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Electronic Supplementary Information (ESI)

Highly active and robust iron quinquepyridine complex for photocatalytic CO_2 reduction in aqueous acetonitrile solution

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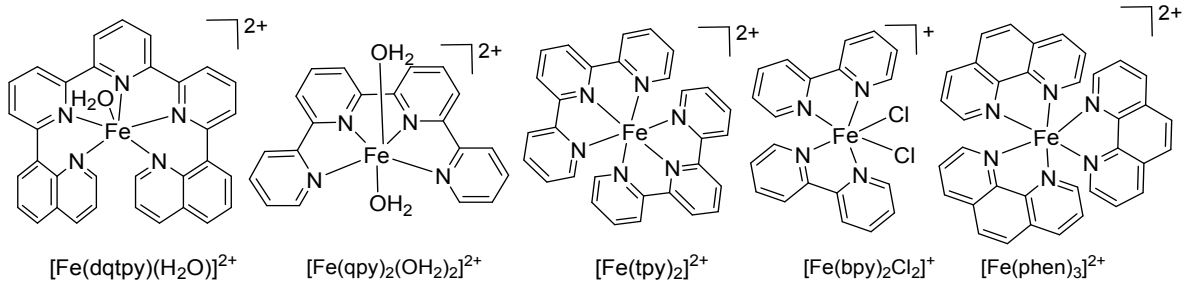

Scheme S1 Structures of $[Fe(dqtpy)(H_2O)]^{2+}$, $[Fe(qpy)(H_2O)_2]^{2+}$, $[Fe(tpy)_2]^{2+}$, $[Fe(bpy)_2Cl_2]^{+}$, and $[Fe(phen)_3]^{2+}$.

2. Experimental details

Chemicals

Iron(II) perchlorate hydrate (Sigma-Aldrich, 98%), sodium formate (Sigma-Aldrich, 99.998%), acetonitrile (Sigma-Aldrich, 99.9%), N,N-Dimethylformamide (DMF, Sigma-Aldrich, 99.9%), 2-phenylbenzimidazole (J&K, 98%), iodomethane (Energy Chemical, 99.5%) and sodium borohydride (Acros, 99%) were used as received. $Ru(phen)_3Cl_2$ (phen = 1,10-phenanthroline),[1] $[Fe(dqtpy)(H_2O)](ClO_4)_2$ (dqtpy = 6,6"-di(quinolin-8-yl)-2,2':6',2"-terpyridine),[2] $[Fe(qpy)(H_2O)_2](ClO_4)_2$ (qpy = 2,2′:6′,2″:6″,2′′′-quaterpyridine),[3] $[Fe(tpy)_2](ClO_4)_2$ (tpy = 2,2':6',2"-terpyridine),[4] $[Fe(bpy)_2Cl_2]Cl$ (bpy = 2,2'-bipyridine),[5] $[Fe(phen)_3]Cl_2$,[6] qnpy (2,2':6',2":6",2"':6"',2""-quinquepyridine)[7] and BIH (1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole)[8] were synthesized according to literature methods.

Synthesis of $[Fe(qnpy)(H_2O)_2](ClO_4)_2$

The iron(II) complex was prepared by reacting the 2,2':6',2":6",2"':6"',2""-quinquepyridine (100 mg, 0.26 mmol) and iron(II) perchlorate hexahydrate (1.2 equivalents, 113 mg) in acetonitrile (20 mL) at room temperature for 12 h under argon. The crude products were recrystallized by diffusion of diethyl ether to CH_3CN solution. $[Fe(qnpy)(H_2O)_2](ClO_4)_2$ was obtained as red solid (58 mg, 35% yield).[9] ESI-MS (MeOH): m/z = 222.0 for $[Fe(qnpy)]^{2+}$ and 542.4 for $\{[Fe(qnpy)](ClO_4)\}^{+}$; Anal. Calcd. (Found) for $C_{25}H_{21}Cl_2N_5FeO_{10}$: C, 44.27 (43.77), H, 3.12 (2.98), N, 10.33 (10.11).

Characterization

Electrospray ionization mass spectrometry (ESI/MS) was conducted on a PE SCIEX API 150 mass spectrometer. The analytic solution was continuously infused with a syringe pump at a constant flow rate into the pneumatically assisted electrospray probe with nitrogen as the nebulizing gas. H^1NMR spectra were recorded on Bruker 400 MHz spectrometer and the chemical shift is expressed in ppm. Elemental analyses were done on an Elementar Vario EL analyzer.

Photocatalytic CO_2 reduction

In a typical run, a 2 mL MeCN/H_2O (1:1, v/v) solution containing 0.05 mM **1**, 0.2 mM $Ru(phen)_3^{2+}$ and 0.11 M BIH (50 mg) was put in a glass tube and then sealed with a rubber septum. The solution was bubbled with CO_2 for 30 min and then irradiated with visible light (blue LED centered at 460nm) for 68 h at 293 K in a thermostatted water bath. The inner volume of the tube is about 12.3 mL. 100 μL aliquots of gaseous products in the headspace were analyzed by gas chromatography-thermal conductivity detector (GC-TCD, Agilent 7820A) fitted with a Molsieve 5Å PLOT column (CP7534, 30 m ⌀ 0.32 mm ⌀10 μm). No alkane, alkene or alkyne was detected. The calibration curves were obtained by filling pure H_2 and CO gas to a tube with a graduated gastight syringe. GC-MS (Agilent 6890-5975 with DB-5MS column, 30 m ⌀ 0.25 mm ⌀ 0.25 μm). Ion chromatography DX-600 (Dionex, IonPac AS19 (0.4 × 250 mm) + AG19 Column (4 × 50 mm)) were used to analyze the liquid reaction products in the solution. The experiments were performed at least in duplicate. ^{13}C-labeling experiments were conducted following the same procedure except $^{13}CO_2$ was used and the gaseous products were analyzed by Agilent 7820A GC-TCD and Agilent 6890GC -5975MS.

Electrochemical studies

Cyclic voltammetry was performed with a CHI 660E instrument. The three-electrode set-up consists of a glassy carbon working electrode (CHI 104, 0.071 cm^2), a Pt wire counter electrode (CHI 115) and a saturated calomel reference electrode (SCE, CHI 150). Working electrode was polished with α-Al_2O_3 (successively 0.3, 0.1, and 0.05 μm, 1 min each), thoroughly rinsed and with H_2O and ethanol. The solution was purged with argon or CO_2. All reported potentials in this study are versus SCE at a scan rate of 0.1 $V \cdot s^{-1}$.

Quantum yield determination

Blue LED light strip (1 modules, centered at 460 nm) was used for evaluating the number of photons. The average light intensity taken before and after photochemical reaction was 6×10^{-9} einstein s^{-1}. Typically for the photochemical reaction, a quartz cell (light path length = 1 cm) containing 0.05 mM **1**, 0.2 mM $Ru(phen)_3^{2+}$ and 0.11 M BIH in a 2 mL CO_2-saturated MeCN/H_2O (1:1, v/v) was irradiated with blue LED light. The solution was vigorously stirred during the irradiation. The amount of CO after irradiation for 24 h was determined by GC-TCD. The quantum yield for CO_2 reduction to CO was calculated using the following equation:

$$\phi_{CO} = \frac{number\ of\ CO\ molecules}{number\ of\ incident\ photons} \times 100\%$$

Fluorescence quenching

The excited-state lifetime (τ_0) of $Ru(phen)_3^{2+*}$ was measured with a FLS 980 fluorescence spectrometer (Edinburgh instruments). The quenching experiments were performed by addition of various amounts of BIH or catalyst **1** to an anaerobic 2 mL CO_2-saturated MeCN/H_2O (1:1, v/v) solution of $Ru(phen)_3^{2+}$ (0.05 mM). The relative emission lifetime of the characteristic emission of $Ru(phen)_3^{2+*}$ at 700 nm in the presence of different concentrations of BIH or catalyst **1** was used to calculate the quenching rate constant (k_q) according to the Stern-Volmer equation.

$\tau_0/\tau = 1 + k_q \tau_0 [Q]$

Where I_0 and I are the emission intensity in the absence and presence of quencher, τ_0 and τ are the excited state lifetime in the absence and presence of quencher, k_q is the bimolecular quenching rate constant, and [Q] is the molar concentration of the quencher.

Dynamic light scattering

Dynamic light scattering (DLS) measurements were performed by using a Zetasizer Nano ZS instrument (Malvern Instruments Ltd., USA), which can detect particle sizes ranging from 0.6–6000 nm. The light source was a HeNe gas laser (4 mW, λ = 632.8 nm). Data were obtained by using a scattering angle of 175° at 23 °C.

2. Additional data

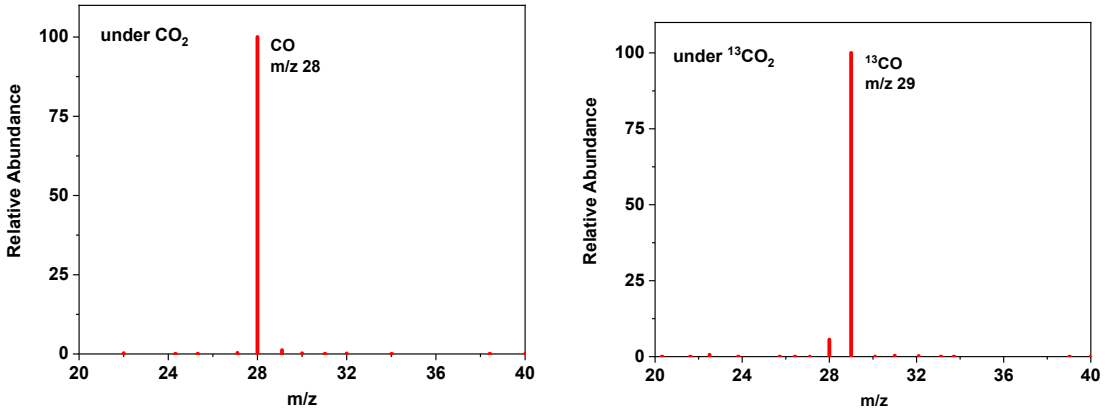

Fig. S1 MS analysis of CO evolved in the headspace of sample flask under CO_2 (left) or $^{13}CO_2$ (right). Sample solution: 0.05 mM **1**, 0.2 mM $Ru(phen)_3^{2+}$ and 0.11 M BIH in MeCN/H_2O (1:1, v/v) solution. Isotopic labeling experiments indicate the peak at m/z 29, assigned to ^{13}CO, is produced under 1 atm $^{13}CO_2$.

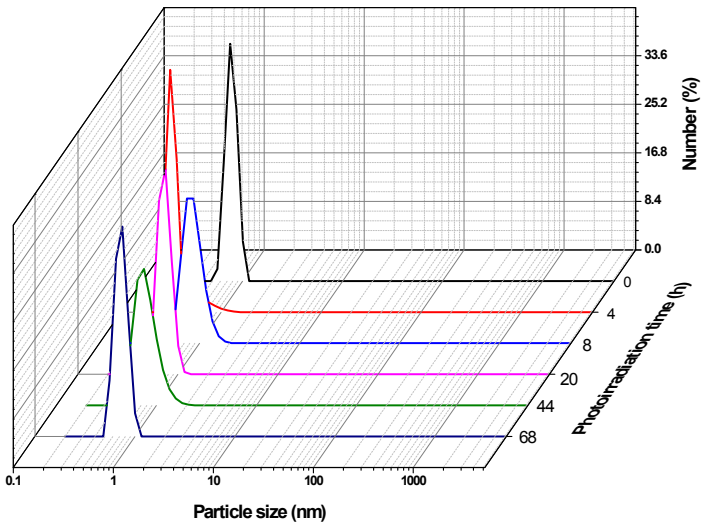

Fig. S2 Particle size distribution of a CO_2-saturated MeCN/H_2O (1:1, v/v) solution containing 0.05 mM **1**, 0.2 mM $Ru(phen)_3^{2+}$ and 0.11 M BIH determined by dynamic light scattering (DLS) measurements during irradiation from 0 to 68 h.

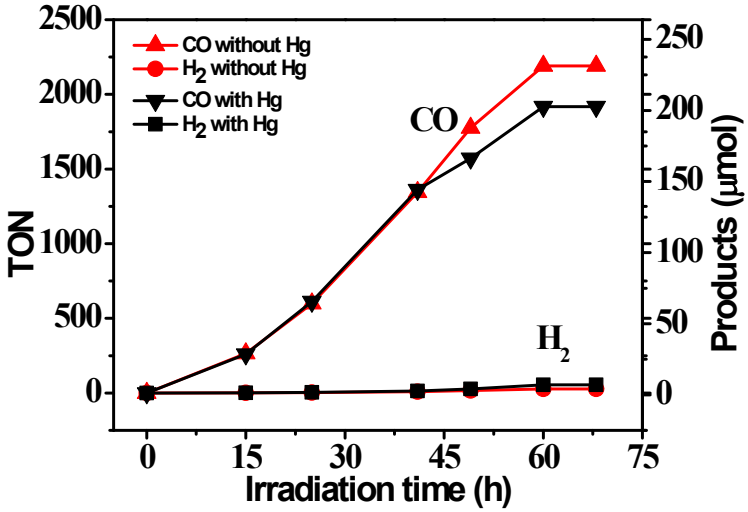

Fig. S3 CO and H_2 production upon visible-light irradiation (blue LED centered at 460 nm) of a CO_2-saturated MeCN/H_2O (1:1, v/v) solution (2 mL) containing 0.05 mM **1**, 0.2 mM $Ru(phen)_3^{2+}$ and 0.11 M BIH without Hg(0) (red) and in the presence of 0.2 mL Hg(0) (black). The TON for CO slightly decreased from 2190 to 1918 when Hg(0) is added. The errors are around 10%.

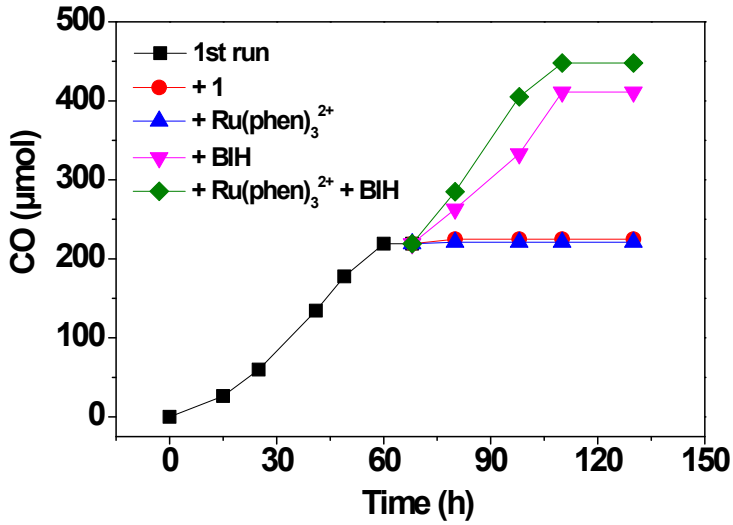

Fig. S4 Stability tests of the photosystem during light irradiation. Plot of CO versus time for the first cycle (■) and second cycle with re-bubbling of CO_2 and the addition of another equiv. of **1** (●), $Ru(phen)_3^{2+}$ (▲), BIH (▼) or $Ru(phen)_3^{2+}$ +BIH (♦). The solution contains initially 0.05 mM **1**, 0.2 mM $Ru(phen)_3^{2+}$ and 0.11 M BIH in 2 mL MeCN/H_2O (1:1, v/v). The errors are around 10%.

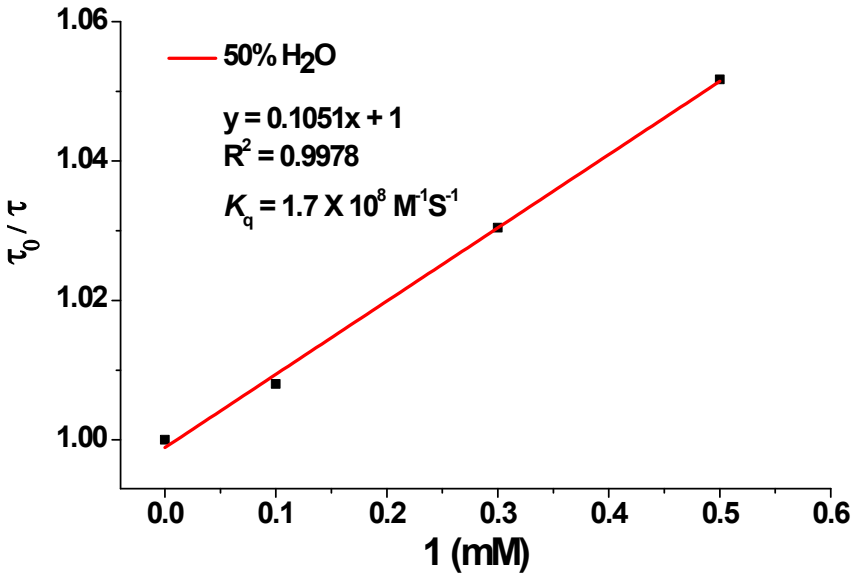

Fig. S5 Stern-Volmer plot for luminescence lifetime quenching of excited $Ru(phen)_3^{2+}$ (0.05 mM) by catalyst **1** in MeCN/H_2O (1:1, v/v) solution.

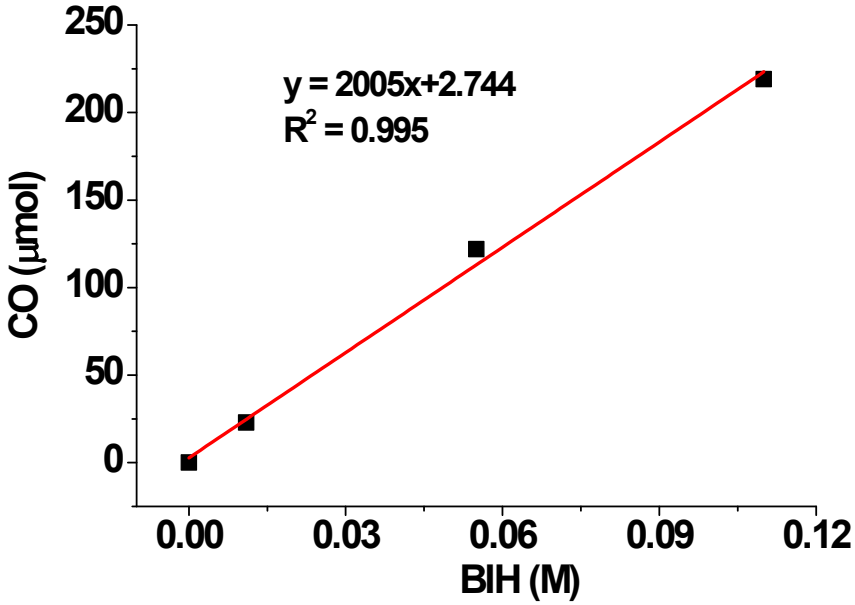

Fig. S6 Plot of amount of CO (μmol) vs. [BIH] in a CO_2-saturated MeCN/H_2O (1:1, v/v) solution containing 0.05 mM **1** and 0.2 mM $Ru(phen)_3^{2+}$.

Table S1 Photocatalytic reduction of CO_2 with **1**.[a]

Entry	**1**	$Ru(phen)_3^{2+}$	Sacrificial	Proton	TON(selectivity %)		
	mM	mM	reductant	source	CO	H_2	HCOOH
1[b]	0.05	0.2	0.11 M BIH+20% TEOA	-	208(94)	14(6)	0(0)
2	0.05	0.2	0.11 M BIH	20% H_2O	1751(97)	32(2)	18(1)
3	0.05	0.2	0 M BIH	50% H_2O	0(0)	0(0)	0(0)
4	0.05	0.2	0.011 M BIH	50% H_2O	229(100)	0(0)	0(0)
5	0.05	0.2	0.055 M BIH	50% H_2O	1219(99)	9(1)	0(0)
6	0.05	0.2	0.11 M BIH	50% H_2O	2190(99)	27(1)	0(0))
7	0.05	0.01	0.11 M BIH	50% H_2O	1793(99)	18(1)	0(0)
8	0.05	0.05	0.11 M BIH	50% H_2O	2130(99)	26(1)	0(0)
9	0.02	0.5	0.11 M BIH	50% H_2O	2008(99)	22(1)	0(0)

[a] In a typical run, a CO_2-saturated MeCN/H_2O (1:1, v/v) containing **1** (0.05 mM), $Ru(phen)_3^{2+}$ (0.2 mM) and BIH (0.11 M) irradiated for 68 h. The errors are around 10%.

Table S2 Comparison of the photocatalytic performances for CO_2 reduction with molecular catalysts based on earth-abundant metal complexes.

Catalyst	Photosensitizer	[Catalyst]/ [Photosensitizer]	TON(selectivity %) based on catalyst			Φ_{CO}	Reaction conditions	Reference
			CO	H_2	HCOOH			
$[Fe(qnpy)(H_2O)_2]^{2+}$	**$[Ru(phen)_3]^{2+}$**	**0.05 mM / 0.2 mM**	**2190(99)**	**27(1)**	**0(0)**	**0.8%**	**0.11 M BIH and 50% H_2O in MeCN, blue LED (centered at 460 nm), 68 h**	***This work***
		5 μM / 0.2 mM	**14095(98)**	**360(2)**	**0(0)**	**-**		
$[Fe(phen)_2(C_2H_5OH)Cl]^+$	$[Ru(bpy)_3]^{2+}$	0.03 mM / 0.67 mM	2567(85.4)	171(14.6)	0(0)	-	0.022 M BIH in 4 mL DMF/TEOA solution (v/v, 7:1), white LEDs (λ ≥ 420 nm), 2 h.	*Molecules* **2019**, *24*, 1-12.[6]
		0.15 μM / 0.67 mM	33167(95.3)	1650(4.7)	0(0)	-		
$[Fe(phen)_3]^{2+}$	$[Ru(bpy)_3]^{2+}$	0.03 μM / 0.67 mM	35417(68)	16667(32)	0(0)	-		
		3 μM / 0.67 mM	1642(90.3)	176(9.7)	0(0)	-		
$[Fe(dqtpy)(H_2O)]^{2+}$	Purpurin	0.05 mM / 0.05 mM	544(99.3)	4(0.7)	0(0)	0.12%	0.1 M BIH and 5% TFE in DMF, blue LED (460 nm), 15 h	*Dalton Trans.* **2019**, *48*, 9596-9602.[2]
$[Fe(qpy)(OH_2)_2]^{2+}$	$[Ru(bpy)_3]^{2+}$	0.05 mM / 0.2 mM	1879(97)	15(1)	48(2)	8.8%	0.1 M BIH in MeCN/TEOA (4:1 v/v), blue LED (centered at 460 nm), 3 h	*J. Am. Chem. Soc.* **2016**, *138*, 9413-9416.[10]
		0.005 mM / 0.2 mM	3844(85)	534(12)	118(3)	-		
	Purpurin	0.05 mM / 0.02 mM	520(97)	0(0)	14(3)	1.1%	0.1 M BIH in DMF, blue LED (460 nm), 11 h	
		0.005 mM/0.02 mM	1365(92)	0(0)	115(8)	-		
	$mpg\text{-}C_3N_4$	0.02 mM / 8.0 mg	155(97)	<1	8(3)	4.2%	MeCN/TEOA (4:1, v/v), λ≥400 nm, 17 h	*J. Am. Chem. Soc.* **2018**, *140*, 7437-7440.[11]
Fe(0) porphyrin	$Ir(ppy)_3$	2 μM / 0.2 mM	140(93)	11(7)	0	0.0013%	0.36 M TEA in MeCN, 150 W Xenon lamp (λ > 420 nm), 55 h	*J. Am. Chem. Soc.* **2014**, *136*, 16768-16771.[12]
Fe-*p*-TMA	$Ir(ppy)_3$	2 μM / 0.2 mM	367(78)	26(5)	0(0) + (CH_4 79(17))	-	0.05M TEA in MeCN, 150 W Xenon lamp (λ> 420 nm), 102 h	*Nature* **2017**, *548*, 74-77.[13]
	Purpurin	2 μM / 0.2 mM	120(95)	6(5)	0(0)	-	0.1 M $NaHCO_3$, 0.05 M TEA, and 0.2 mM purpurin	*ChemSusChem* **2017**, *10*, 4447-

							in MeCN/H_2O (1:9 v/v), λ > 420 nm, 94 h	4450.[14]
	Phen2	10 μM / 1 mM	140(73)	23(12)	0(0) + (CH_4 29(15))	-	0.1 M TEA and 0.1 M TFE in DMF, visible Light (λ > 435 nm), 102 h	*J. Am. Chem. Soc.* **2018**, *140*, 17830-17834.[15]
$Fe(dmp)_2(NCS)_2$	$Cu(dmp)(P)_2^+$	0.05 mM / 0.25 mM	273(78)	75(22)	0(0)	6.7%	0.05 M BIH in MeCN-TEOA (5:1 v/v) mixed solution (4 mL), λ=436 nm (high-pressure Hg lamp), 12 h	*J. Am. Chem. Soc.* **2016**, *138*, 4354-4357.[16]
	Cu(3Bzth)	0.05 mM / 0.5 mM	~ 50(71)	~ 20(29)	0(0)	4.1%	0.01 M BIH in MeCN-TEOA (5:1 v/v) mixed solution (4 mL), λ=436 nm by Xe lamp, 2 h (CO production is still continued.)	*Front. Chem.* **2019**, *7*, 1-12.[17]
cyclopentadienone iron complex	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]^+$	5 μM / 1.67 mM	596(100)	0(0)	0(0)	34%	NMP-TEOA (5:1 v/v) mixed solution (7.5 mL), Hg-lamp (400–700 nm), 5 h	*Chem. Commun.* **2016**, *52,* 8393-8396.[18]
Cyclopentadienone iron complex	5 μmol $[Cu(MeCN)_4]PF_6$, 15 μmol xantphos P–P ligand and 5 μmol N–N ligand	0.13 mM / 0.67 mM	487(99)	7(1)	0(0)	13.3%	0.1 M BIH in 7.5 mL NMP/TEOA (5:1,v/v), Hg-lamp (400–700 nm), 5 h	*Green Chem.* **2017**, *19,* 2356-2360.[19]
$Fe(CO)_3bpy$	$[Ru(bpy)_3]^{2+}$	0.25 μmol / 25 μmol	173(51)	168(49)	0(0)	5.2%	$Fe(CO)_3bpy$ 0.25 μmol, $[Ru(bpy)_3]Cl_2$ (25 μmol), ligand (1.25), 15 mL NMP/TEOA (5 : 1, v/v), visible light (400–700 nm), 5 h	*Catal. Sci. Technol.* **2016**, *6*, 3623-3630[20]
CoZn cryptate	$[Ru(phen)_3]^{2+}$	0.025 μM / 0.4 mM	65000(98)	1280(2)	0(0)	0.15%	0.3 M TEOA in H_2O/MeCN (v/v, 1:4), LED light (450 nm), 10 h	*Angew. Chem. Int. Ed. Engl.* **2018**, *57*, 16480-16485.[21]
CoCo cryptate	$[Ru(phen)_3]^{2+}$	0.025 μM / 0.4 mM	17000(98)	368(2)	0(0)	0.04%		
$[Co(qpy)(H_2O)_2]^{2+}$	$[Ru(bpy)_3]^{2+}$	0.05 mM / 0.3 mM	497(98)	3(1)	5(1)	2.8%	0.1 M BIH in MeCN/TEOA (4:1 v/v), blue LED (centered at 460 nm) for 3 h	*J. Am. Chem. Soc.* **2016**, *138*, 9413-9416.[10]
		0.005 mM / 0.3 mM	2660(98)	23(1)	35(1)	-		
$[Ni(^{Pr}bimiq1)]^{2+}$	$Ir(ppy)_3$	2 nm / 0.2 mM	98000(100)	0(0)	0(0)	0.01%	0.07 M TEA in MeCN,Xe lampequipped with an AM 1.5 filter, 7 h	*J. Am. Chem. Soc.* **2013**, *135,* 14413-

		0.2 μm / 0.2 mM	1500(100)	0(0)	0(0)	-		14424.[22]
$[Ni(bpet)(MeCN)_2]^{2+}$	$[Ru(bpy)_3]^{2+}$	0.03 mM / 0.5 mM	713(99)	7(1)	0(0)	1.42%	0.1 M BIH in DMA/H_2O solution (4.0 mL, 9:1 v/v), 450 nm, 55 h	*J. Am. Chem. Soc.* **2017**, *139*, 6538-6541.[23]
$[Ni(bpet\text{-}py_2)(H_2O)_2]^{2+}$	$[Ru(bpy)_3]^{2+}$	0.03 mM / 0.5 mM	120(99.7)	0.4(0.3)	0(0)	11.1%	5.0 mM $Mg(ClO_4)_2$ and 0.1 M BIH in DMA/H_2O solution (4.0 mL, 9:1 v/v), 450 nm, 4 h	*J. Am. Chem. Soc.* **2019**, *141*, 20309-20317.[24]
$[Cu(pyN_2^{Me2})(HCO_2)]^-$	$[Ru(phen)_3]^{2+}$	0.05 μM / 0.4 mM	9900(98)	200(2)	0(0)	-	TEOA (0.3 M) in MeCN/H_2O (5 mL, v/v=4:1), LED light (450 nm), 10 h	*Chem. Eur. J.* **2018**, *24*, 4503-4508.[25]
$[Cu(qpy)]^{2+}$	$[Ru(bpy)_3]^{2+}$	1 μM / 2 mM	12400(97)	410(3)	0(0)	1.2%	TEOA (15% v/v) and H_2O (3% v/v) in 2.5 mL MeCN, white LED lamp, 3 h.	*ChemSusChem* **2017**, *10*, 4009-4013.[26]
$[Mn(pyrox)(CO)_3Br]$	5.0 μmol $[Cu(CH_3CN)_4]PF_6$, 5.0 μmol bathocuproine, and 15.0 μmol xantphos	1 μM / 0.1 mM	1058(>99)	0(0)	0(0)	0.47%	0.1 M BIH in 10 mL MeCN/TEOA (5:1, v/v); Hg-lamp, 5 h.	*ACS Catal.* **2019**, *9*, 2091-2100.[27]
[Mn(4OMe)]	$[Cu_2(P_2bph)_2]^{2+}$	0.05 mM / 0.25 mM	1314(CO+HCOOH)			57%	0.1 M BIH in 4 mL DMA−TEOA (4:1, v/v) solution, Hg lamp, 36 h	*J. Am. Chem. Soc.,* **2018,** *140,* 17241-17254.[28]

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