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Supporting Information

for

Highly Efficient and Selective Photochemical Reduction of CO_2 to CO using Cyclopentadienone Iron Complexes

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Materials and methods

Anhydrous *N*-methyl-2-pyrrolidone (NMP) was purchased from Sigma-Aldrich and stored under an Ar atmosphere. Triethanolamine (TEOA) was degassed and also stored under Ar prior to use. CO_2 tanks (>99.998%) were purchased from Linde and used as received. $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (**IrPS**) was either purchased from commercial sources or synthesized according to the literature,[1] iron hydride complex **9** and all tricarbonyl (cyclopentadienone)iron complexes were prepared using known literature protocols.[2,3] All other reagents were of reagent-grade quality and were used as received. Analyses of the headspace of the photocatalytic reactions were performed using a gas chromatograph equipped with a TCD detector (Agilent Technologies 6890N, carboxen 1000, external calibration). ^1H and ^{13}C NMR spectra were recorded on a Bruker Fourier 300 instrument by using the residual solvent signal as an internal standard. Analyses of the reaction mixture liquid phase was performed using a capillary electrophoresis (Agilent Technologies, capillary 75 μm/40 cm, 300 μA current) equipped with a DAD detector (400 μm). The analysis temperature was maintained at 25 ^oC and the method employed an organic acids buffer (Agilent) at pH 5.6. Emission spectra were recorded in a Varian Cary Eclipse fluorescence spectrophotometer. Cyclic voltammograms (scan rate 100 mV s^{-1}) were carried out in a conventional three electrode cell using a Parstat 4000 potentiostat (Princeton Applied Research), a glassy carbon disc (diameter: 1 mm) as working electrode, and a platinum wire as counter electrode. As reference a $Ag/AgNO_3$ electrode (silver wire in 0.1 M NBu_4BF_4/CH_3CN solution; $c(AgNO_3) = 0.01$ M; $E^0 = -87$ mV vs. ferrocene redox couple) was used and this compartment was separated from the rest of the cell with a Vycor frit.

Typical procedure for photocatalytic reactions

A double-walled temperature-controlled 100-mL reaction vessel was evacuated and refilled with Ar three times followed by an additional three cycles using CO_2. **IrPS**, the corresponding Fe complex (as a solid or solution in NMP/TEOA) and 7.5 mL of a 5:1 mixture of NMP/TEOA were then added. Prior to irradiation, the reaction mixture was bubbled with CO_2 for 30 min. The temperature was maintained at 25 °C using a thermostat. The solution was irradiated through a plain borosilicate-glass wall in the reaction vessel using a Hg-lamp (Lumatec Superlite 400, output 2.5 W), equipped with a 400-700 nm filter. The gaseous reaction products (H_2 and CO) were analyzed using calibrated GC and $HCOO^-$ in the liquid phase was quantified by use of capillary electrophoresis techniques. Calculations of TONs for carbon monoxide were performed using its van der Waals molar volume (24.44323 mol/L) at 25 °C and 1.01325 bar.

Table S1. Photocatalytic CO_2 reduction in the absence of key reaction components: iron catalyst (**3**), photosensitizer (**IrPS**), triethanolamine (TEOA) or light.[a]

Modification	**H_2 (µmol)[b]**	**CO (µmol)[b]**	**TON**
No addition of 3	0	2.99	0
No addition of IrPS	0	3.82	4
No addition of TEOA	0	0.24	0
No irradiation	0	0	0

[a] Reaction conditions: *N*-methyl-2-pyrrolidone and triethanolamine (5:1, v/v) 7.5 mL; catalyst 0.13 mM; photosensitizer **IrPS** 1.67 mM; Hg-lamp (light output 2.5 W) equipped with a 400-700 nm filter. [b] Determined using calibrated GC.

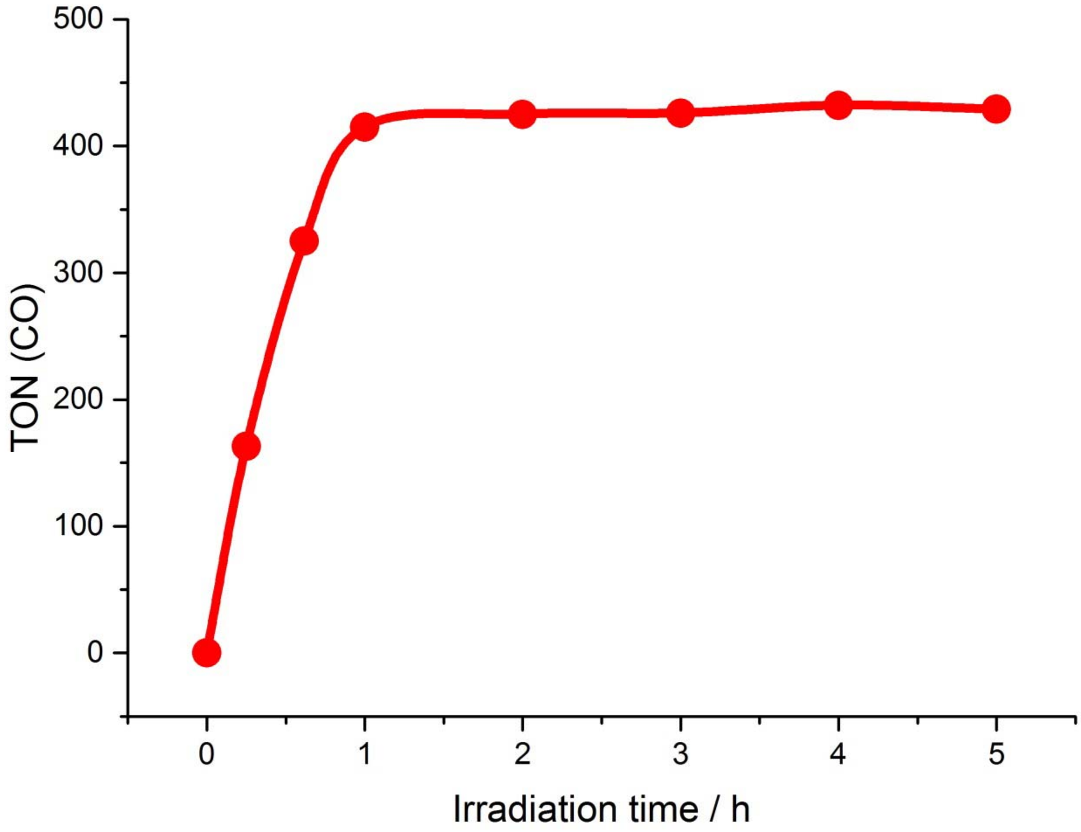


Figure S1. Photocatalytic formation of CO as a function of irradiation time. Reaction conditions: *N*-methyl-2-pyrrolidone and triethanolamine (5:1, v/v) 7.5 mL; iron catalyst (**3**) 0.13 mM; photosensitizer **IrPS** 1.67 mM; Hg-lamp (light output 2.5 W) equipped with a 400-700 nm filter.

Quantum yield calculations

The quantum yields for the photocatalytic CO_2 reduction reactions were determined using the following equation:

$$\Phi(\%) = \frac{\text{CO molecules} \times 2}{\text{incident photons}} \times 100\% \qquad (1)$$

where the CO molecules were quantified using a calibrated GC and the incident photons were measured using $K_3Fe(C_2O_4)_3$[4] as chemical actinometer. Thus, 3mL (V_1) of an aqueous solution containing the iron actinometer (0.15 M) and H_2SO_4 (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 (V_2) was taken and 2 mL of a buffered solution of phenanthroline (0.015 M / 0.5 M H_2SO_4) were added together with distilled H_2O to give a final volume of 25 mL (V_3). The absorbance of the solution at 510 nm was recorded and the value was used to calculate the number of Fe^{2+} ions (nFe^{2+}) generated during the irradiation process through the following equation:

$$nFe^{2+} = \frac{V_1 \cdot V_3 \cdot (A - A_0)}{1000 \cdot V_2 \cdot \varepsilon_0} \qquad (2)$$

where V_1 = volume of actinometer solution irradiated (mL)

V_2 = volume of aliquot taken for analysis (mL)

V_3 = final volume to which the aliquot V_2 is diluted (mL)

A = measured optical density at 510 nm

A_0 = measured optical density at 510 nm of a non-irradiated sample

ε_0 = experimental value of the molar extinction coefficient of the Fe^{2+} complex (11100 L mol^{-1} cm^{-1})

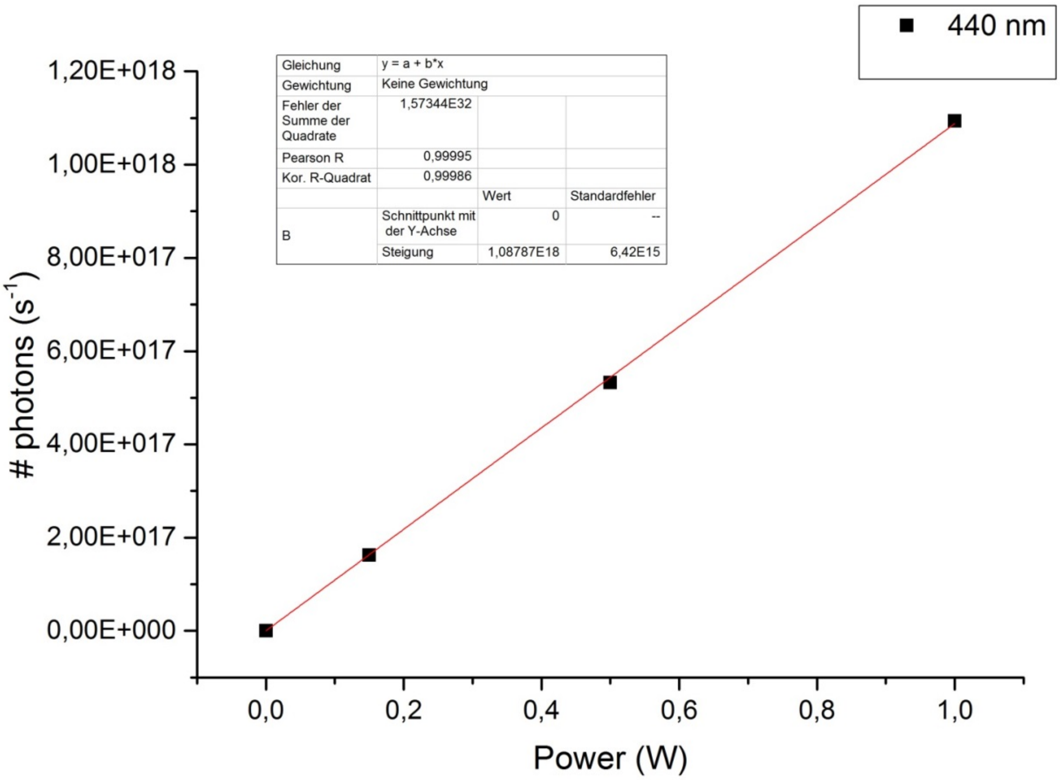
Finally, the number of incident photons per second (# photons) is calculated using the following equation:

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

Where Φ_λ = quantum yield of Fe^{2+} formation

t = time of irradiation (s)

The number of incident photons were determined at 440 nm using 3 different power outputs (0.07 W, 0.15 W, and 0.50 W) as shown in Figure S1.



Gleichung	y = a + b*x		
Gewichtung	Keine Gewichtung		
Fehler der Summe der Quadrate	1,57344E32		
Pearson R	0,99995		
Kor. R-Quadrat	0,99986		
		Wert	Standardfehler
B	Schnittpunkt mit der Y-Achse	0	--
	Steigung	1,08787E18	6,42E15

Figure S2. Measurement of incident photons at 440 nm using different power outputs of the lamp.

Table S2. Quantum yield results for the photocatalytic CO_2 reduction at various loadings of iron catalyst **3**[a]

Catalyst Loading (µmol)	H_2 (µmol)[b]	CO (µmol)[b]	Φ (%)
1	0	366	32.1
5	0	665	58.4
15	0	752	66.1
20	0	826	72.5
40	0	777	68.3
60	0	744	65.4

[a] Reaction conditions: *N*-methyl-2-pyrrolidone and triethanolamine (5:1, v/v) 7.5 mL; photosensitizer **IrPS** 1.67 mM; Hg-lamp (light output 0.07 W, 440 nm); 5 h of irradiation. [b] Determined using calibrated GC.

Operando FTIR measurements

Reactions were performed as described above for a typical photocatalytic setup and incorporated continuous FTIR monitoring. Operando FTIR spectroscopic measurements were carried out on a Bruker Tensor 27 spectrometer equipped with a mercury-cadmium-telluride (MCT) detector. The optics was purged with nitrogen. The reaction was carried out under argon in a vitreous reaction vessel. The reaction solution was irradiated by a Hg-vapor lamp (Lumatec Superlite 400, 400-700 nm filter) and continuously circulated by a micro gear pump via capillary tubes through an IR-transmission cell (pathlength = 0.1 mm, window material = CaF_2). The reaction temperature was maintained at 25°C with a thermostat. This experimental operando FTIR setup allows for the drawing of conclusions between activity and the IR absorption of the catalysts. The pure component spectra and the associated concentration profiles (chapter IR spectra) were extracted with an algorithm based on factor analysis.[5]

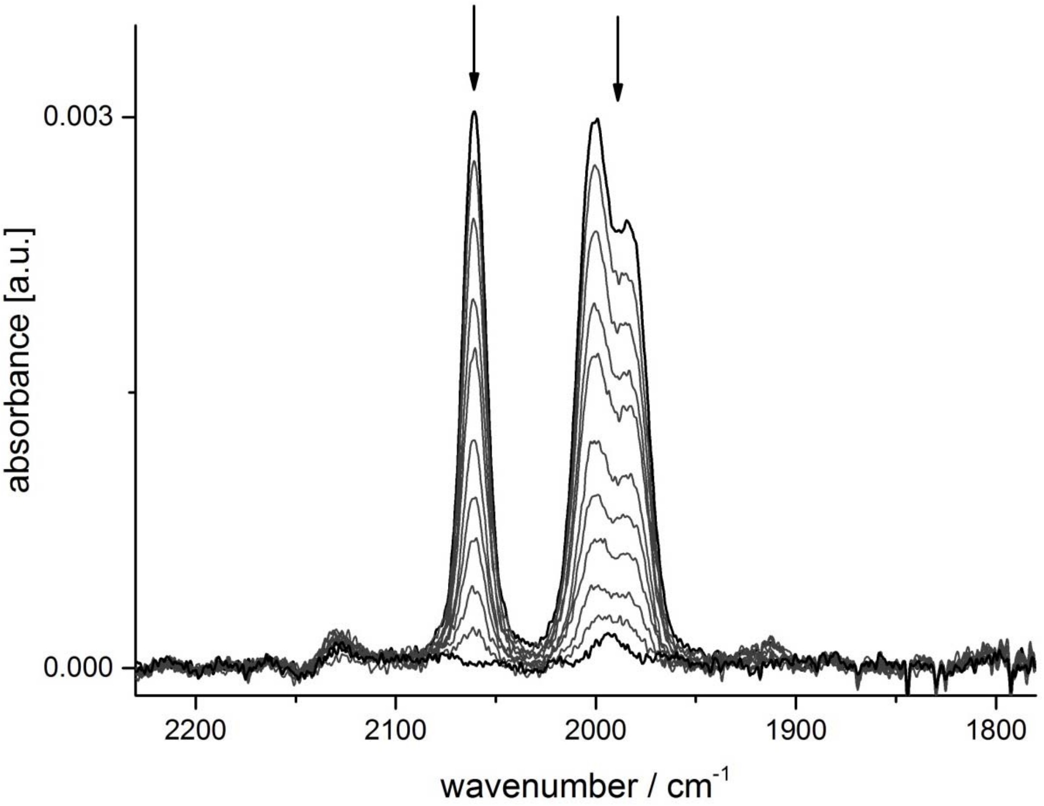


Figure S3. Operando FTIR measurement during the irradiation with visible light (400-700 nm) of a solution of iron complex **3** (0.1 mM) in NMP/TEOA (5:1, v/v) under Ar atmosphere.

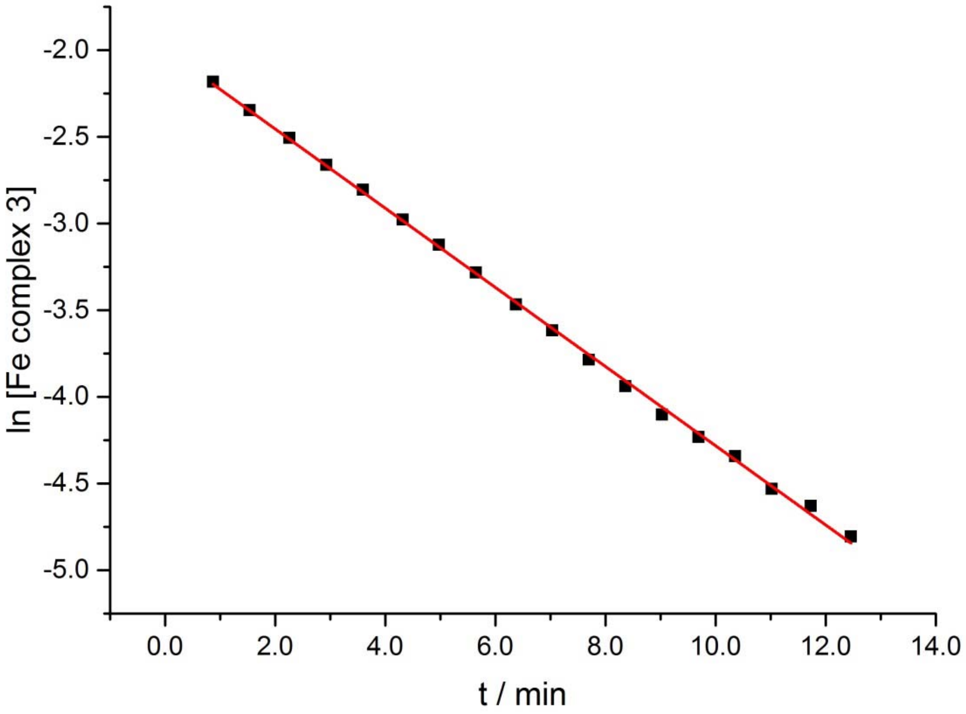


Figure S4. Kinetic analysis for the decarbonylation reaction of complex **3** under visible light irradiation (y = -0.22853x – 1.99633, R^2 = 0.99913). Absorbance data from FTIR spectra shown in Figure S3 were converted to the corresponding concentration values.

Emission-quenching experiments

Solutions of **IrPS** (0.1 mM) in anhydrous acetonitrile were prepared containing different concentrations of the corresponding quencher. In the case of complex **3**, the concentration varied from 0.06 mM to 0.30 mM, while for TEOA from 3 mM to 15 mM. Thus, steady-state emission spectrum (excitation wavelength 360 nm) of each solution was recorded, and the intensity of the luminescence for the ^{3}MLCT excited state of the photosensitizer (480 nm) was recorded. Quenching rate constants k_q were calculated from the linear Stern-Volmer plots obtained, and the knowledge of the lifetime of the excited stated of **IrPS**.[1]

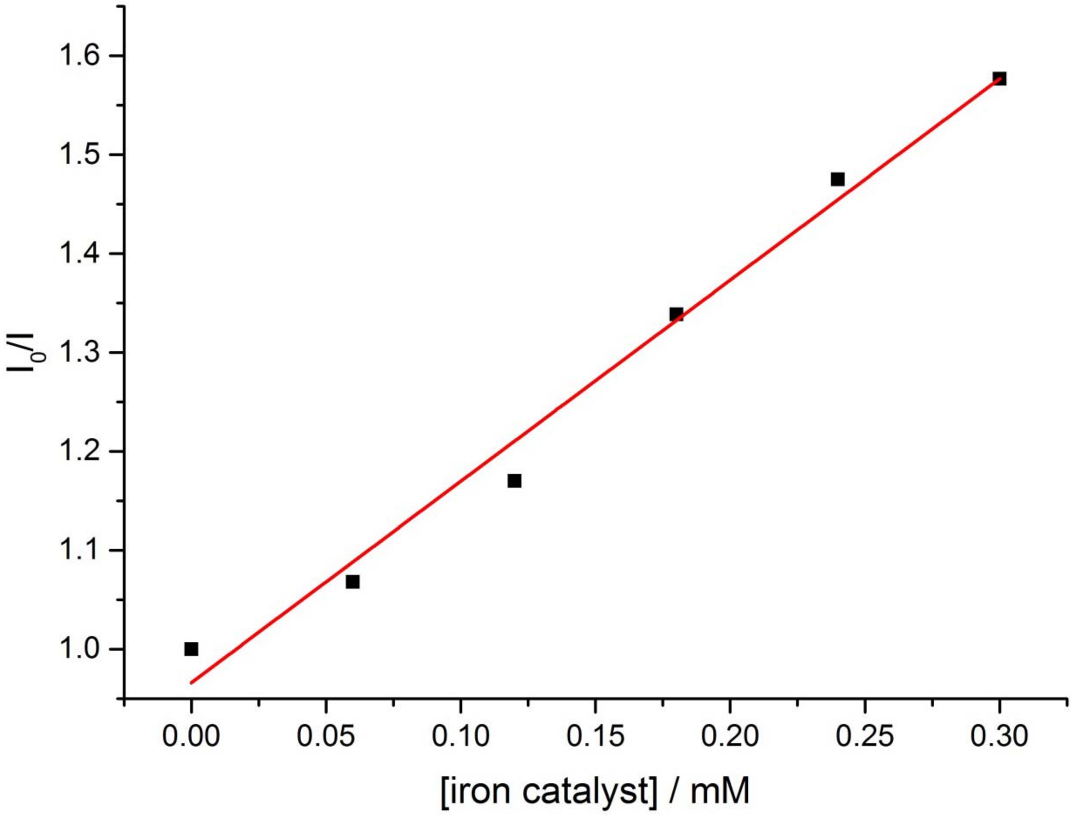


Figure S5. Stern-Volmer plot for the quenching of luminescence of **IrPS** in the presence of iron catalyst **3**. ($y = 2.03555x + 0.96605$, $R^2 = 0.9827$).

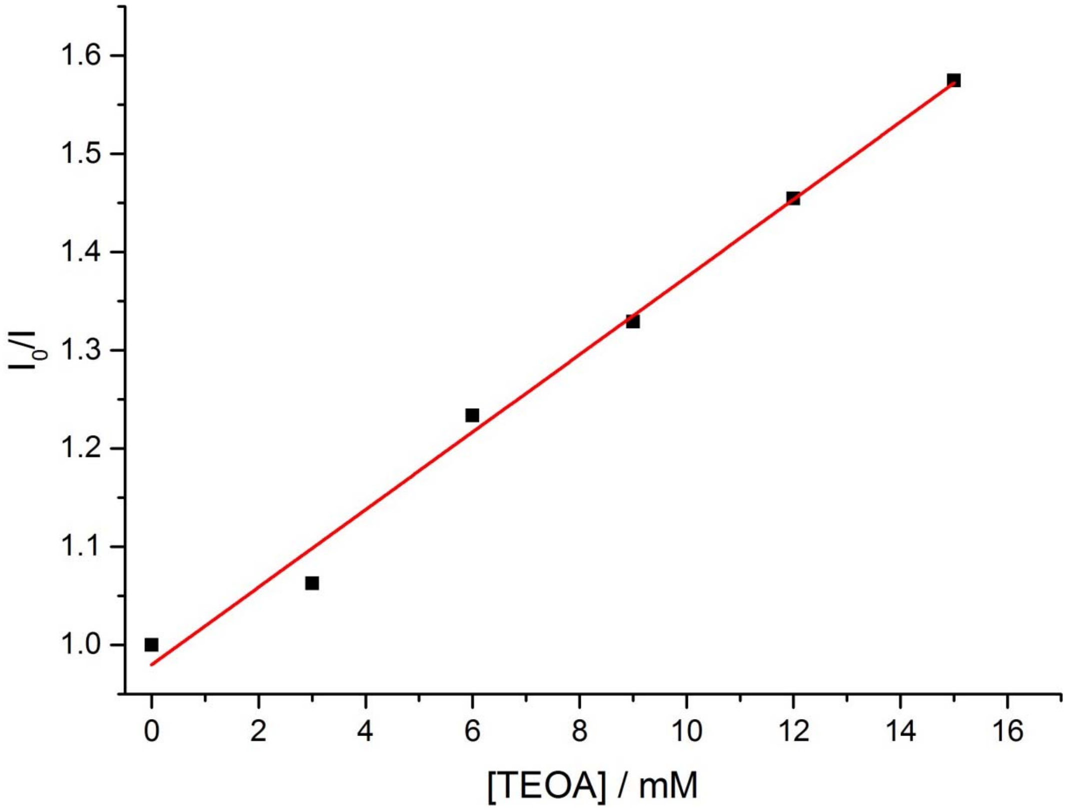


Figure S6. Stern-Volmer plot for the quenching of luminescence of **IrPS** in the presence of triethanolamine ($y = 0.03949x + 0.97965$, $R^2 = 0.9899$).

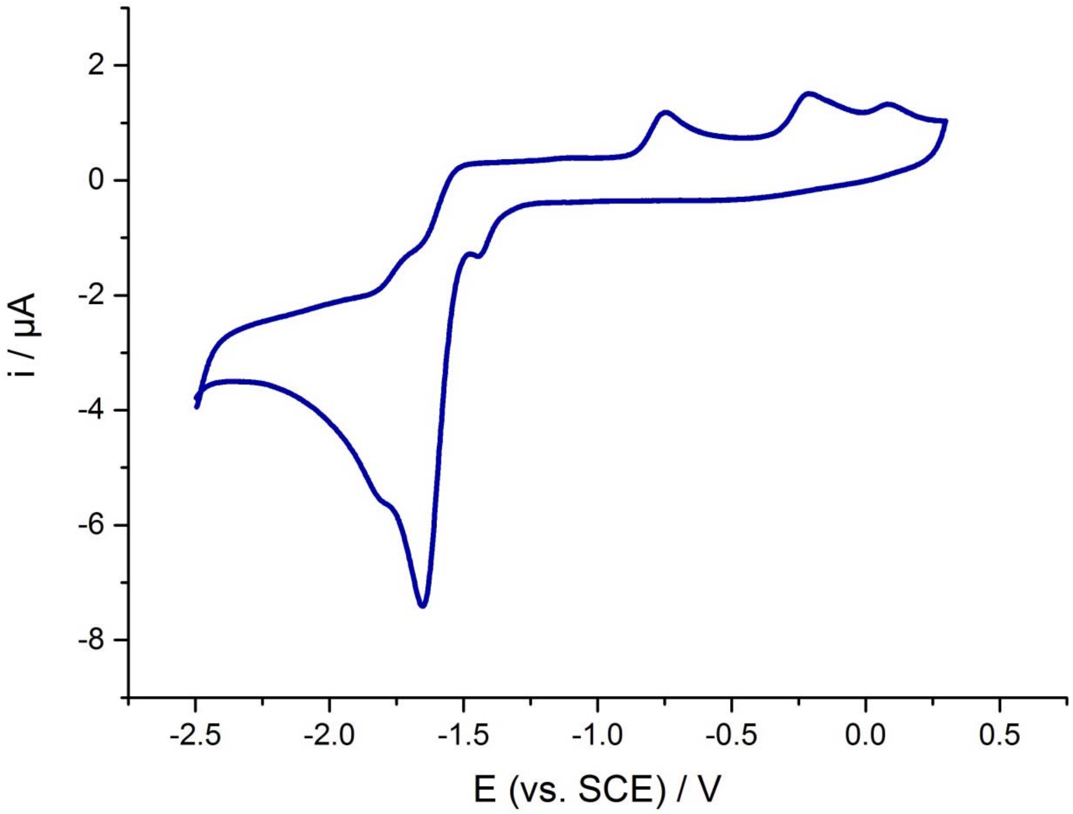


Figure S7. Cyclic voltammogram of complex **3** in CH_3CN using 0.1 M NBu_4BF_4 as supporting electrolyte.

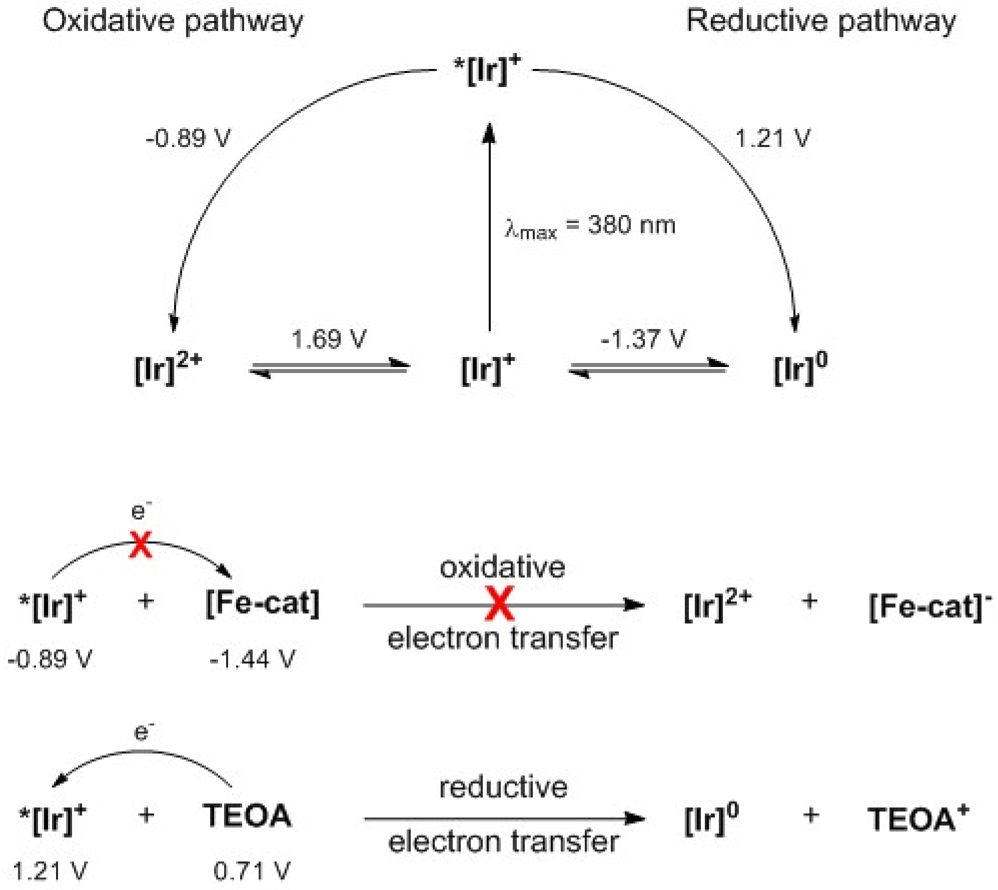


Figure S8. Schematic diagram showing an example of the molecular quantities relevant for energy and electron transfer processes based on [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)](PF$_6$). Values were obtained from literature[1,6] or own measurements and converted to values with respect to SCE.

Reactions between iron hydride complex 9 and CO_2

Complex **9** (19.6 mg, 50 µmol) was weighted inside a glovebox and transferred to a J. Young NMR tube. NMP (0.5 mL) and benzene-d_6 (0.1 mL) were added and the resulting solution was degassed by 3 freeze-pump-thaw cycles, filling the atmosphere with CO_2 in the last cycle. The NMR tube was kept under dark conditions for 30 min and a ^{13}C NMR spectrum was recorded (Figure S9b).

A second J. Young NMR tube was prepared as previously described and irradiated with a 300 W Xenon lamp (power output = 1.5 W) for 30 min. During irradiation, the NMR tube was immersed in a cooling bath controlled by a thermostat to maintain the temperature at 25 °C. Immediately after, a ^{13}C NMR spectrum of the resulting solution was recorded (Figure S9c).

For comparison purpose, ^{13}C NMR spectra of complex **9** (Figure S9a) and complex **3** (Figure S9d) in the same solvent mixture (NMP/C_6D_6) and under Ar atmosphere were also recorded.

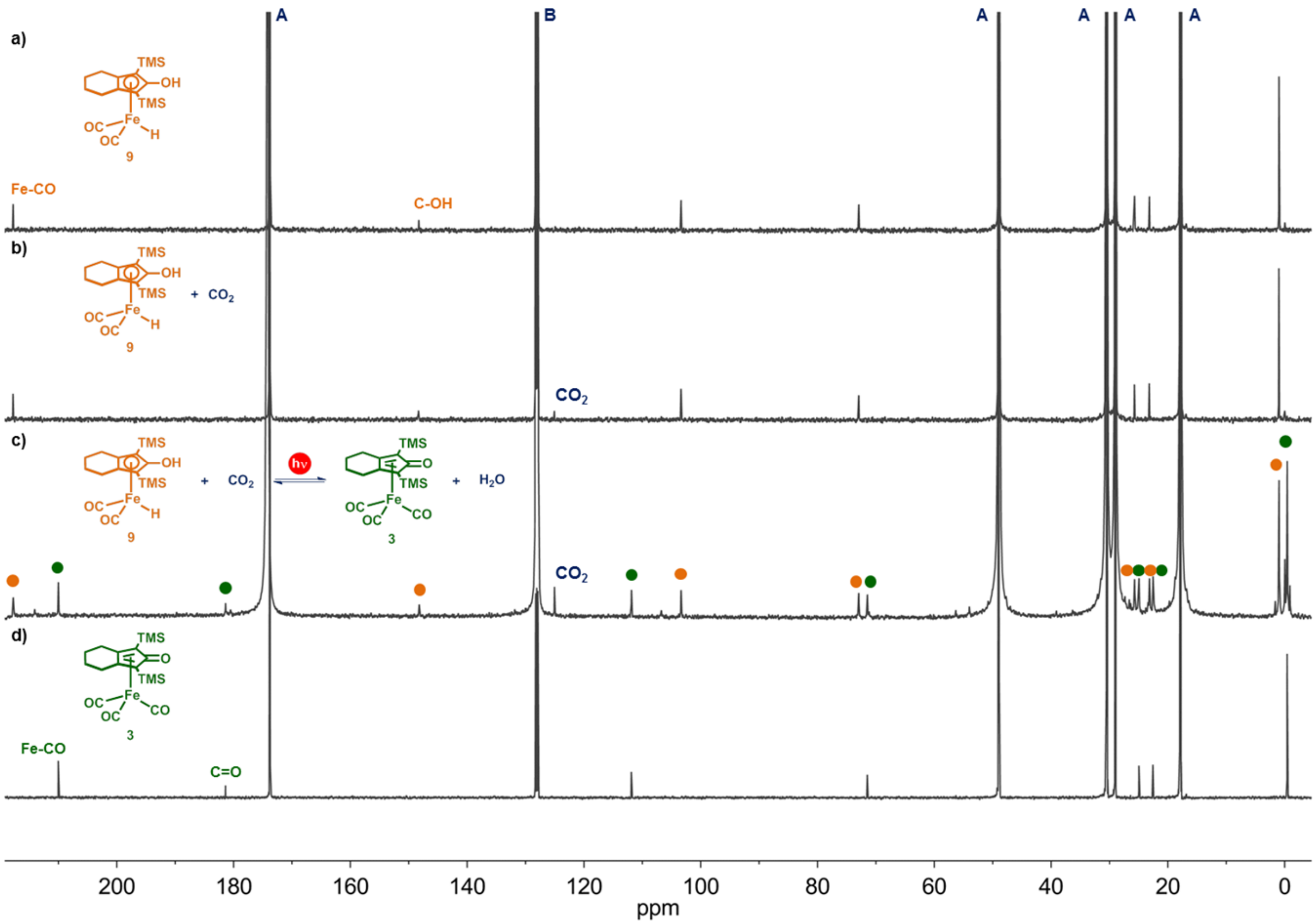


Figure S9. ^{13}C NMR spectra of the experiments with iron hydride complex **9** and CO_2 (A = NMP; B = C_6D_6). (a) Solution of complex **9** in NMP/C_6D_6 under Ar atmosphere. (b) Solution of complex **9** in NMP/C_6D_6 under 1 atm of CO_2 after 30 min of reaction in dark conditions. (c) Solution of complex **9** in NMP/C_6D_6 under 1 atm of CO_2 after 30 min of reaction with light irradiation. (d) Solution of complex **3** in NMP/C_6D_6 under Ar atmosphere.

References

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