Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

for

A fully earth-abundant photocatalytic system for the visible-light-driven reduction of CO_2 to CO

Alonso Rosas-Hernández[1], Christoph Steinlechner[1], Henrik Junge[1], Matthias Beller[*,1]

[1] Leibniz Institute for Catalysis at the University of Rostock, Albert Einstein-Str. 29a, 18059 Rostock, Germany.

[*]Corresponding author email address: matthias.beller@catalysis.de

Content

Materials and Methods

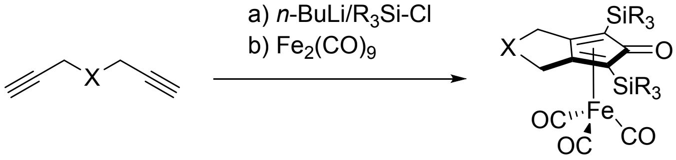
Anhydrous *N*-methyl-2-pyrrolidone (NMP) was purchased from Sigma-Aldrich and stored under an Ar atmosphere. Triethanolamine (TEOA) was degassed and also stored under Ar prior to use. CO_2 tanks (>99.998%) were purchased from Linde and used as received. $[Cu(CH_3CN)_4]PF_6$ was either purchased from commercial sources. N-N and P-P ligands were purchased by commercial sources or synthesized according to the literature[1]. Knölker complexes and BIH were synthesized according to literature[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). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Fourier 300 instrument by using the residual solvent signal as an internal standard. Emission spectra were recorded in a Varian Cary Eclipse fluorescence spectrophotometer.

Typical procedure for photocatalytic reactions

A double-walled temperature-controlled 100 mL reaction vessel was evacuated and refilled with Ar three times followed by additional three cycles using CO_2. $[Cu(CH_3CN)_4]PF_6$, N∩N ligand, P∩P ligand, 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 1.5 W), equipped with a 400-700 nm filter. The gaseous reaction products (H_2 and CO) were analyzed using calibrated GC. Calculations of amount of carbon monoxide were performed using its van der Waals molar volume (24.44323 mol/L) at 25 °C and 1.01325 bar. TONs for carbon monoxide and hydrogen were calculated by following equation 1.

$$TON = \frac{n_{product}}{n_{catalyst}} \tag{1}$$

General procedure for complexes 1-4

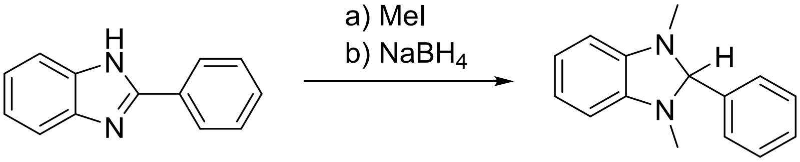


1 eq. of diyne is dissolved in dry THF and 1.1 eq. of *n*-BuLi are added at -78 °C (dry ice/acetone) and stirred for 10 min under argon. Subsequently it is allowed to warm up to room temperature and is stirred for further 1 h. 2.2 eq. of R_3Si-Cl are added and stirred over night with a slight stream of argon. A saturated NH_4Cl-solution is poured into the mixture. The aqueous phase is extracted 2x with diethyl ether and the combined organic phases dried with $MgSO_4$. Purification over silica gel with *n*-pentane/ethyl acetate (9:1) gave a colorless oil with a yield of 90 %.

[2+2+1]-Cycloaddition

In the glovebox 1 eq. of $Fe_2(CO)_9$ is weighed into a Schlenk tube. 1 eq of diyne-SiR_3 and dry toluene are added and the solution refluxed 15 h under argon atmosphere. The solvent was removed under vacuum and purification by column chromatography (*n*-pentane/ethyl acetate 9:1) gave the complex with a yield of 60 %.

Synthesis of BIH



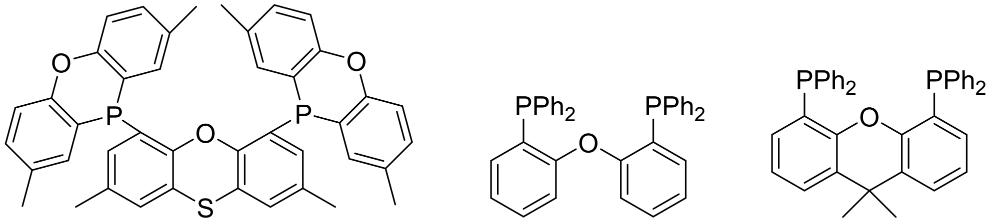
1 eq of phenylbenzimidazole, 1.8 eq NaOH-powder, 6.5 eq methyliodide and dry methanol are added into a pressure tube and heated up to 110 °C for 72 h under argon. The solvent was removed and the solution was decolorized with activated carbon in ethanol/water 5:1 and recrystallized in ethanol, filtered off and dried *in vacuo*. The methylated phenylbenzimidazol salt was dissolved in 80 mL dry methanol. Thereafter 3.4 eq $NaBH_4$ was added slowly. After 1 h the product precipitates and the solvent is evaporated. Recrystallisation in ethanol/water 2:1 gives white crystals in a yield of 65%.

^{1}H-NMR (DMSO-*d*6, 300 MHz): δ = 2.47 (s, 6H), 4.87 (s, 1H), 6.45 (m, 2H), 6.62 (m, 2H), 7.45 (m, 3H), 7.55 (m, 2H); **^{13}C-NMR** (DMSO-*d*6, 75 MHz): δ = 33.6, 93.7, 106.2, 119.5, 129.0, 129.7, 139.2, 142.4

Table S1. Screening of various P∩P ligands with Bathocuproine.

Entry	P∩P	TON (CO)	TON (H_2)	Selec. (CO)
1	**10**	430	30	94%
2	**11**	340	14	96%

Reaction conditions: 5 µmol of $[Cu(CH_3CN)_4]PF_6$; N∩N = Bathocuproine; 1 µmol of [Fe]; BNAH 0.1 M; 7.5 mL NMP/TEOA (5:1); Hg-lamp 1.5 W output, 400-700 nm.



10 **11** **12**

Figure S1. Thixantphos **10**, DPEphos **11** and Xantphos **12**.

Table S2. Screening of different ratios between copper, diimine and diphosphine ligands.

Entry	[Cu]:P∩P:N∩N	TON (CO)	TON (H_2)	Selec. (CO)
1	1:1:1	246	39	86%
2	1:0:2	4	0	--
3	1:1:2	225	26	90%
4	1:1:3	207	27	88%
5	1:2:1	271	14	95%
6	1:3:1	270	9	97%

Reaction conditions: 5 µmol of $[Cu(CH_3CN)_4]PF_6$; P∩P = Xantphos; N∩N = Bathocuproine; 1 µmol of [Fe]; BNAH 0.1 M; 7.5 mL NMP/TEOA (5:1); Hg-lamp 1.5 W output, 400-700 nm.

Table S3. Comparison between BNAH and BIH

Entry	Electron donor	TON (CO)	TON (H2)	Selec. (CO)
1	BNAH	245	6	98%
2	BIH	487	7	99%

5 µmol of $[Cu(CH_3CN)_4]PF_6$; 15 µmol of Xantphos; 5 µmol of Bathocuproine; 1 µmol of [Fe]; electron donor 0.1 M; 7.5 mL NMP/TEOA (5:1); Hg-lamp 1.5 W output, 400-700 nm.

Table S4. Comparison between "in situ" generated and molecular defined Cu PS.

Entry	[Cu]	TON (CO)	TON (H_2)	Selec. (CO)
1[a]	in situ	487	7	99%
2[b]	isolated	427	5	99%
3[c]	in situ	308	8	97%

[a] 5 µmol of $[Cu(CH_3CN)_4]PF_6$; 15 µmol of Xantphos; 5 µmol of Bathocuproine; 1 µmol of [Fe]; BIH 0.1 M; 7.5 mL NMP/TEOA (5:1); Hg-lamp 1.5 W output, 400-700 nm.

[b] 5 µmol of $[Cu(Xantphos)(Bathocuproine)]PF_6$; 1 µmol of [Fe]; BIH 0.1 M; 7.5 mL NMP/TEOA (5:1); Hg-lamp 1.5 W output, 400-700 nm.

[c] 5 µmol of $[Cu(CH_3CN)_4]PF_6$; 15 µmol of Xantphos; 5 µmol of Bathocuproine; 0.5 µmol of [Fe]; BIH 0.1 M; 7.5 mL NMP/TEOA (5:1); Hg-lamp 1.5 W output, 400-700 nm.

Table S5. Downscaling of the Photocatalytic reduction of CO_2.

Entry	[Cu]:P∩P:N∩N	TON (CO)	TON (H_2)	Selec. (CO)
1	1:3:1	292	55	84%
2	1:3:1	301	81	79%

Reaction conditions: 0.5 µmol of [Cu]; 0.1 µmol of [Fe]; BIH 0.1 M; 2.0 mL NMP/TEOA (5:1); Hg-lamp 1.5 W output; 5 h, 400-700 nm.

Table S6. Long-time irradiation experiments

Entry	Time (h)	CO (μmol)	H_2 (μmol)	Selec. (CO)
1	5	85	26	77%
2	16	75	20	79%

Reaction conditions: 0.5 μmol $[Cu(CH_3CN)_4]PF_6$; 0.5 μmol Bathocuproine; 0.5 μmol Xantphos; 0.5 μmol [**1**]; BNAH 0.1 M; 7.5 mL NMP/TEOA (5:1); Hg-lamp 1.5 W output, 400-700 nm.

Quantum yield calculation

The quantum yields for the photocatalytic CO_2 reduction reactions were determined using the following equation 2:

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

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, 3 mL (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, 120 W) 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 3:

$$nFe^{2+} = \frac{V_1 \cdot V_3 \cdot (A - A_0)}{1000 \cdot V_2 \cdot \varepsilon_0} \tag{3}$$

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})

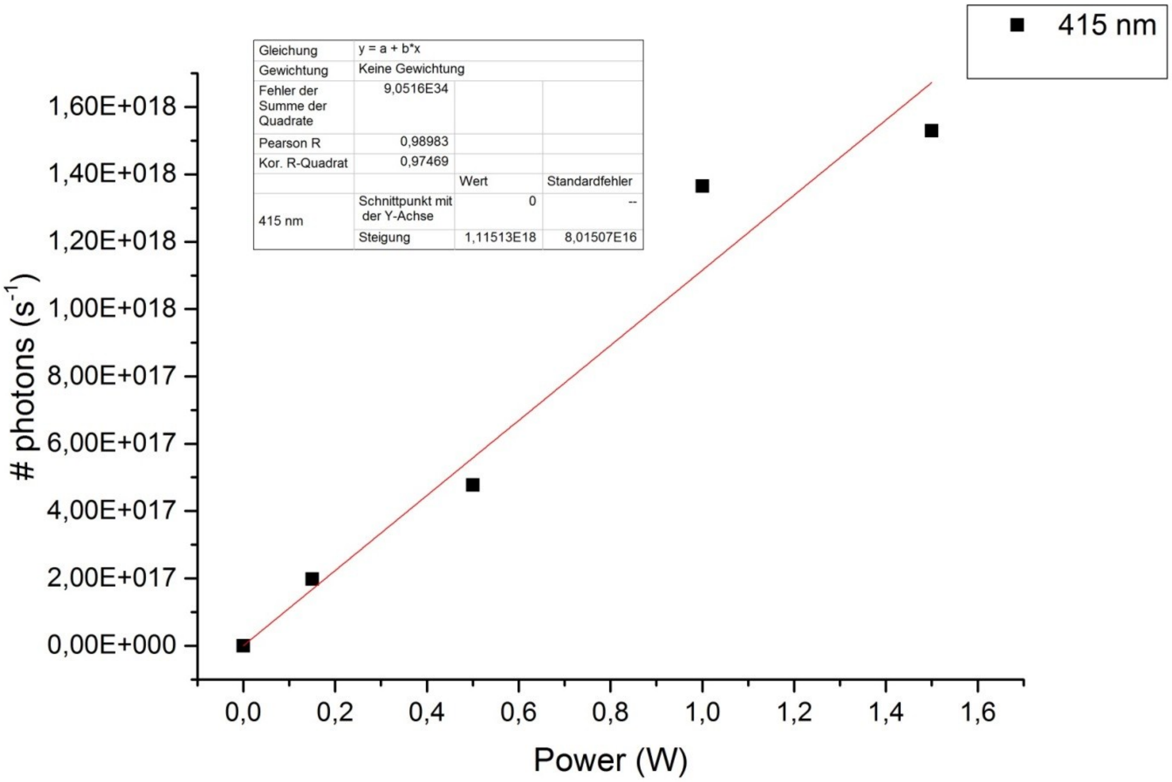
Finally, the number of incident photons per second (# photons) is calculated using the following equation 4:

$$\#\, photons\ (s^{-1}) = \frac{6.022 \cdot 10^{23} \cdot nFe^{2+}}{\Phi_\lambda \cdot t} \tag{4}$$

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

t = time of irradiation (s)

The numbers of incident photons were determined at 415 nm using 4 different power outputs (0.15 W, 0.5 W, 1.0 W and 1.50 W) as shown in Figure S2.



Gleichung	y = a + b*x		
Gewichtung	Keine Gewichtung		
Fehler der Summe der Quadrate	9,0516E34		
Pearson R	0,98983		
Kor. R-Quadrat	0,97469		
		Wert	Standardfehler
415 nm	Schnittpunkt mit der Y-Achse	0	--
	Steigung	1,11513E18	8,01507E16

Figure S2. Numbers of photons vs. power output.

Emission-quenching experiments

In situ solutions of **CuPS** (0.1 mM [$Cu(CH_3CN)_4$]PF_6, 0.1 mM Bathocuproine, 0.3 mM Xantphos) in anhydrous acetonitrile were prepared containing different concentrations of the corresponding quencher. In the case of BIH, the concentration varied from 0.375 mM to 1.875 mM (figure S3), while for complex **1** concentrations from 0.06 mM to 0.3 mM (figure S4) were used. Thus, steady-state emission spectrum (excitation wavelength 450 nm) of each solution was recorded, and the intensity of the luminescence for the ^{3}MLCT excited state of the photosensitizer (550 nm) was recorded. Quenching rate constants k_q were calculated from the linear Stern-Volmer plots.

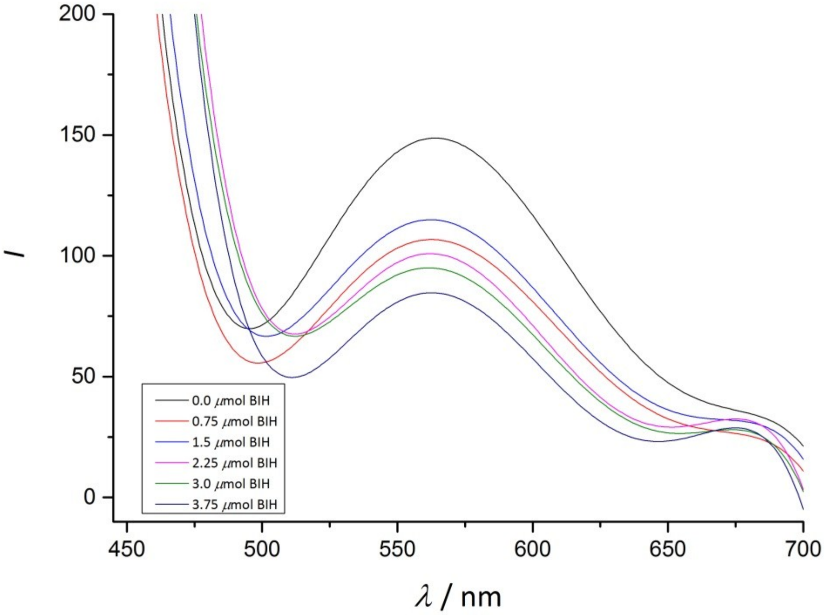


Figure S3. Emission-spectra from the quenching experiments with BIH.

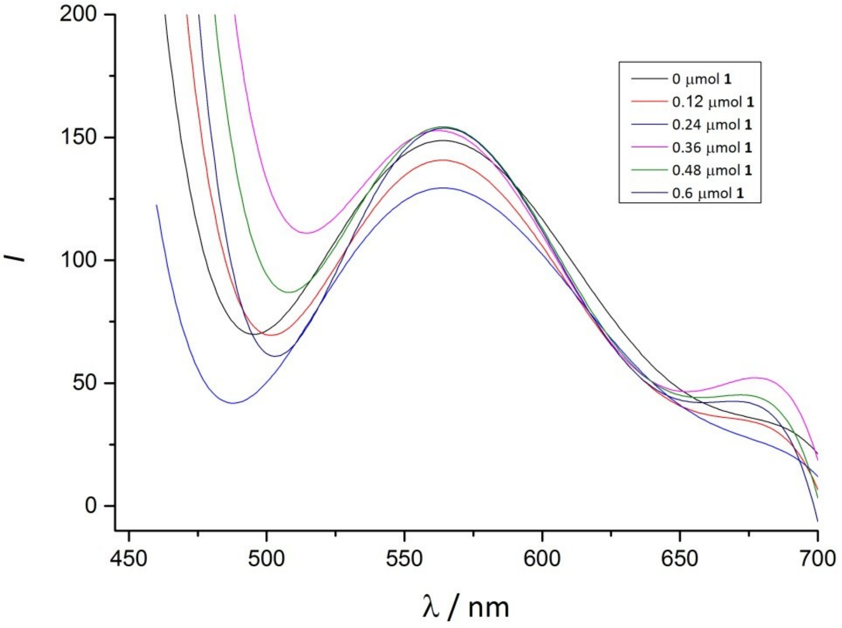


Figure S4. Emission-spectra from quenching experiments with complex **1**.

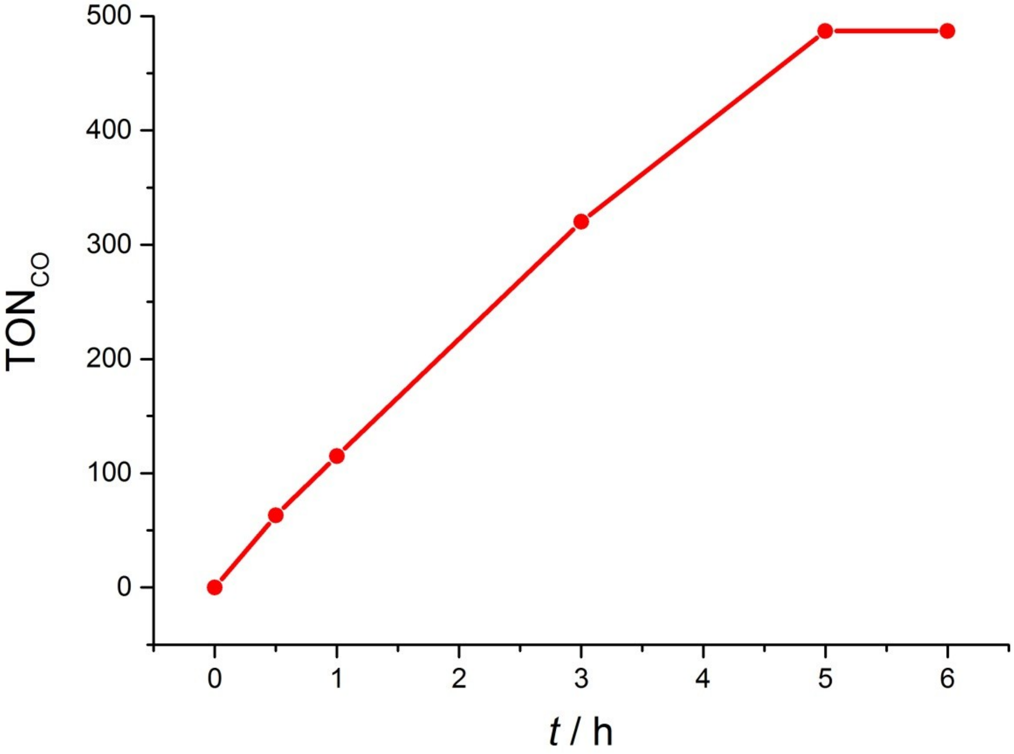


Figure S5. Photocatalytic formation of CO as a function of irradiation time. Reaction conditions: *N*-methyl-2-pyrrolidone and triethanolamine (5:1, v/v) 7.5 mL; iron catalyst (**1**) 1 µmol; $[Cu(CH_3CN)_4]PF_6$ 5 µmol; xantphos ligand 15 µmol; bathocuproine ligand 5 µmol; Hg-lamp (light output 1.5 W) equipped with a 400-700 nm filter.

References

[1] T. Moragas, M. Gaydou, R. Martin, *Angew. Chem. Int. Ed.*, **2016**, *55*, 5053 –5057

[2] H.-J. Knölker, J. Heber, C. H. Mahler; *Synlett*, **1992**, 1002-1004.

[3] I. H. Lee, E. H. Jeoung, M. M. Kreevoy, *J. Am. Chem. Soc.*, **1997**, 2722-2728.

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