** (orange dotted line) and **Ru-Re** (red dotted line). The solvent is MeCN.

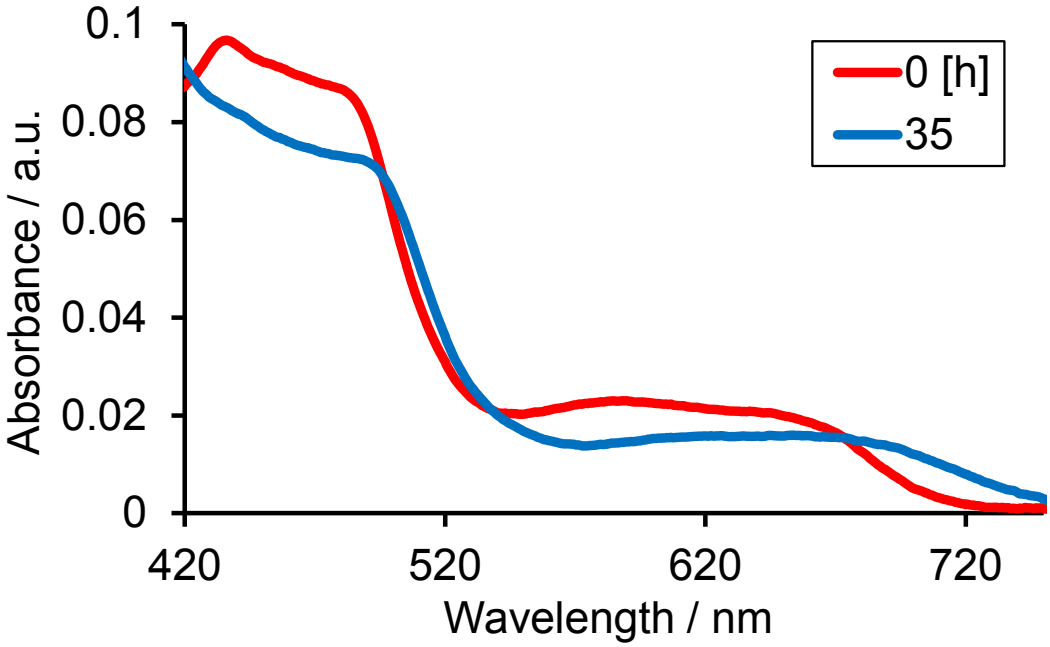

Figure S5. Absorption spectrum of **Os-Re** before (red) and after 35-h photocatalysis (blue).

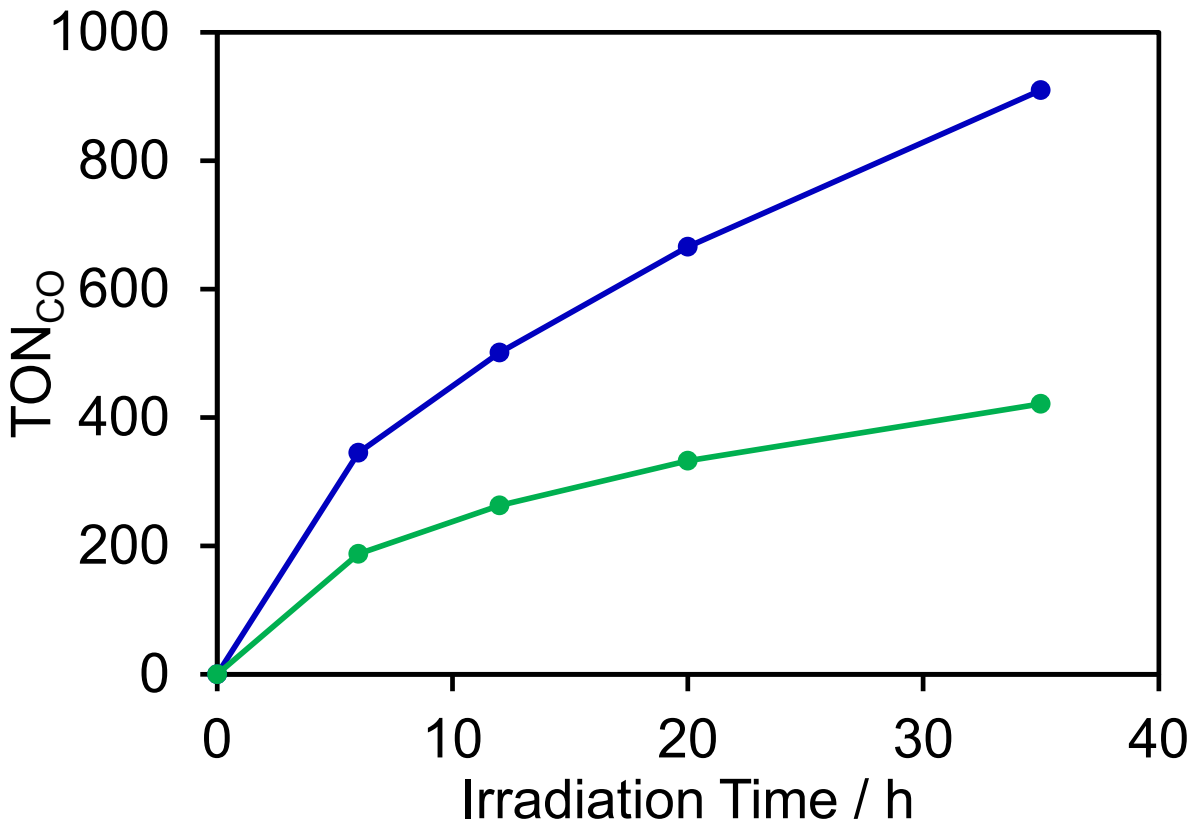

Figure S6. Time courses of the TON of CO formation during photocatalytic reactions (λ_{ex} > 620 nm) using a mixture of DMA and TEOA (5:1 v/v) containing 0.2 M BIH and metal complexes (blue: **Os-(5-Re)-Ru**, green: **Os-Re**). The concentration of each complex was 0.01 mM.

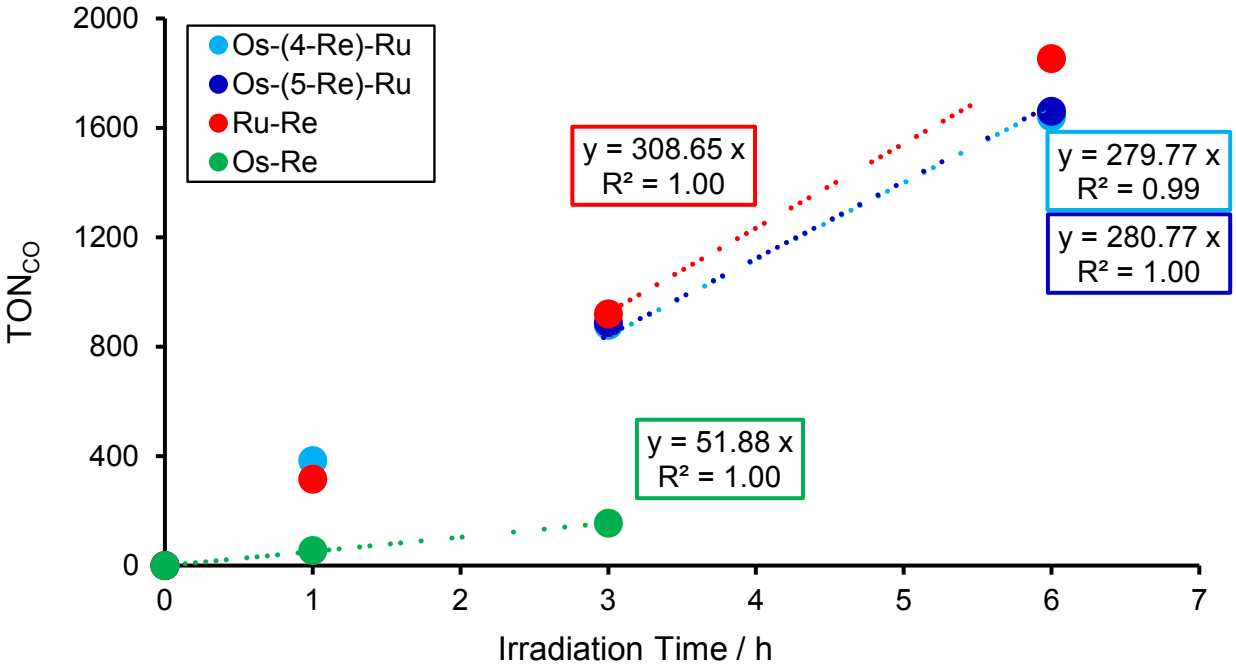

Figure S7. Time courses of the TON of CO formation in the initial stage of photocatalytic reactions (< 6 h, λ_{ex} > 500 nm) using a mixture of DMA and TEOA (5:1 v/v) containing 0.2 M BIH and metal complexes (sky blue: **Os-(4-Re)-Ru**, blue: **Os-(5-Re)-Ru**, red: **Ru-Re**, green: **Os-Re**). The concentration of each complex was 0.01 mM. TOF_{CO} was determined from the slopes of the fitting curves. In the case of the **Os-Re**, the fitting curve was drawn with plots recorded within 3 h because decrease of the reaction rate was observed after 3-h irradiation.

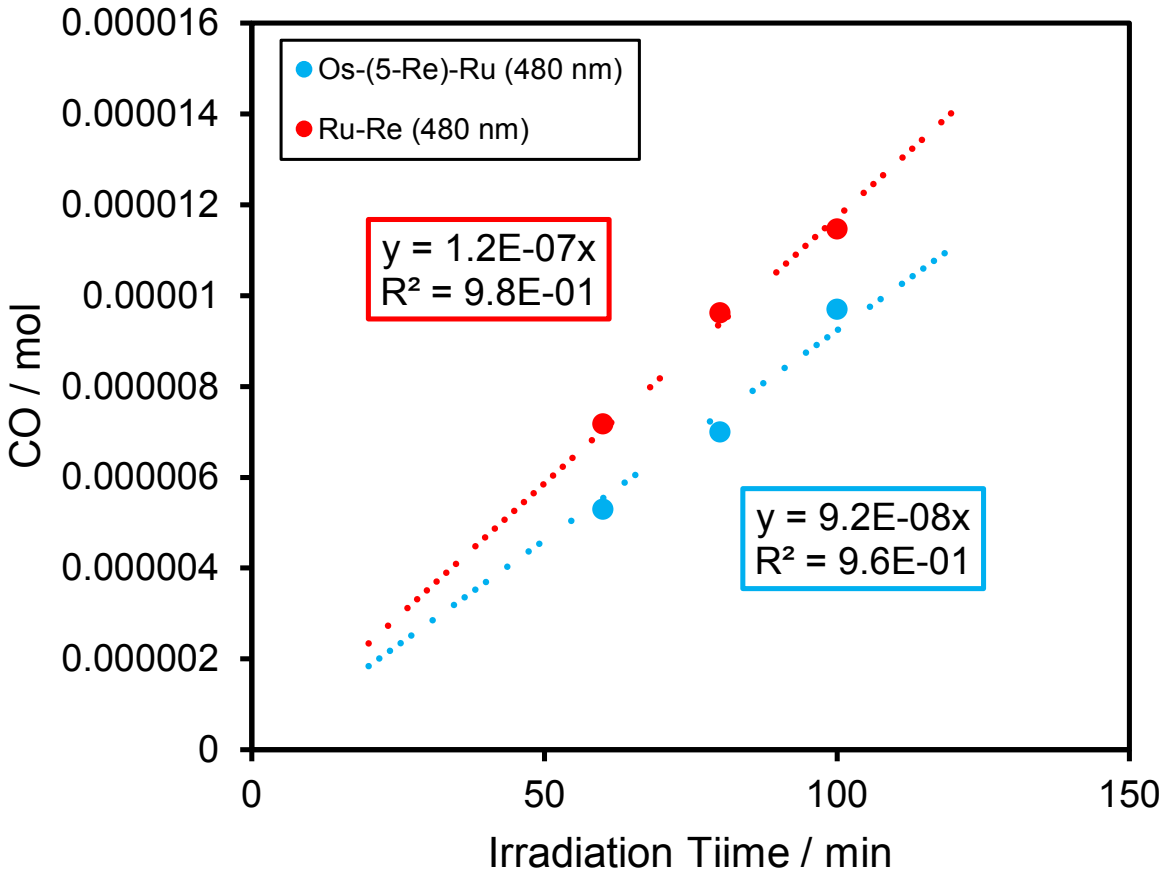

Figure S8. The relationship between the absorbed photon numbers and the amount of the produced CO using a mixture of DMA and TEOA (5:1 v/v) containing 0.1 M BIH and metal complexes with various excitation light source (blue: **Os-(5-Re)-Ru** (λ_{ex} = 480 nm), red: **Ru-Re** (λ_{ex} = 480 nm)). The concentration of each complex was 0.01 mM. Φ_{CO} were determined from the slopes of the fitting curves, and light intensity was 3×10^{-8} einstein/s.

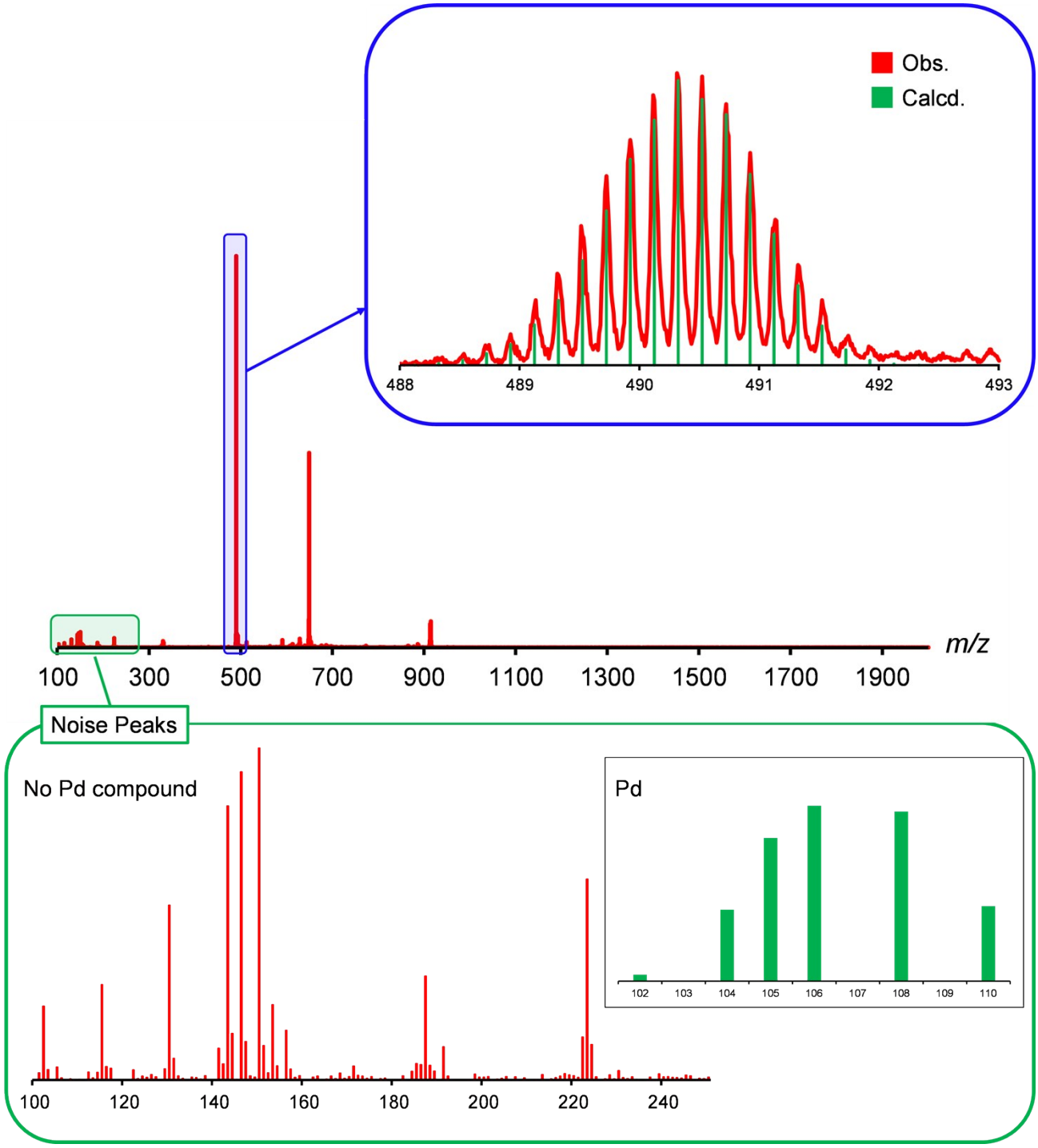

Figure S9. ESI-mass spectrum of **Os-(5-Re)-Ru**.