Electronic Supplementary Material (ESI) for Chemical Science.

Electronic Supporting Information for

Efficient Trinuclear Ru(II)-Re(I) Supramolecular Photocatalysts for CO_2 Reduction Based on a New Tris-chelating Bridging Ligand Build Around a Central Aromatic Ring

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Materials, methods, and equipments

DMA was dried over activated molecular sieves 4 Å, distilled under reduced pressure and stored under argon before use. TEOA was distilled under reduced pressure. BNAH[1] and BIH[2] were synthesized as reported in literature.

Electrospray ionization time-of-flight mass spectroscopy (ESI-TOFMS) was undertaken with a Waters LCT Premier, with acetonitrile as mobile phase. UV-Vis spectra were measured in acetonitrile on a JASCO V-560 UV/VIS. Emission spectra were measured with a SpexJobin Yvon FluoroMax-2 spectrofluorimeter equipped with a photomultiplier Hamamatsu R3896. Emission lifetimes were obtained using a Horiba FluoroCube time-correlated single photon counting system. The excitation light source was a LED pulse lamp (NanoLED, 401 nm). The samples were dissolved in MeCN and purged with Ar for 20 min before lifetime measurements. The emission quantum yields were evaluated with emission from $[Ru(bpy)_3]Cl_2$ in water (Φ_{em} = 0.040).[3] IR spectra were recorded with a JASCO FT/IR-6600 in MeCN. UHPLC measurement was conducted by SHIMADZU UPLC Nexera X2 with a UPLC BEH125 SEC 1.7 μm 4.6 x 150 mm column kept at 40 °C. A mixed solvent of acetonitrile-methanol (1:1 v/v) containing CH_3COONH_4 (0.5 M) was used as a mobile phase. Emission quenching experiments were performed at 25 °C under an Ar atmosphere using a JASCO FP-8600 spectrofluorimeter in DMA/TEOA (5:1 v/v) solutions containing complex and four different concentrations of sacrificial agents. Quenching rate constants k_q were calculated from linear Stern–Volmer plots for the luminescence of the triplet metal-to-ligand-charge-transfer (^{3}MLCT) excited state of the photosensitizer units together with knowledge of their lifetimes.

Redox potentials were measured in an Ar purged acetonitrile solution containing the complex (0.5 mM) and Bu_4NPF_6 (0.1M) as supporting electrolyte through CV, DPV and SW using an Autolab equipment with a glassy carbon electrode as working electrode, a Pt wire as counter electrode and a silver wire as pseudo-reference electrode. As internal reference was used the redox couple ferrocene/ferrocenium (395 mV vs. SCE in acetonitrile).

For the TONs determination, 3 mL of DMA/TEOA (5:1 v/v) solution of complex (0.05 mM) and sacrificial agent (0.1 M) in 11 mL (i.d. = 8 mm) pyrex tubes were purged with CO_2 and irradiated with a Merry-go-round type irradiation apparatus using LED (530 nm, 4 mW) as a light source, Iris-MG (CELL System co.).

For the quantum yield determination, 4 mL of DMA/TEOA (5:1 v/v) solution of complex (0.05 mM) and sacrificial agent (0.1 M) in 11 mL quartz cubic cell (optical path length: 1 cm) was purged with CO2 for 20 min, and then irradiated with a SHIMADZU QYM-01 apparatus with light at 480 nm using a 500-W Xe lamp (Asahi Spectra Co.) with a bandpass filter. The temperature of the solutions was maintained at 25 ± 0.1 ◦C using an IWAKI CTS-134A constant-temperature system.

H_2 and CO (the gaseous photoreaction product) were quantified with a GC-TCD (GL science GC323) with an active carbon column and argon as gas carrier and the amount of formic acid was analysed by capillary electrophoresis system (Agilent7100L) with buffer solution and water dilution.

Synthesis

Synthesis of bpy_3Ph.

4,4′-Dimethyl-2,2′-dipyridyl (1.83 g, 10 mmol) was dissolved in 140 mL of dry THF under argon atmosphere. The solution was cooled at -33°C and a solution 1M of lithium diisopropylamide (12 mmol, 12 mL) were added dropwise. After stirring for 90 min, 38 mL of a solution of 1,3,5-Tris(bromomethyl)benzene (1g, 2.8 mmol) was added dropwise. The solution was left stirring overnight for 48h. After this period, the reaction was quenched adding 15 mL of water. The mixture was extracted with diethylether (3 x 250 mL) and dichloromethane (2 x 100 mL). The organic phase was dried over sodium sulfate anhydrous. The yellow residue was purified by chromatography on a silica column eluted with DCM/Methanol (9:1). Yield: 1.08g, 57%.

^1H NMR (500 MHz, 25°C, CD_2Cl_2) δ = 8.53 (d, J = 4.9 Hz, 6H), 8.28-8.25 (m, 6H), 7.14-7.11 (m, 3H), 7.06 (dd, J = 4.9, 1.7 Hz, 3H), 6.80 (s, 3H), 2.87 (s, 12H), 2.36 (s, 9H). ^{13}C NMR (126 MHz, 25°C, CD_2Cl_2) δ = 156.16, 156.01, 151.65, 148.99, 148.89, 148.14, 141.38, 126.63, 124.66, 124.63, 124.03, 121.80, 121.18, 37.45, 36.68, 21.01. $^1H\{^{13}C\}$ HQSC δ = {8.53, 149.00}, {8.53,148.91}, {7.14-7.11,124.65}, {7.06, 124.05}, {6.80, 126.65}, {8.28-8.25, 121.82}, { 8.28-8.25, 121.19}, {2.87,37.46}, {2.87,36.69}, {2.36, 21.02}. Anal. Calcd for $C_{45}H_{42}N_6$: C, 81.05; H, 6.35; N, 12.60. Found: C, 81.09; H, 6.40; N, 12.58.

Synthesis of Cis-$[Ru(dmb)_2Cl_2]\cdot 2H_2O$

4,4′-Dimethyl-2,2′-dipyridyl (2.81 g, 15 mmol), $RuCl_3{\cdot}3H_2O$ (2.06 g, 8 mmol) e LiCl (1 g, 24 mmol) were dissolved in 14 mL of DMF. This mixture was refluxed for 15 h. After this time the solution was cooled to room temperature and 65 mL of acetone was added. The mixture was left at 0°C overnight. The formed purple solid was collected by filtration. Yield: 2.02 g, 45%.

Synthesis of Ru

The ligand **bpy₃Ph** (0.101g, 0.15 mmol) was dissolved in 5 mL methanol under argon atmosphere. Cis-[Ru(dmb)$_2$Cl$_2$] ·2H$_2$O (0.078 g, 0.13 mmol) was dissolved in 5 mL of ethanol and added dropwise to the mixture during 60 min at reflux temperature. The solution was left at reflux temperature for 24 h. The residue was purified by ion exchange chromatography on CM Sephadex C-25 eluted with a solution of NaCl in water/acetone (5:3, v/v). Yield: 70 mg, 46%. ESI-TOFMS (in MeCN) m/z: Calculated for $C_{69}N_{10}H_{64}Ru$ (M – 2 PF6) 568.2267, found 568.2239.

Synthesis of Ru2

The ligand **bpy$_3$Ph** (0.101g, 0.15 mmol) was dissolved in 5 mL methanol under argon atmosphere. Cis-[Ru(dmb)$_2$Cl$_2$] ·2H$_2$O (0.18 g, 0.31 mmol) was dissolved in 5 mL of ethanol and added dropwise to the reaction mixture over 80 min at reflux temperature. The solution was left under stirring at reflux temperature for 24 h. The residue was purified by ion exchange chromatography on CM Sephadex C-25 eluted with a solution of NaCl in water/acetone (5:3, v/v). The product was precipitated from the concentrate by addition of NH_4PF_6 and filtered out. Yield: 220.9 mg, 67%. ESI-TOFMS (in MeCN) m/z: Calculated for $C_{93}N_{14}H_{86}Ru_2$ (M – 4 PF_6) 401.6400, found 401.6376.

Synthesis of Ru3

The ligand **bpy$_3$Ph** (0.101g, 0.15 mmol) was dissolved in 5 mL methanol under argon atmosphere. Cis-[Ru(dmb)$_2$Cl$_2$] ·2H$_2$O (0.26 g, 0.45 mmol) was dissolved in 5 mL of ethanol and added dropwise to the mixture during 60 min at reflux temperature. The solution was left at reflux temperature for 24 h. The residue was purified by ion exchange chromatography on CM Sephadex C-25 eluted with a solution of NaCl in water/acetone (5:3, v/v). The product was precipitated from the concentrate by addition of NH_4PF_6 and filtered out. Yield: 334.4 mg, 75%. ESI-TOFMS (in MeCN) m/z: Calculated for $C_{117}N_{18}H_{108}Ru_3$ (M – 6 PF_6) 345.9444, found 345.9446.

Synthesis of RuRe2

Ru (20 mg, 0.017 mmol) and $Re(CO)_5Cl$ (12.7 mg, 0.035 mmol) were dissolved in 32 mL of 1,2-dichloroethane for 4 h at reflux under argon atmosphere. After this period, the product was precipitated by addition of NH_4PF_6 and filtered out. Yield: 33.1 mg, 94%. ESI-TOFMS (in MeCN) m/z: Calculated for $C_{75}N_{10}H_{64}Cl_2O_6RuRe_2$ (M – 2 PF_6) 874.1349, found 874.1372. FT-IR (in CH_3CN) ν_{CO}/cm^{-1}: 2021, 1915, 1896.

Synthesis of Ru2Re

Ru2 (50.6 mg, 0.023 mmol) and $Re(CO)_5Cl$ (8.9 mg, 0.025 mmol) were dissolved in 30 mL of 1,2-dichloroethane for 6 h at reflux under argon atmosphere. After this period, the product was precipitated by addition of NH_4PF_6 and filtered out. Yield: 34.5 mg, 61%. ESI-TOFMS (in MeCN) m/z: Calculated for $C_{96}N_{14}H_{86}ClO_3Ru_2Re$ (M – 4 PF_6) 478.1170, found 478.1149. FT-IR (in CH_3CN) ν_{CO}/cm^{-1}: 2021, 1915, 1895.

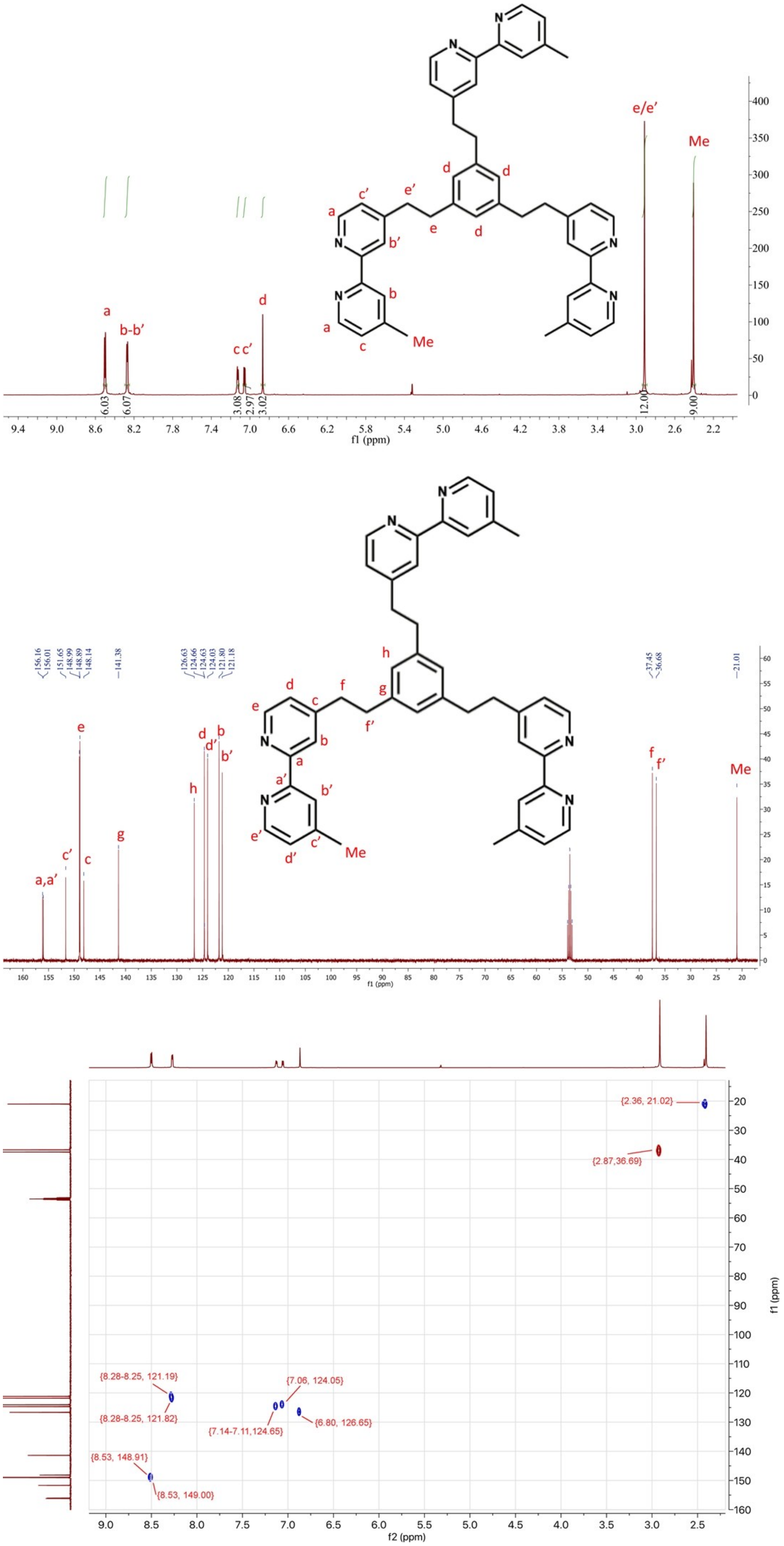

Figure S1. ^{1}H-NMR spectrum (top panel); ^{13}C-NMR spectrum (middle panel) and ^{1}H–^{13}C HSQC (bottom panel) of **bpy$_3$Ph** in CD$_2$Cl$_2$

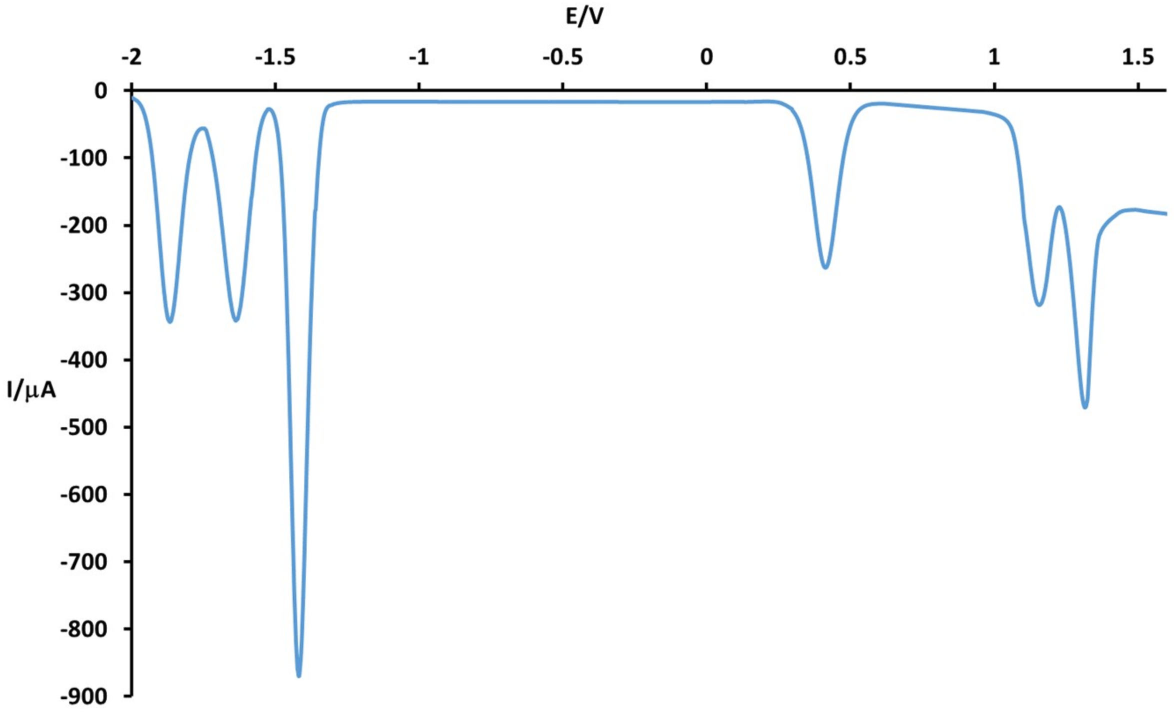

Figure S2. Differential pulsed voltammogram of **RuRe2** (0.5 mM) in argon purged MeCN at room temperature using Bu_4NPF_6 (0.1 M) as supporting electrolyte. As internal reference was used the redox couple ferrocene/ferrocenium (395 mV vs. SCE in acetonitrile). Scan rate 200 mV/s.

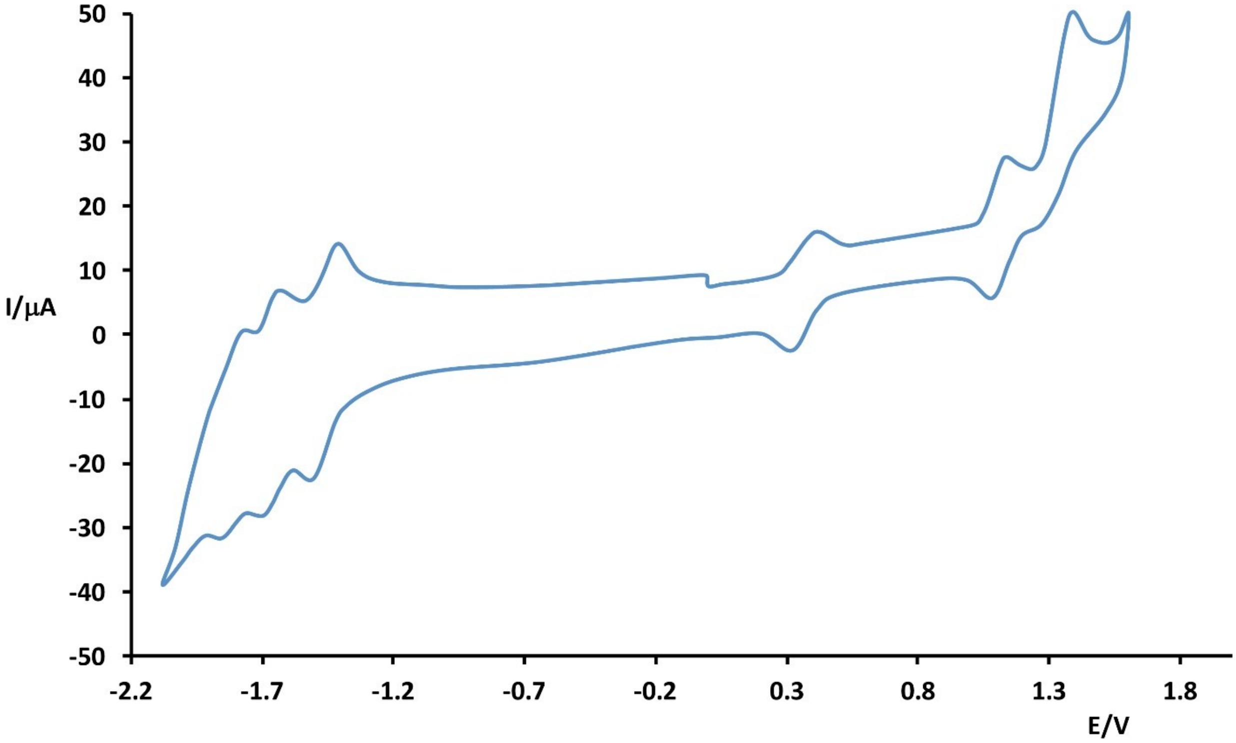

Figure S3. Cyclic voltammogram of **RuRe2** (0.5 mM) in argon purged MeCN at room temperature using Bu_4NPF_6 (0.1 M) as supporting electrolyte. As internal reference was used the redox couple ferrocene/ferrocenium (395 mV vs. SCE in acetonitrile). Scan rate 200 mV/s.

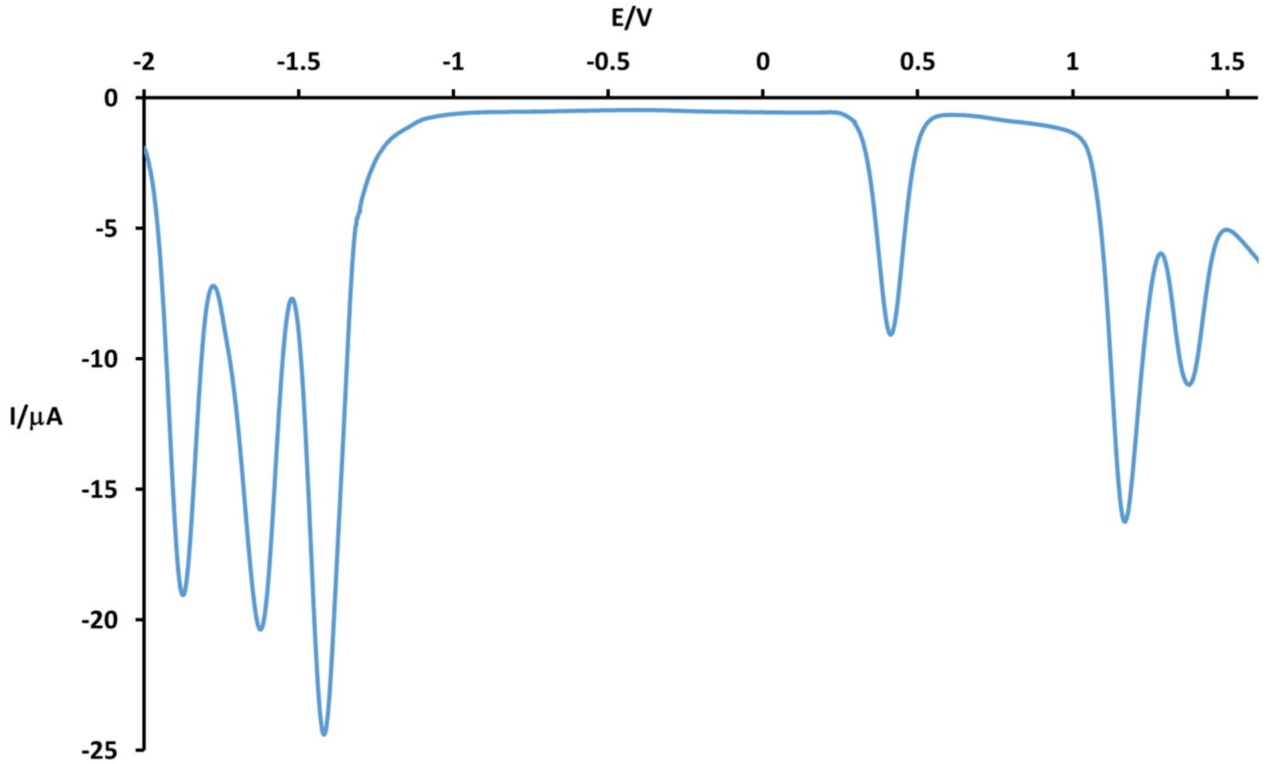

Figure S4. DPV analysis of **Ru2Re** (0.5 mM) in argon purged MeCN at room temperature using Bu_4NPF_6 (0.1 M) as supporting electrolyte. As internal reference was used the redox couple ferrocene/ferrocenium (395 mV vs. SCE in acetonitrile). Scan rate 200 mV/s.

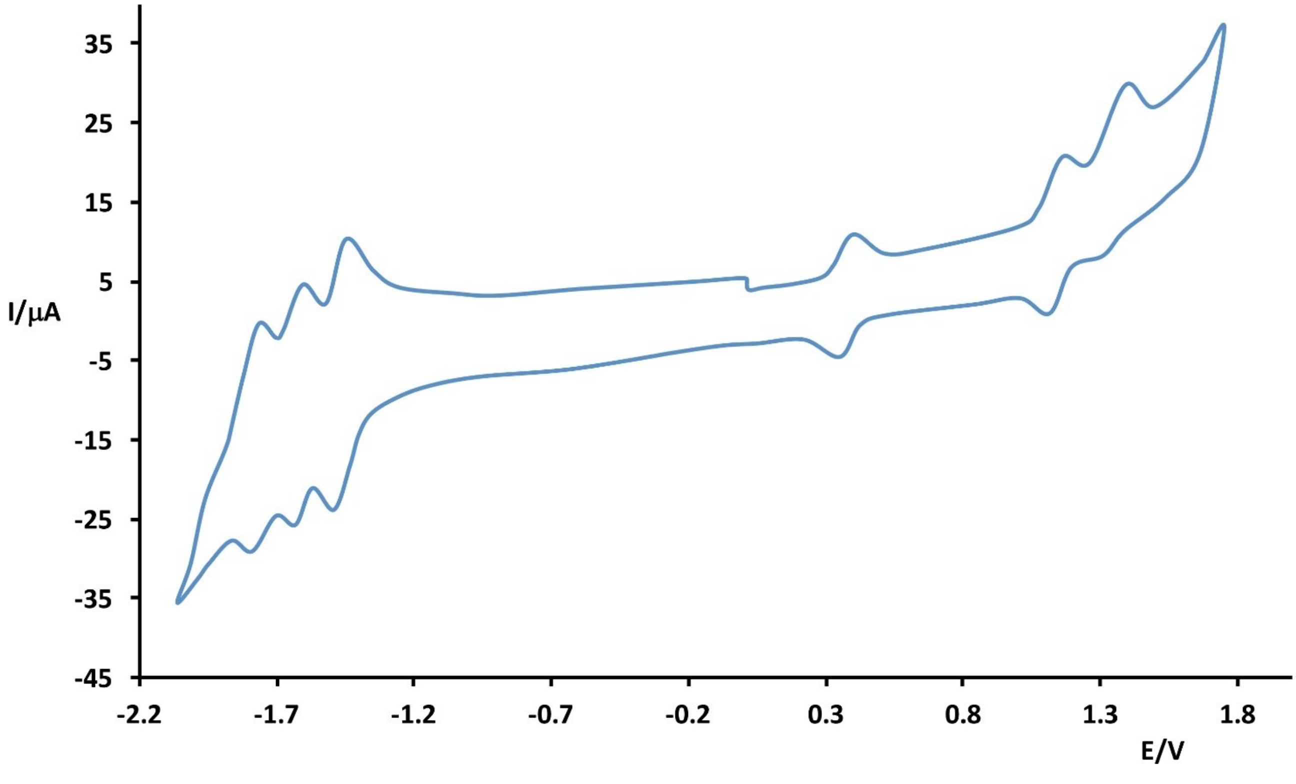

Figure S5. Cyclic voltammogram of **Ru2Re** (0.5 mM) in argon purged MeCN at room temperature using Bu_4NPF_6 (0.1 M) as supporting electrolyte. As internal reference was used the redox couple ferrocene/ferrocenium (395 mV vs. SCE in acetonitrile). Scan rate 200 mV/s.

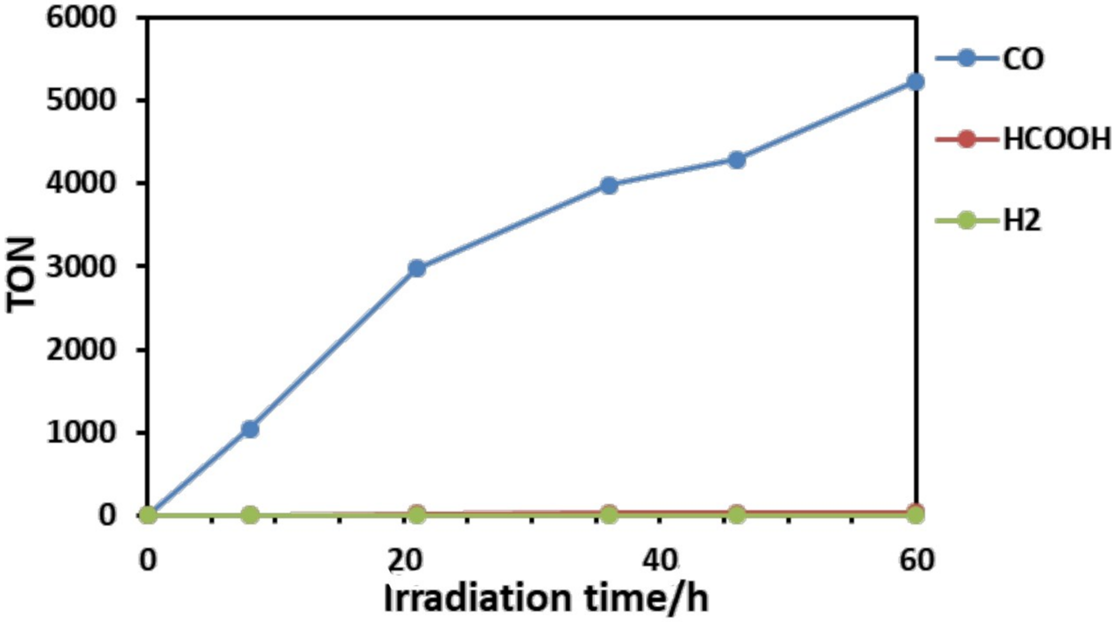

Figure S6. Photocatalytic formation of CO (blue line), formic acid (red line) and H_2 (green line) as function of irradiation time for **RuRe2** in CO_2-saturated DMA-TEOA (5:1 v/v, 3 mL) solutions containing **RuRe2** (10 µM) and BIH (0.1 M); λ_{ex} = 530 nm, 4mW.

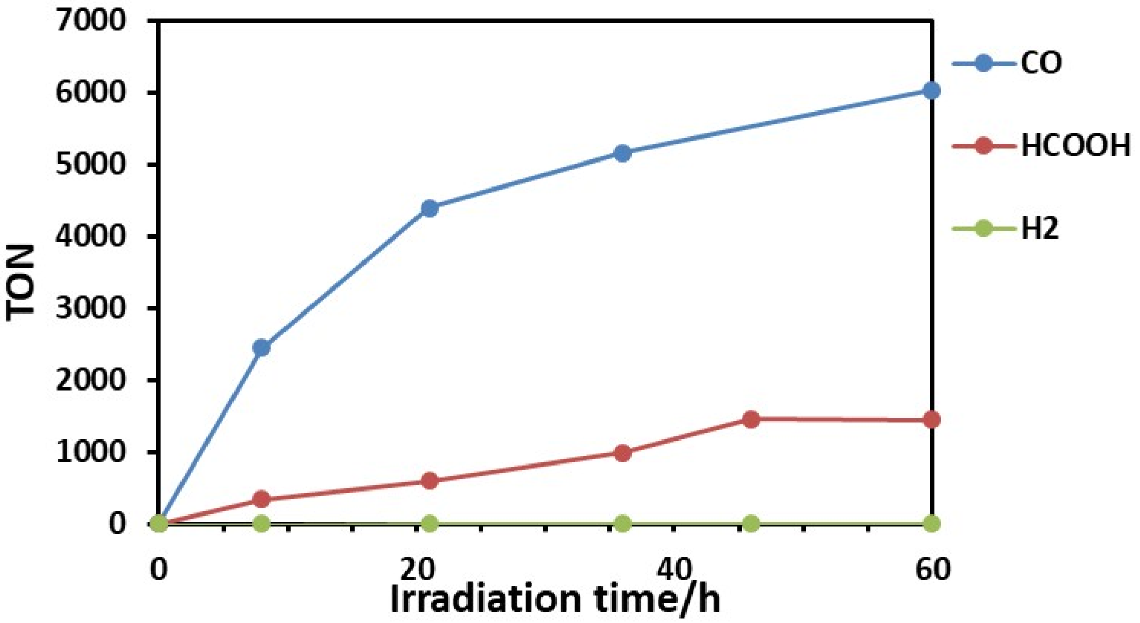

Figure S7. Photocatalytic formation of CO (blue line), formic acid (red line) and H_2 (green line) as function of irradiation time for **Ru2Re** in CO_2-saturated DMA-TEOA (5:1 v/v, 3 mL) solutions containing **Ru2Re** (5 µM) and BIH (0.1 M); λ_{ex} = 530 nm, 4mW.

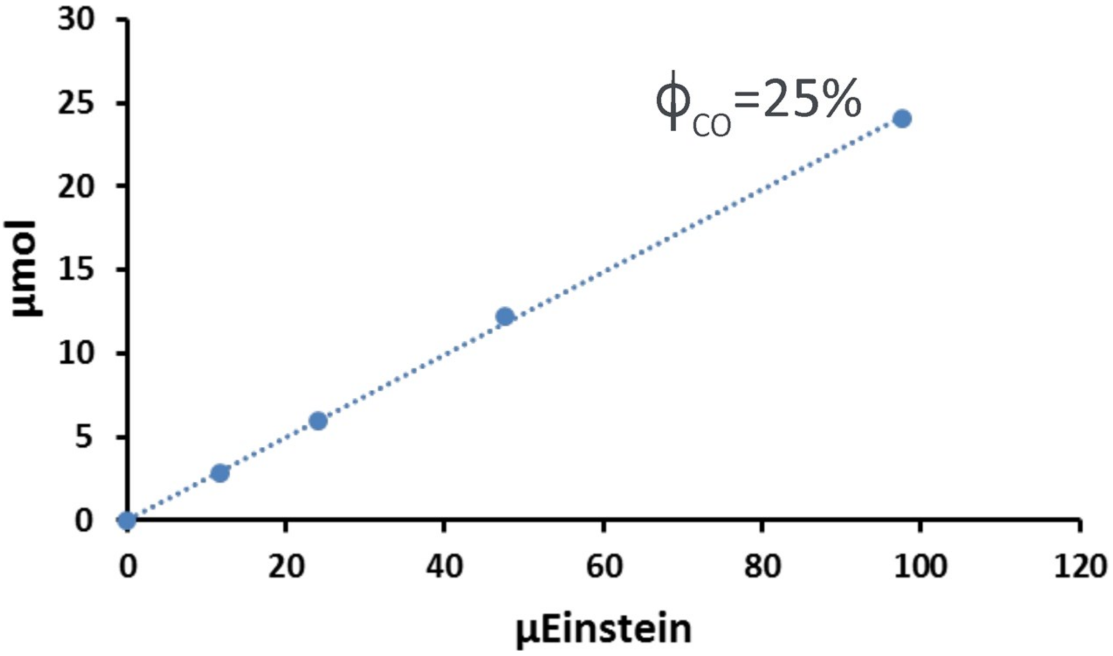

Figure S8. CO formation as a function of absorbed photons using 480-nm light (light intensity: 1.0 × 10^{-8} einstein s^{-1}) for **RuRe2** in CO_2-saturated DMA-TEOA (5:1 v/v, 4 mL) solution containing **RuRe2** (50 μM) and BIH (0.1 M).

Refererences

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