

## Supporting Information

### **Conjugation effect of the bridging ligand on the CO<sub>2</sub> reduction properties in difunctional photocatalysts**

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## Experimental Section.

**Instrumentation and Measurements.** NMR spectra were measured on a Bruker Avance DPX 400 MHz resonance spectrometer. Absorption spectra were measured on a Hitach U-3010 spectrophotometer. Electrospray ionization–mass spectroscopy (ESI-MS) was performed with an APEXII FT-ICR system, using HPLC-grade acetonitrile or methanol as the mobile phase. FT-IR spectra were taken as KBr pellets using a Varian 3010 FT-IR spectrometer. Raman spectra were measured in powder state on a Renishaw inVia-Reflex confocal laser micro-Raman spectrometer with excitation wavelength of 785 nm. Redox potentials of metal complexes were measured by cyclic voltammetry (CV) using a CHI660 electrochemical analyzer in a standard three-electrode cell arrangement. Voltammograms were recorded using a glass-carbon working electrode (diameter, 3 mm) in acetonitrile solutions of the complexes (1 mM) containing 0.1 M supporting electrolyte, tetrabutylammonium hexafluorophosphate.

Photocatalytic reduction was performed in a quartz test tube containing a DMF/TEOA (5:1) solution of the metal complexes (0.05 mM) and a sacrificial electron donor (BNAH, 0.1 M) after purging with CO<sub>2</sub> for 20 min. For a selective excitation of the ruthenium moiety, solutions were irradiated at  $\lambda \geq 500$  nm using a Xe lamp, in a merry-go-round irradiation apparatus, combined with a K<sub>2</sub>CrO<sub>4</sub> (30% w,  $d = 2$  cm) solution filter. All experiments were conducted at the ambient temperature. Gas samples were taken using a gas-tight syringe. The gaseous reaction products were detected by GC-TCD.

**Computational methods:** All computations were performed with the Gaussian 03

package.[1] Geometry optimizations and molecular orbital calculations were performed on the density functional theory (DFT) level using B3LYP/6-31G(d) and LANL2DZ basis set.

**Materials.** Diisopropylamine and acetonitrile were freshly distilled from CaH<sub>2</sub> before use. Tetrahydrofuran (THF) was freshly distilled from Na before use. DMF was dried over 4 Å molecular sieves and distilled at reduced pressure. Triethanolamine (TEOA) was also distilled at reduced pressure. All of the purified solvents were kept under nitrogen pressure before use. The spectroscopic data were obtained on samples dissolved in the purified or spectral-grade solvents. All other reagents were reagent grade quality and were used without further purification.

**Synthesis.** *cis*-[Ru(dmb)<sub>2</sub>Cl<sub>2</sub>]•2H<sub>2</sub>O was synthesized by a modification of the literature procedure.[2] All transfer of solutions was carried out by using glass syringes and/or steel cannulas under the positive nitrogen pressure. All glassware were completely dried. Reactions were conducted under a nitrogen atmosphere. Chromatographic purifications were carried out on silica gel 60 (230-400 mesh) otherwise noted. All complexes were protected from light during synthesis and measurement processes.

1,2-bis(4-methyl-2,2'-bipyridyl-4'-yl)ethane (**L1**) and 1,2-bis(4-methyl-2,2'-bipyridyl-4'-yl)ethene (**L2**) were synthesized by the literature procedures.[3,4]

The synthesis and purification methods used for the heteronuclear complexes **Ru-Re**, **Ru=Re** are described below. These complexes were characterized by NMR, ESI-MS, Elemental Analyses.

### **Ru-Re**

A solution of **L1** (74 mg, 0.2 mmol) in deoxygenated ethanol (20 mL) was purged

with N<sub>2</sub> for 15 min. *cis*-[Ru(dmb)<sub>2</sub>Cl<sub>2</sub>]•2H<sub>2</sub>O (58 mg, 0.1 mmol) in 100 mL of deoxygenated ethanol was added dropwise while the mixture was heated at reflux under Nitrogen pressure. When the addition was completed, the resulting mixture was stirred for additional 4 h. After that, the dark-red solution was cooled to room temperature and concentrated to 2 mL, and charged on a Sephadex LH-20 column using ethanol as an eluent. The middle of main red band was collected and evaporated to dryness.

[Re(CO)<sub>5</sub>Cl] (48 mg, 0.14 mmol) was dissolved in deoxygenated ethanol (200 mL) under N<sub>2</sub> pressure. To the solution, the prepared mono ruthenium L1 complex (64 mg, 0.07 mmol) was added under N<sub>2</sub> pressure. The mixture was heated at reflux for 8 h. After this period, the resulting red solution was cooled to room temperature and concentrated to 10 mL. The product was changed to PF<sub>6</sub> salt by addition of excess aqueous ammonium hexafluorophosphate. The precipitate was collected by filtration and purified on a silica gel column (Eluent: MeCN/ H<sub>2</sub>O/ KNO<sub>3</sub> 80/20/0.05 M) to give **Ru-Re**.

Yield: 57 mg, 40%.

ESI-MS: *m/z* = 571.1 (100%, [M-2(PF<sub>6</sub>)]<sup>2+</sup>).

FT-IR (CO bands in the Re<sup>I</sup> center, cm<sup>-1</sup>): 2019, 1911, and 1892 (shoulder).

Anal. Calcd for C<sub>51</sub>H<sub>46</sub>N<sub>8</sub>O<sub>3</sub>P<sub>2</sub>F<sub>12</sub>ClRuRe•2H<sub>2</sub>O: C, 41.74; H, 3.43; N, 7.63%. Found: C, 41.67; H, 3.42; N, 7.58%.

<sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN; δ(ppm)): 2.59-2.45 (m, 18H); 3.22-3.26 (m, 4H); 7.16-7.39 (m, 7H); 7.47-7.54 (m, 7H); 8.23-8.35 (m, 8H); 8.76-8.84 (m, 2H).

### **Ru=Re**

The synthesis procedure was similar with that of **Ru-Re** unless **L2** used other than **L1**. The

product was purified three times on a silica gel column.

Yield: 50 mg, 35%.

ESI-MS:  $m/z = 569.9$  (100%,  $[M-2(PF_6)]^{2+}$ ).

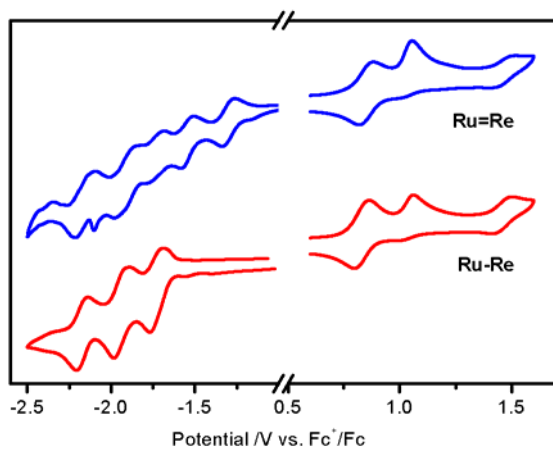
FT-IR (CO bands in the  $Re^I$  center,  $cm^{-1}$ ): 2019, 1913, and 1896.

Anal. Calcd for  $C_{51}H_{44}N_8O_3P_2F_{12}ClRuRe \cdot 3H_2O$ : C, 41.29; H, 3.40; N, 7.55%. Found: C, 41.40; H, 3.41; N, 7.51%.

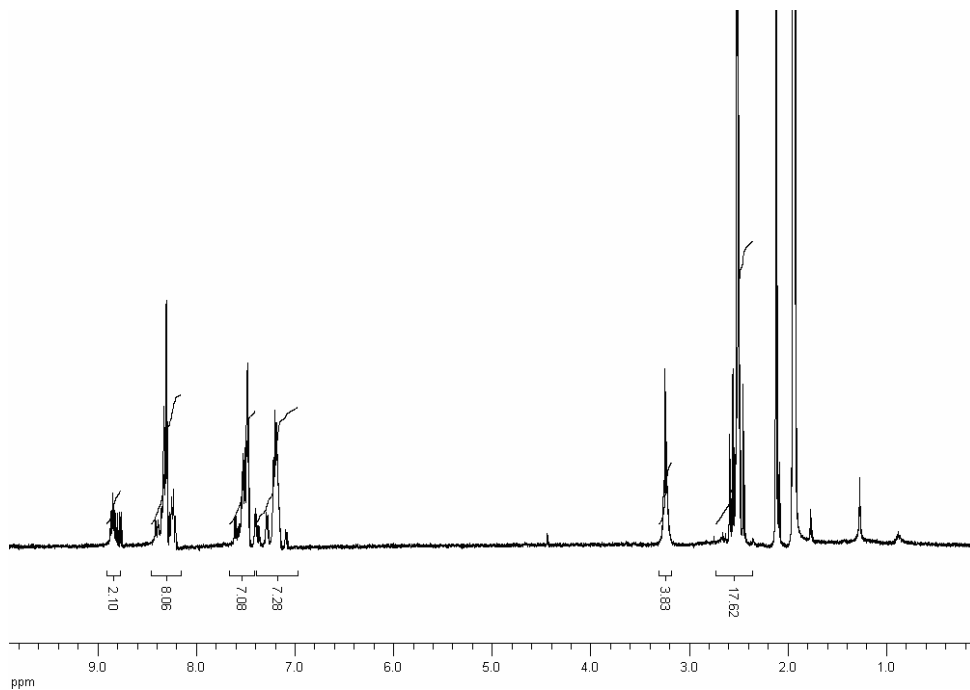
$^1H$  NMR (400 MHz,  $CD_3CN$ ;  $\delta$ (ppm)): 2.52(s, 12H), 2.56(s, 3H), 2.58(s, 3H), 7.22-7.25(m, 4H), 7.46-7.60(m, 8H), 7.70-7.75(m, 4H), 8.34-8.68(m, 8H), 8.84(d, 1H), 8.99(d, 1H).

**Table S1.** Raman energy bands ( $\text{cm}^{-1}$ ) of **Ru-Re** and **Ru=Re** in comparison to those observed in  $[\text{Ru}(\text{dmb})_3]^{2+}$  and  $[\text{Re}(\text{dmb})(\text{CO})_3\text{Cl}]$ , which was used as a reference substance to assign the vibrational modes associated with the ligands.

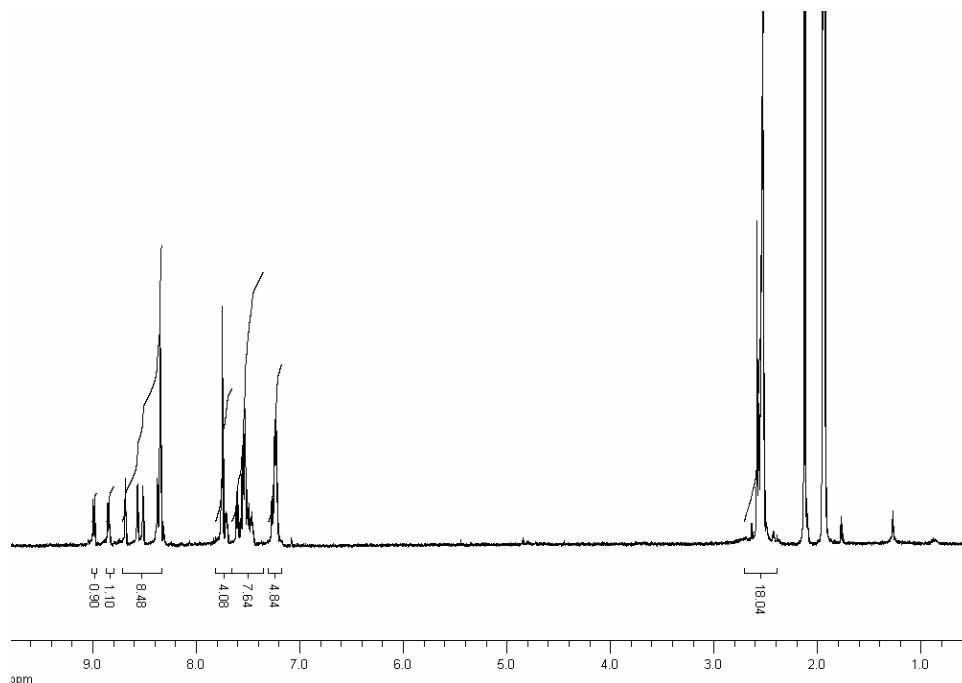
$[\text{Ru}(\text{dmb})_3]^{2+}$	$[\text{Re}(\text{dmb})(\text{CO})_3\text{Cl}]$	<b>Ru-Re</b>	<b>Ru=Re</b>	ligand assignments
1031	1034	1032	1028	L2, dmb
1040		1040		dmb
			1189	-C(ring)-C=C- of L2
1196				dmb
			1218	L2
1258		1262		dmb
1274	1287	1276	1274	dmb
1319	1323	1321	1322	dmb
			1334	L2
			1428	L2
1482	1491	1485	1485	dmb, L2
1550	1556	1552	1544	dmb, L2
1619	1622	1622	1612	dmb, L2
			1640	-C=C- of L2



**Figure S1.** Cyclic voltammograms of **Ru=Re** and **Ru-Re** in acetonitrile with TBAPF<sub>6</sub> as the supporting electrolyte.



**Figure S2.** Proton NMR spectrum of **Ru-Re** in acetonitrile-d<sub>3</sub> at room temperature.



**Figure S3.** Proton NMR spectrum of **Ru=Re** in acetonitrile- $d_3$  at room temperature.

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