

Supporting Information

for

Iron-Catalyzed Photochemical Reduction of Carbon Dioxide to Synthesis Gas

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Details on the quantum yield calculations

The quantum yields for the photocatalytic CO₂ reduction reactions were determined using the following equation:

$$QY(\%) = \frac{\text{products molecules} \times 2}{\text{incident photons}} \times 100\% \quad (1)$$

where the products molecules were quantified using a calibrated GC and the incident photons were measured using K₃Fe(C₂O₄)₃¹ as chemical actinometer. Thus, 3mL (V₁) of an aqueous solution containing the iron actinometer (0.15 M) and H₂SO₄ (0.05 M) was irradiated with a high pressure Hg-lamp (Lumatec Superlite 400, 120W) equipped with built-in band pass filters, and using the same experimental setup as in the case of the photocatalytic reactions. The time of the irradiation was kept as short as possible to avoid more than 10% decomposition of the actinometer. Before each measurement, the power output of the Hg-lamp was measured using a thermopile (Fa. LOT Quantum Design). After irradiation, an aliquot of 0.180 mL (V₂) was taken and 2 mL of a buffered solution of phenanthroline (0.015 M / 0.5 M H₂SO₄) were added together with distilled H₂O to give a final volume of 25 mL (V₃). The absorbance of the solution at 510 nm was recorded and the value was used to calculate the number of Fe²⁺ ions (nFe²⁺) generated during the irradiation process through the following equation:

$$nFe^{2+} = \frac{V_1 \cdot V_3 \cdot (A - A_0)}{1000 \cdot V_2 \cdot \epsilon_0} \quad (2)$$

where

V₁ = volume of actinometer solution irradiated (mL)

V₂ = volume of aliquot taken for analysis (mL)

V₃ = final volume to which the aliquot V₂ is diluted (mL)

A = measured optical density at 510 nm

A₀ = measured optical density at 510 nm of a non-irradiated sample

ε₀ = experimental value of the molar extinction coefficient of the Fe²⁺ complex (11100 L mol⁻¹ cm⁻¹)

Finally, the number of incident photons per second (# photons) is calculated using the following equation:

$$\# \text{ photons } (s^{-1}) = \frac{6.022 \cdot 10^{23} \cdot nFe^{2+}}{\Phi_{\lambda} \cdot t} \quad (3)$$

where Φ_{λ} = quantum yield of Fe²⁺ formation

t = time of irradiation (s)

The number of incident photons were determined for 2 wavelengths (415 and 440 nm) using 3 different power outputs (0.07 W, 0.15 W, and 0.50 W).

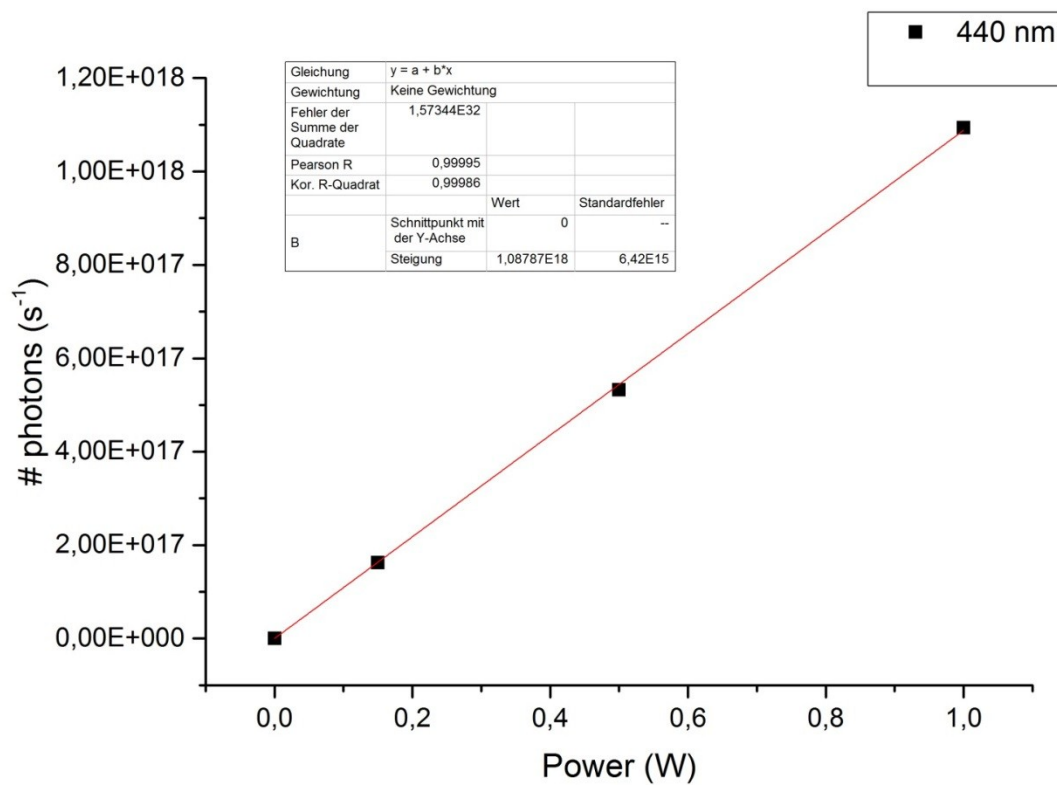


Figure S1. Measurement of incident photons at 440 nm using 3 different power outputs of the lamp.

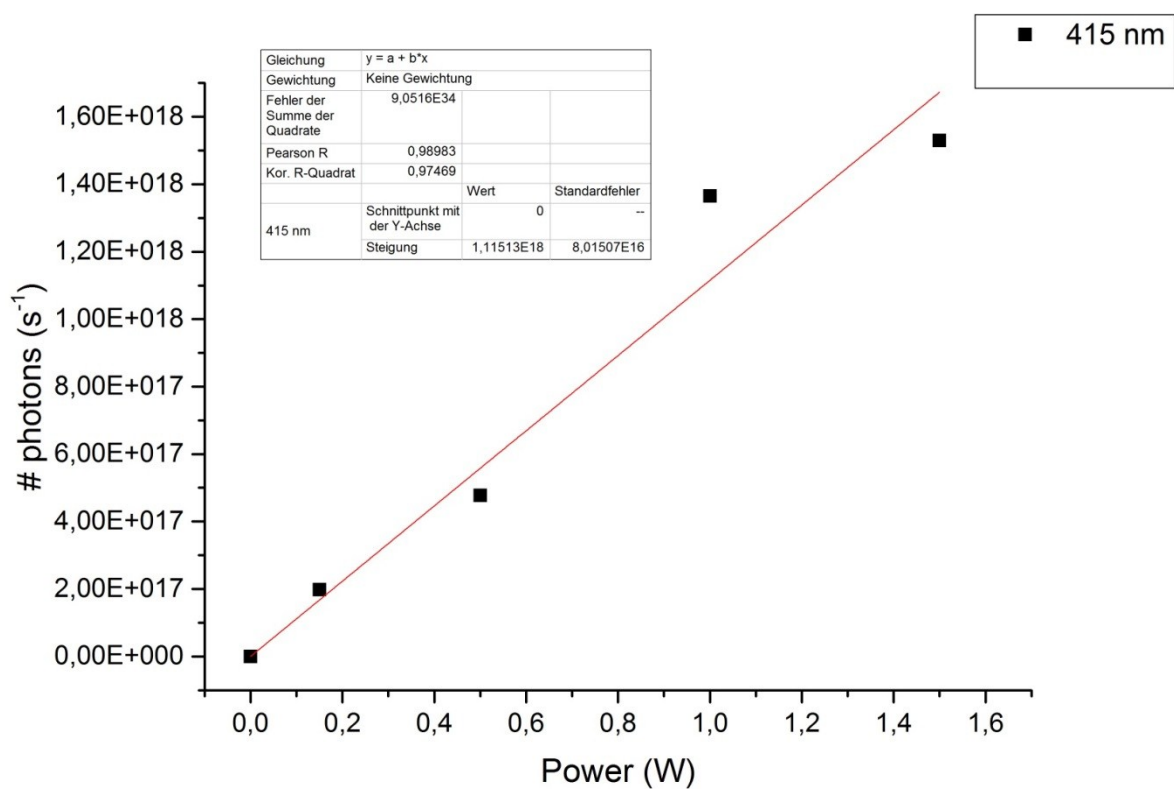


Figure S2. Measurement of incident photons at 415 nm using 4 different power outputs of the lamp.

PS	Power (W)	Wavelength (nm)	H₂ (μmol)	CO (μmol)	Total (μmol)	Φ (%)
PS2	0.15	440	51	33	84	4.3
PS1	0.15	440	85	105	190	9.7
PS2	0.50	440	54	102	156	2.4
PS1	0.50	440	153	188	341	5.2
PS1	0.50	415	134	179	313	4.7
PS1	0.07	440	70	68	138	15.1

Table S1. Measurement of the quantum yield using photosensitizers **PS1** or **PS2** at 440 nm and 415 nm.

Synthesis of [Fe(bpy)(CO)₃]: This complex was prepared based on a previously reported method.² 2,2'-bipyridine (87.47 mg, 0.56 mmol) was placed in 100 mL Schlenk tube and a solution of [Fe(CO)₅] (200 mg, 1.02 mmol) in dioxane (15 mL) was added. The reaction mixture was heated to 95 °C for 26 h. The reaction vessel was quickly evacuated and refilled with Ar three times (after 1.5 h, 3.5 h and 18 h). The reaction mixture was allowed to reach room temperature, the insoluble residue was filtered off and washed with dioxane. The solutions were combined and all volatiles were removed in vacuo to obtain a dark green powder (116.06 mg, 70%). ¹H NMR (300 MHz, THF-d₈): δ = 9.62 – 9.25 (m, 1H), 8.82 – 8.15 (m, 3H), 7.99 – 7.53 (m, 2H), 7.41 – 7.07 (m, 2H); ¹³C NMR (75 MHz, THF-d₈): δ = 121.32, 122.86, 123.43, 124.43, 132.02, 137.32, 149.89, 151.96, 154.53, 157.00, 221.78.

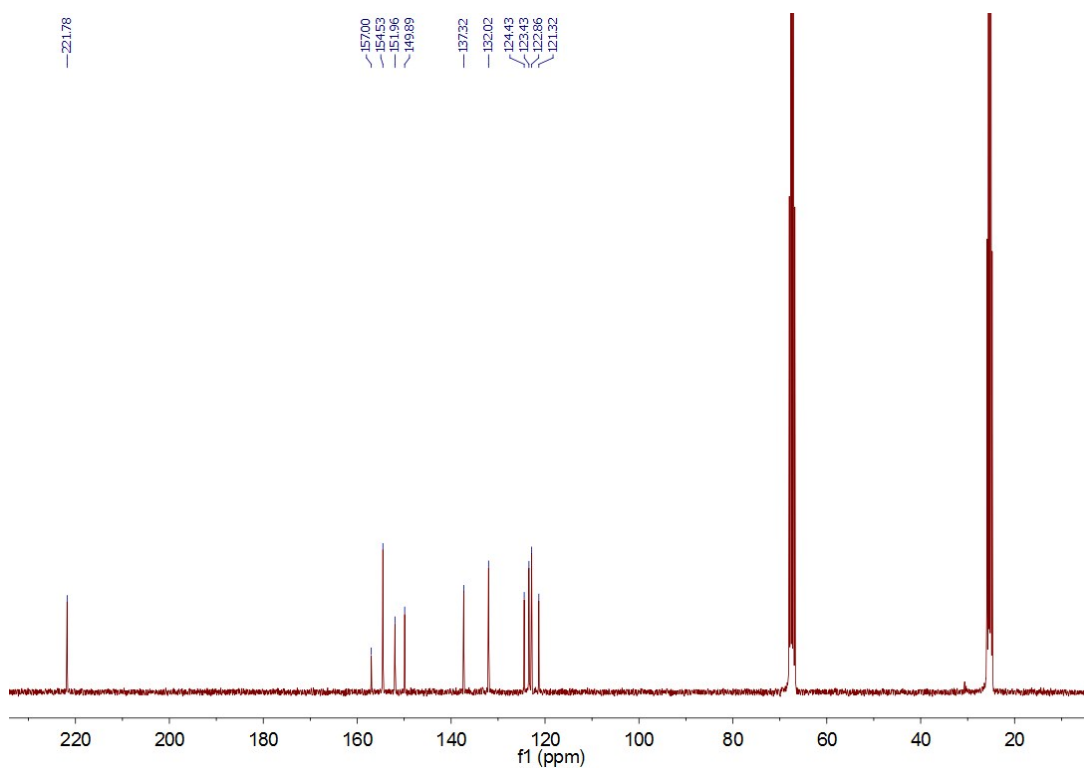
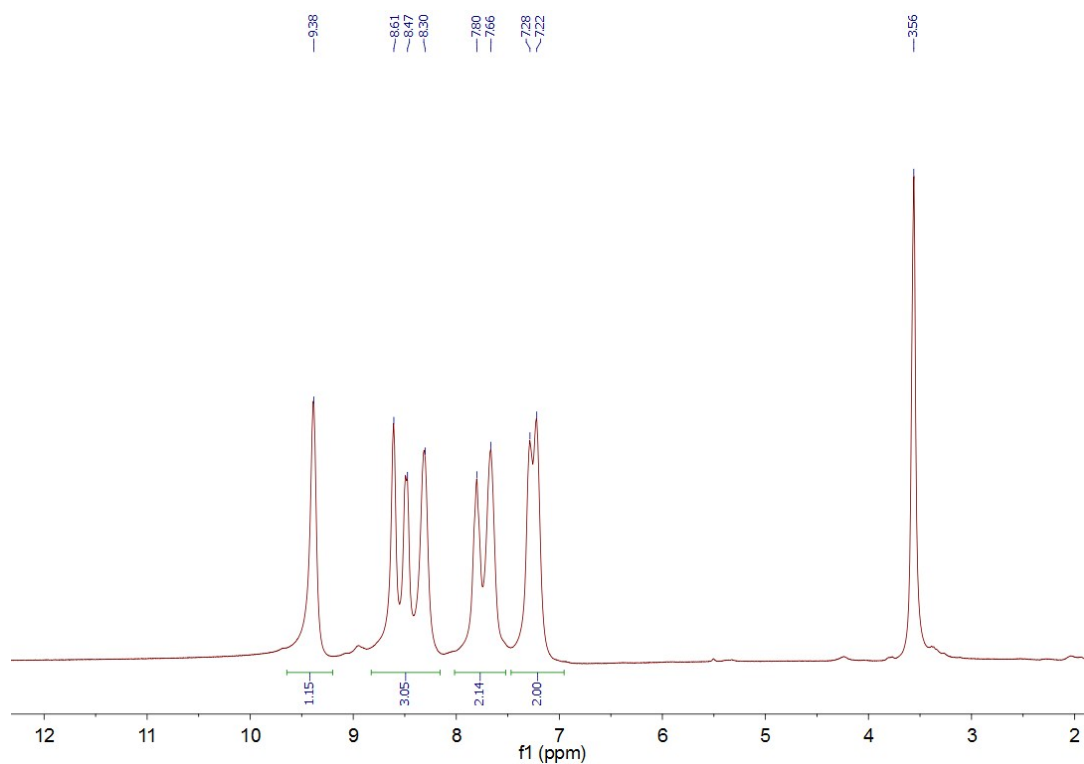


Figure S3. ^1H NMR (top) and ^{13}C NMR (bottom) spectra of $[\text{Fe}(\text{bpy})(\text{CO})_3]$ measured in THF-d_8 .

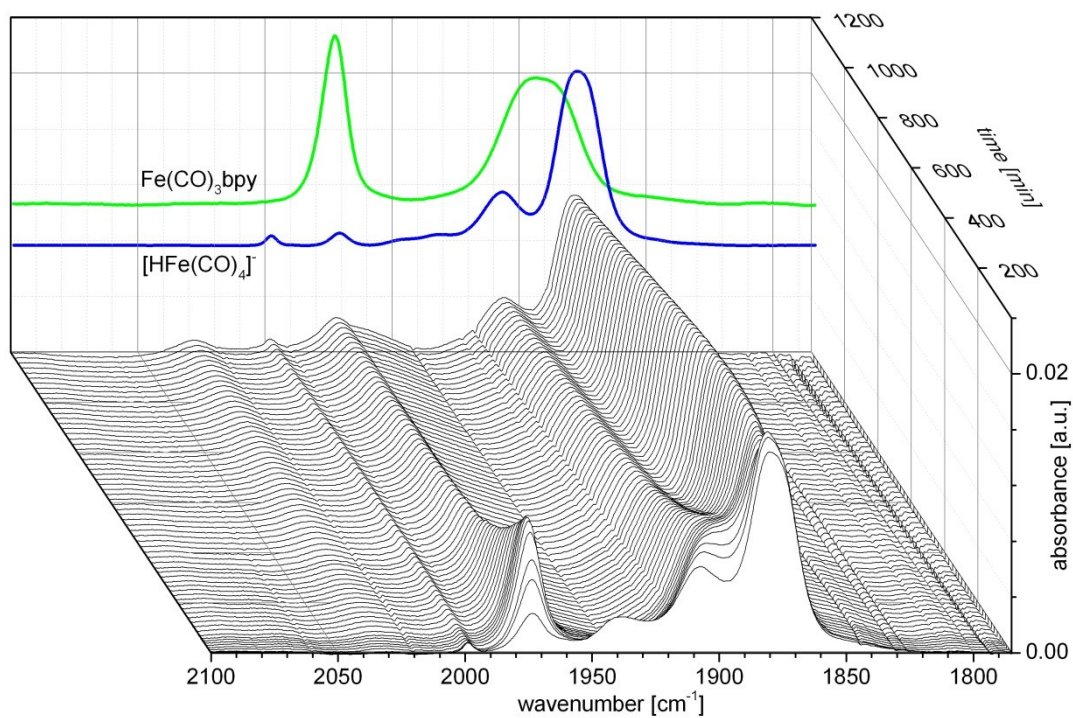


Figure S4. Operando FTIR spectra of a CO_2 -saturated solution (NMP:TEOA = 5:1, v/v), containing $[\text{Fe}_3(\text{CO})_{12}]$ (1 μmol), $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ (25 μmol), and 2,2'-bipyridine (15 μmol) during irradiation with visible light (400-700 nm).

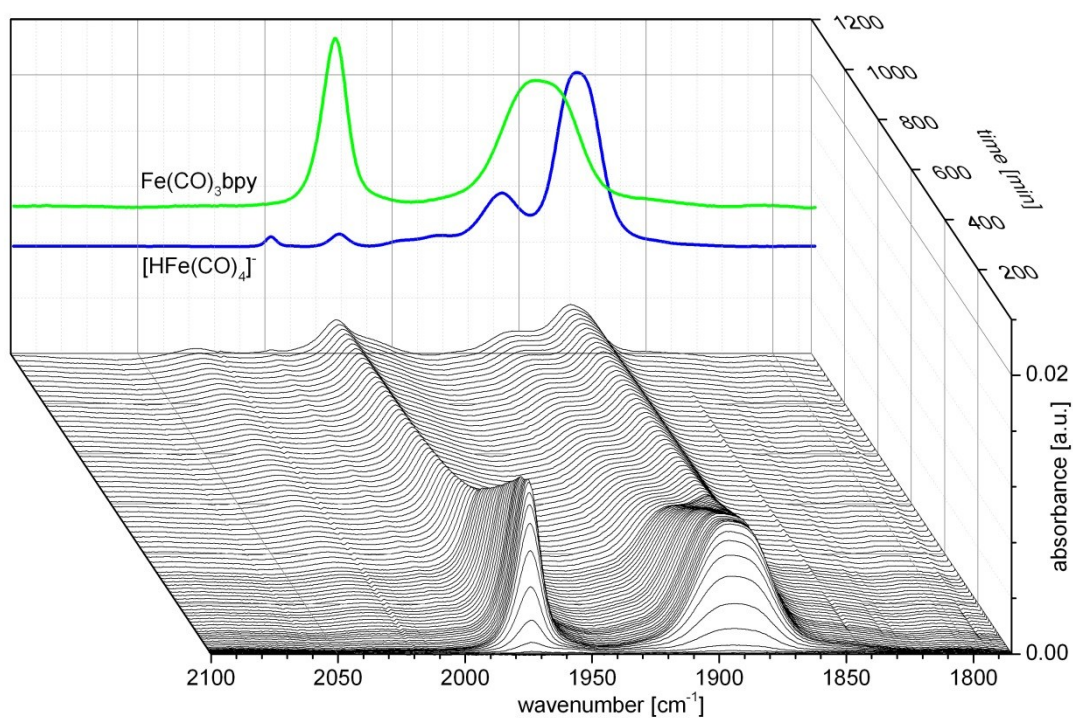


Figure S5. Operando FTIR spectra of a CO_2 -saturated solution (NMP:TEOA = 5:1, v/v), containing $[\text{FeBr}_2]$ ($3 \mu\text{mol}$), $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ ($25 \mu\text{mol}$), and 2,2'-bipyridine ($15 \mu\text{mol}$) during irradiation with visible light (400-700 nm).

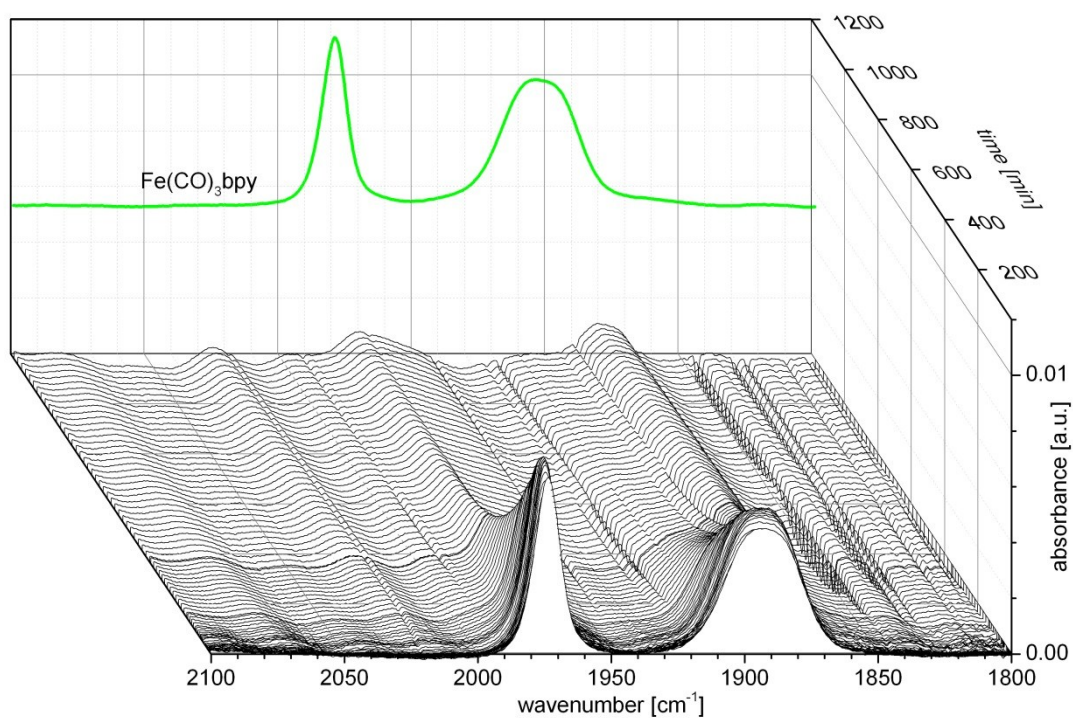


Figure S6. Operando FTIR spectra of a CO_2 -saturated solution (NMP:TEOA = 5:1, v/v), containing $[\text{Fe}(\text{bpy})(\text{CO})_3]$ ($3 \mu\text{mol}$) and $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ ($25 \mu\text{mol}$) during irradiation with visible light (400-700 nm).

References

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- ² T. Zell, P. Milko, K. L. Fillman, Y. Diskin-Posner, T. Bendikov, M. A. Iron, G. Leitius, Y. Ben-David, M. L. Neidig and D. Milstein, *Chem. Eur. J.* **2014**, *20*, 4403-4413.