Electronic Supplementary Information (ESI)

A Molecular Noble Metal-Free System for Efficient Visible Light-Driven Reduction of CO_2 to CO

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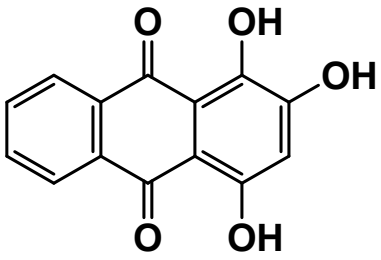
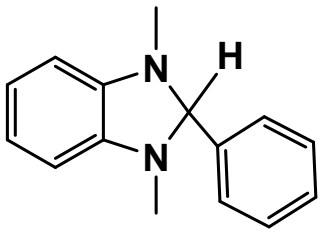
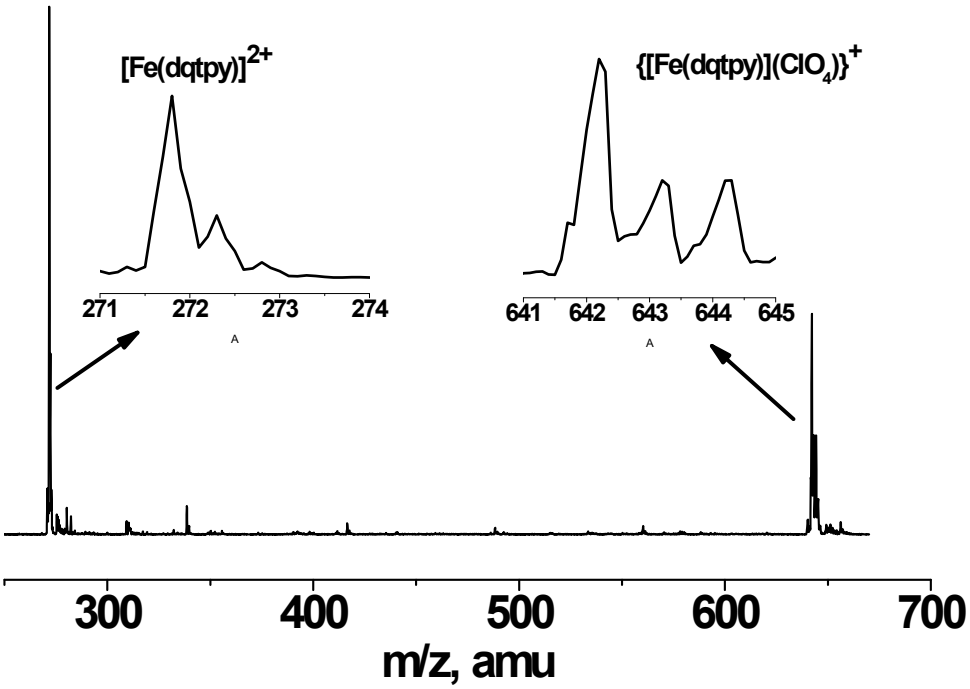


Purpurin



BIH

Scheme S1 Structures of photosensitizer (purpurin) and sacrificial reductant (BIH).



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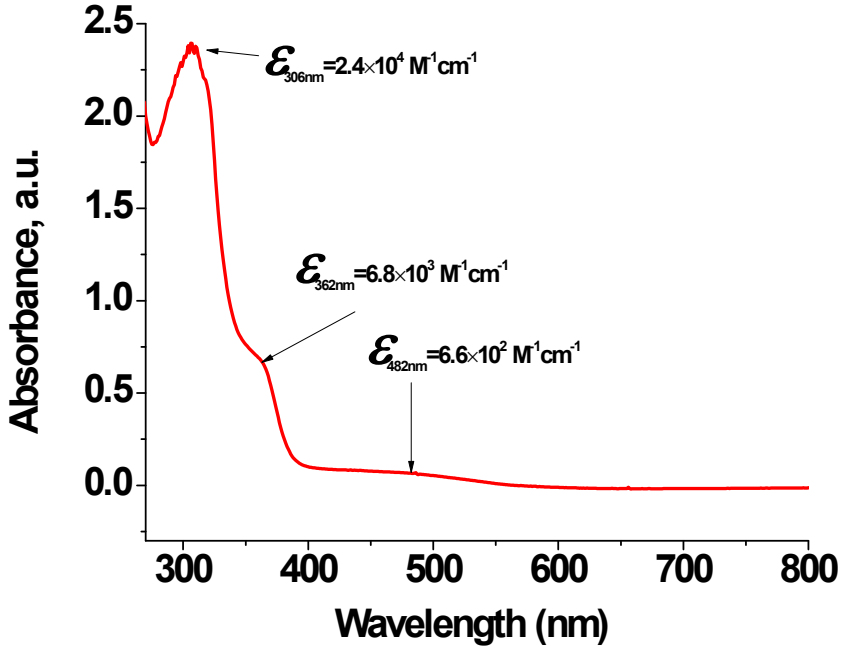
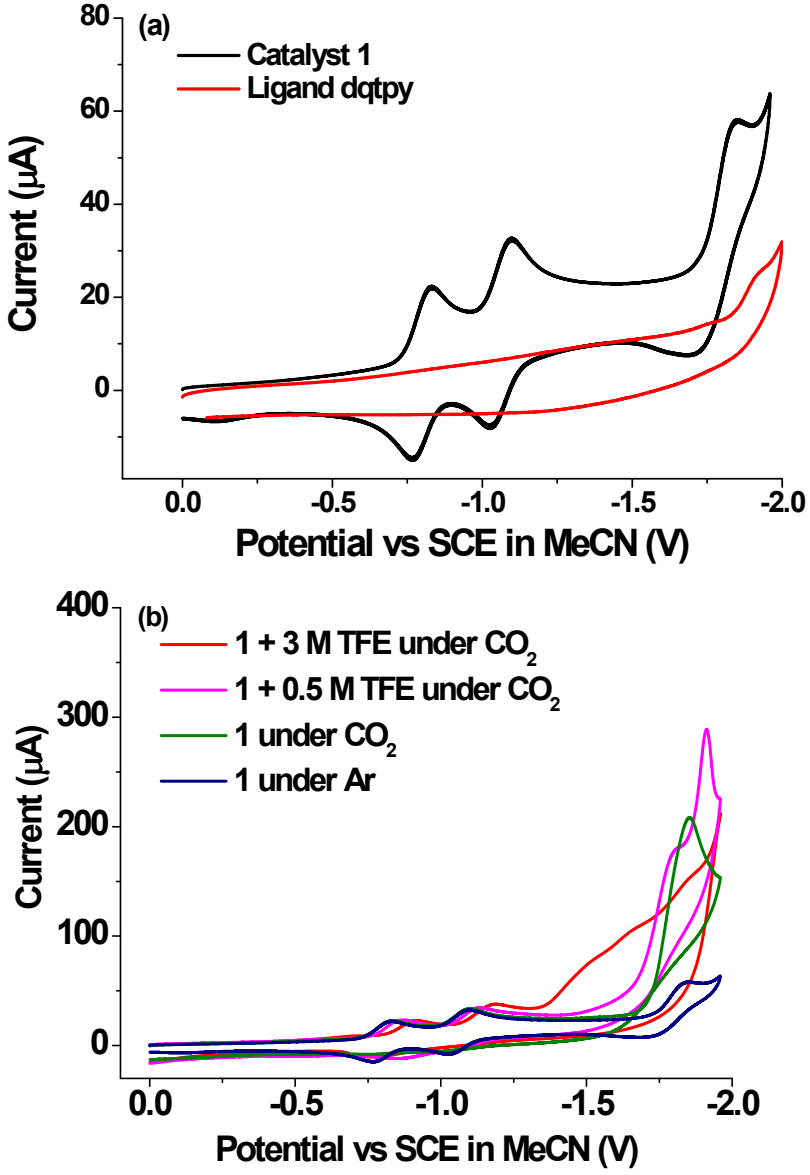


Figure S2 UV-vis spectra of 0.1 mM solution of **1** in DMF.



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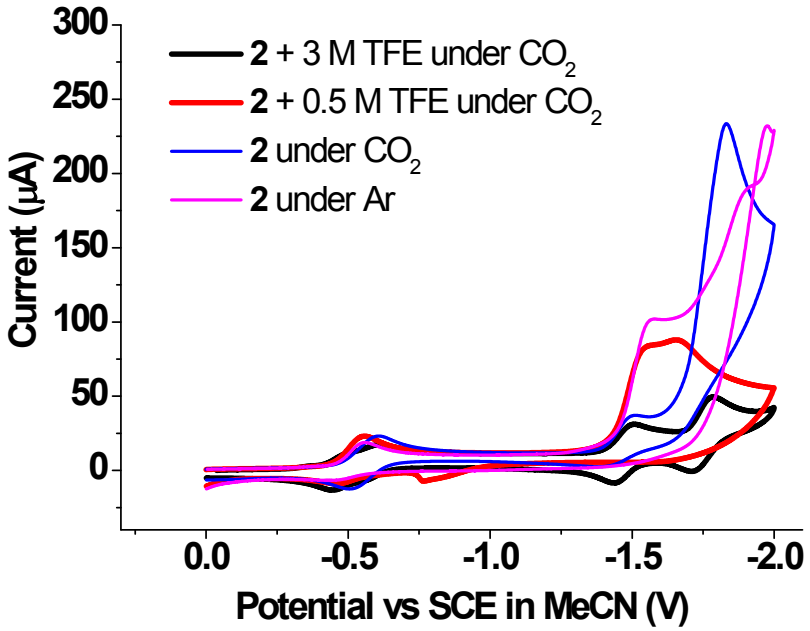

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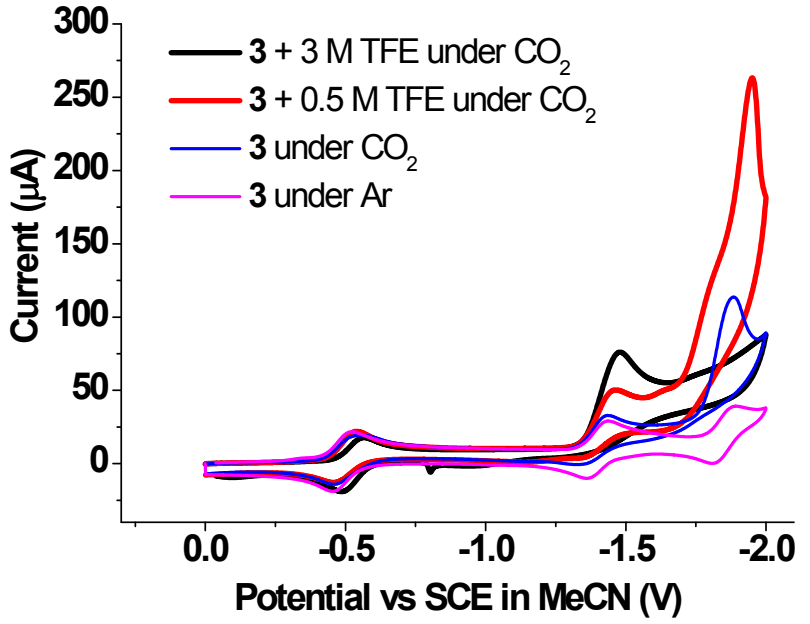

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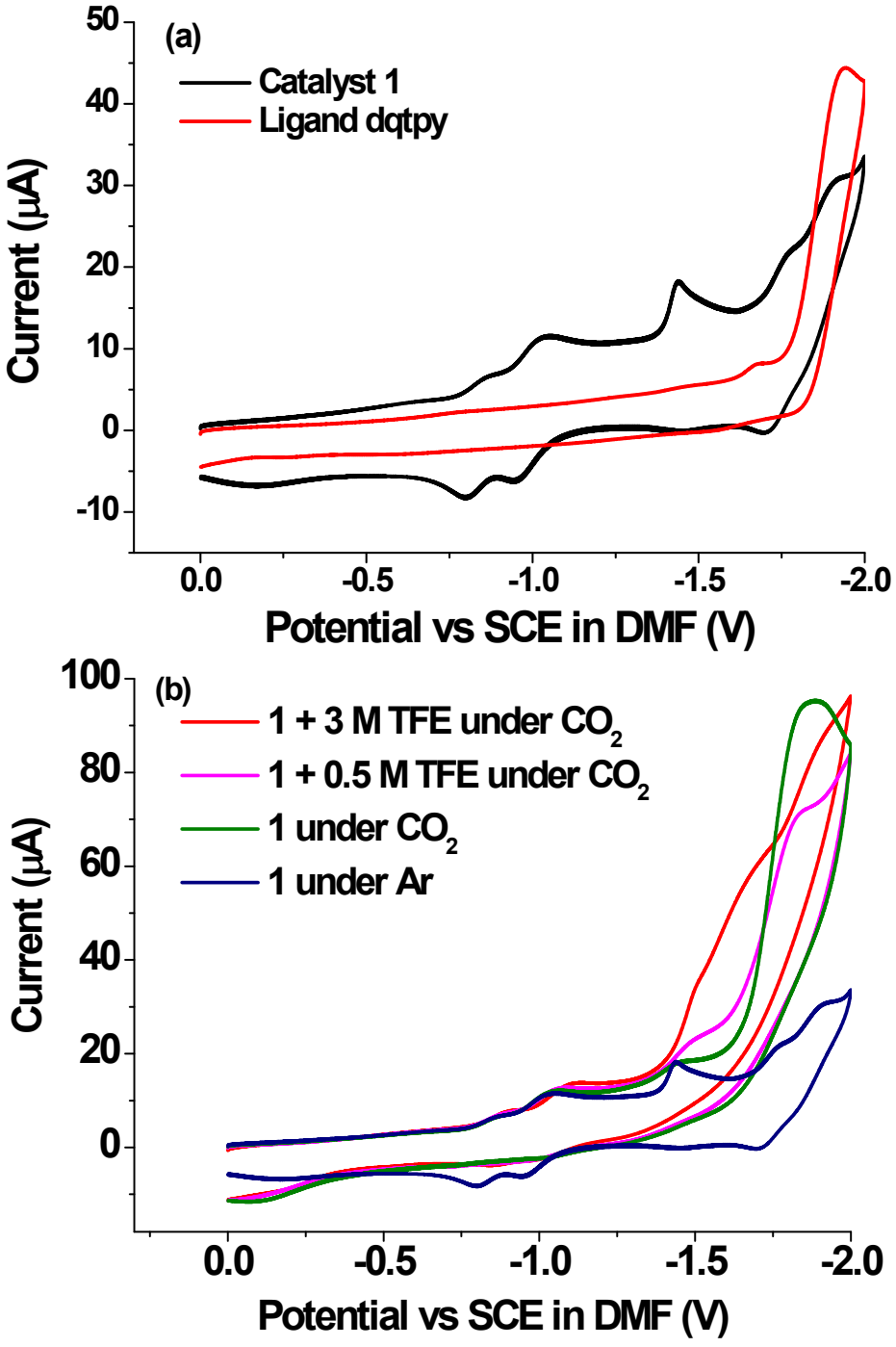

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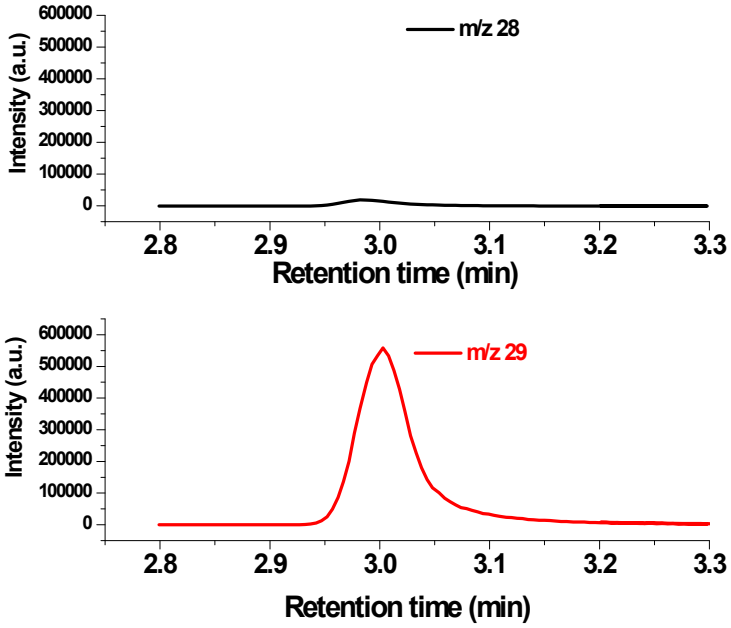

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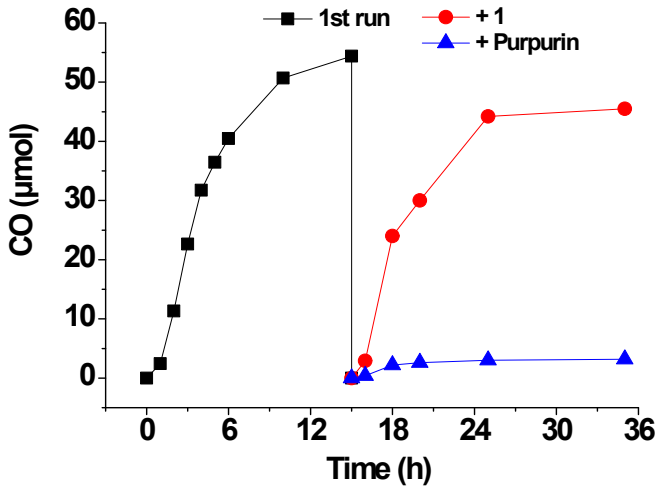

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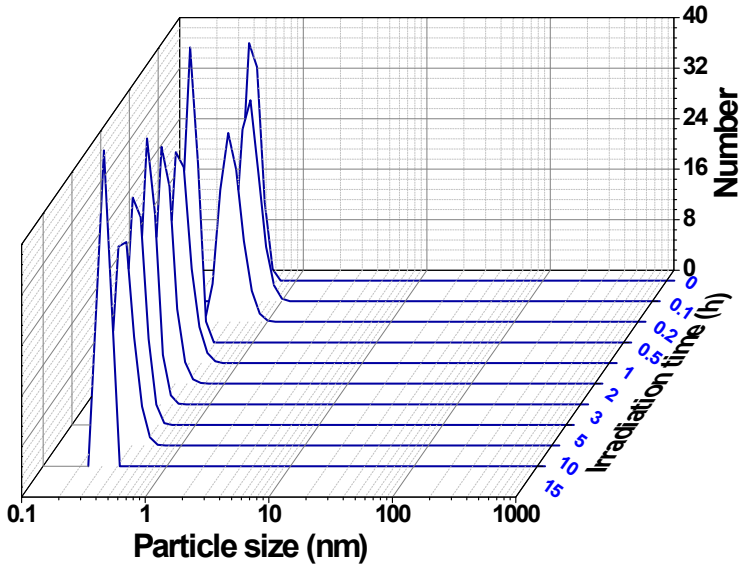

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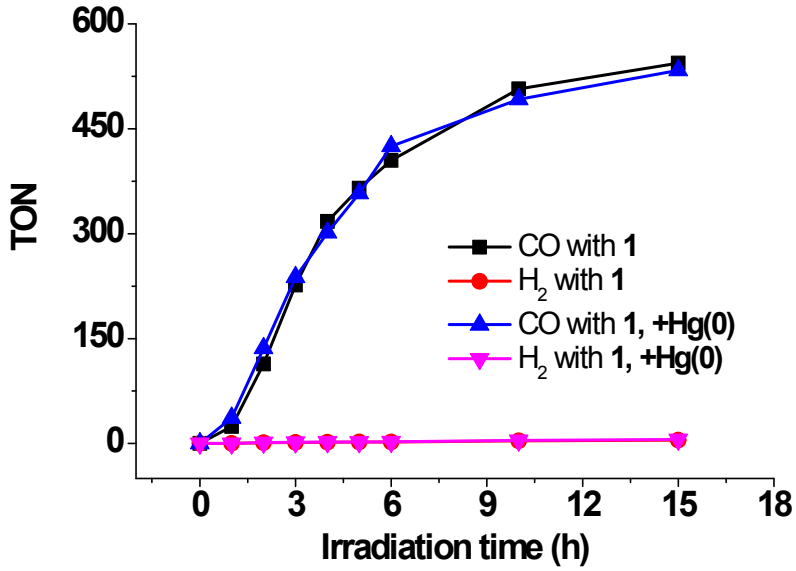

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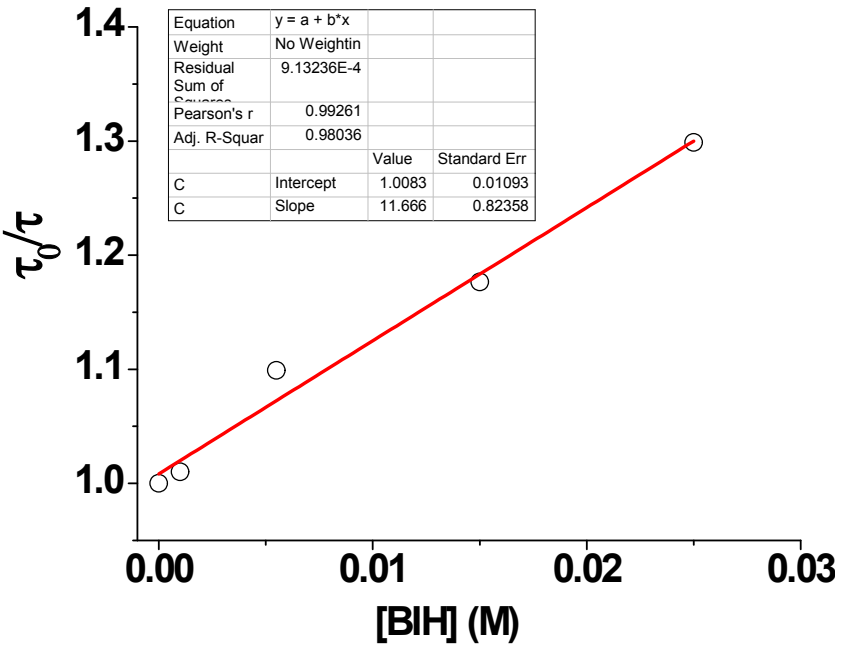

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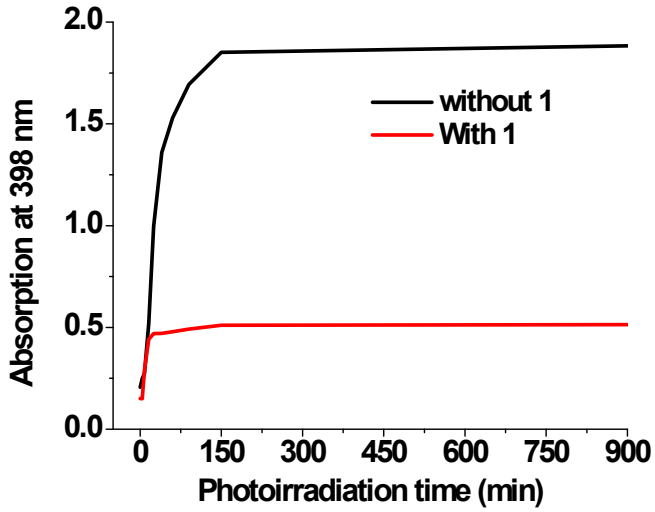

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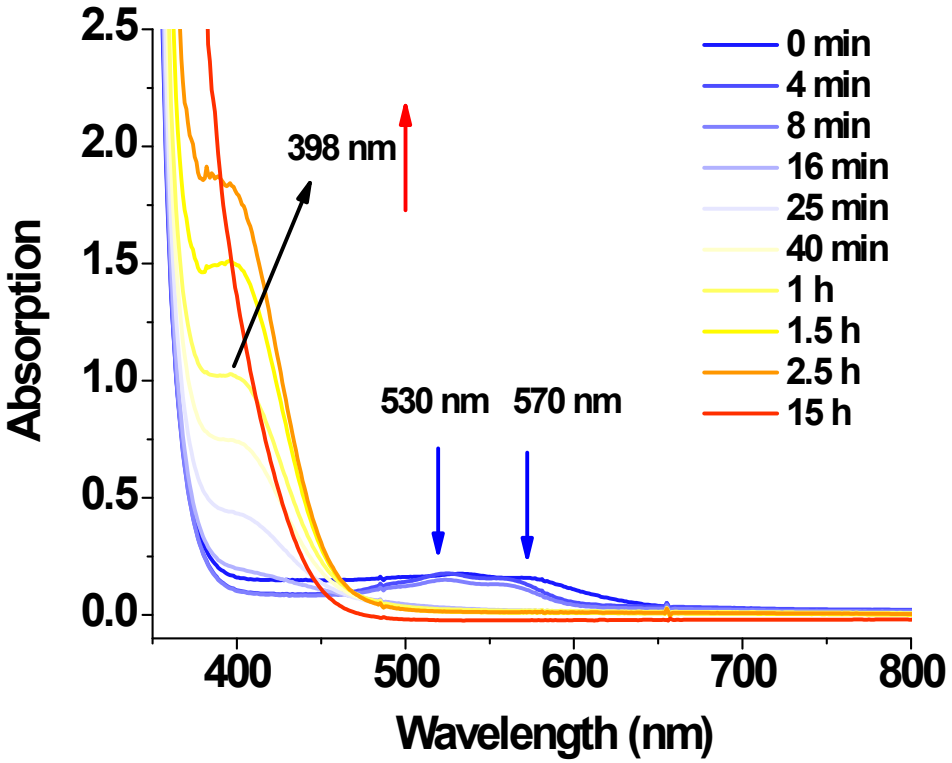

Figure S13 UV-Vis spectral of the solution (a CO_2-saturated DMF solution containing 0.05 mM $Fe(ClO_4)_2$, 0.05 mM purpurin, 0.1 M BIH and 5% TFE) during irradiation.

Table S1 Experiment details of X-ray crystallography of $[Fe(dqtpy)(CH_3CN)](ClO_4)_2$.

Formula sum	C35 H24 Cl2 Fe N6 O8
Formula weight	783.36 g/mol
Crystal system	triclinic
Space-group	P -1 (-2)
Cell parameters	a=11.4470(5) Å b=11.5457(5) Å c=13.5944(6) Å α=94.038(3)° β=105.644(4)° γ=103.365(4)°
Cell ratio	a/b=0.9915 b/c=0.8493 c/a=1.1876
Cell volume	1666.29(13) $Å^3$
Z	2
Calc. density	1.5612 g/cm^3
RAll	0.0614
Pearson code	aP152
Formula type	NO2P6Q24R35...
Wyckoff sequence	i76
CCDC number	1868077

Table S2 Selected bond lengths (Å) and angels (°) of $[Fe(dqtpy)(CH_3CN)](ClO_4)_2$.

Selected bond lengths (Å)					
Fe1-N1	2.123(3)	Fe1-N2	2.137(3)	Fe1-N3	2.097(3)
Fe1-N4	2.138(3)	Fe1-N5	2.231(3)	Fe1-N6	2.206(3)
Selected angels (°)					
N1-Fe1-N2	86.05(13)	N2-Fe1-N5	104.09(13)	N3-Fe1-N5	114.01(12)
N1-Fe1-N4	125.59(12)	N2-Fe1-N6	95.83(13)	N3-Fe1-N6	81.12(13)
N1-Fe1-N5	85.90(11)	N3-Fe1-N1	155.52(13)	N4-Fe1-N5	77.64(11)
N1-Fe1-N6	84.77(12)	N3-Fe1-N2	75.65(13)	N4-Fe1-N6	91.17(12)
N2-Fe1-N4	148.15(12)	N3-Fe1-N4	74.81(12)	N6-Fe1-N5	157.33(12)

Table S3 Experiment details of X-ray crystallography of $[Co(dqtpy)(CH_3CN)](ClO_4)_2$.

Formula sum	C35 H24 Cl2 Co N6 O8
Formula weight	786.44 g/mol
Crystal system	triclinic
Space-group	P -1 (-2)
Cell parameters	a=11.4087(4) Å b=11.6129(4) Å c=26.4344(7) Å α=78.865(2)° β=81.873(2)° γ=76.817(3)°
Cell ratio	a/b=0.9824 b/c=0.4393 c/a=2.3170
Cell volume	3328.35(17) $Å^3$
Z	4
Calc. density	1.610 g/cm^3
CCDC number	1893393

Table S4 Selected bond lengths (Å) and angels (°) of $[Co(dqtpy)(CH_3CN)](ClO_4)_2$.

Selected bond lengths (Å)					
Co1-N1	2.222(2)	Co1-N2	2.090(2)	Co1-N3	2.052(2)
Co1-N4	2.114(2)	Co1-N5	2.087(2)	Co1-N6	2.175(2)
Selected angels (°)					
N2-Co1-N1	78.38(8)	N3-Co1-N4	76.42(9)	N5-Co1-N1	83.99(8)
N2-Co1-N4	148.48(9)	N3-Co1-N5	158.61(9)	N5-Co1-N2	122.36(9)
N2-Co1-N6	93.23(9)	N3-Co1-N6	82.09(9)	N5-Co1-N4	87.91(9)
N3-Co1-N1	112.31(8)	N4-Co1-N1	98.24(9)	N5-Co1-N6	85.83(9)
N3-Co1-N2	76.09(9)	N4-Co1-N6	97.97(9)	N6-Co1-N1	160.49(9)

Table S5 Redox potentials for the investigated complexes **1**, **2** and **3** in anhydrous MeCN.

Complex	$M^{II/I}$	$M^{I/0}$	dqtpy/dqtpy$^{-\bullet}$
1	-0.80	-1.06	-1.78
2	-0.58	-1.47	-1.75
3	-0.49	-1.40	-1.85

Experimental conditions: 0.1 M $^{n}Bu_4NPF_6$ in MeCN using glassy carbon as working electrode, SCE as reference electrode and platinum wire as counter electrode with scan rate of 0.1 Vs^{-1}.

Table S6 Photocatalytic CO_2 reduction data with **1** using purpurin as photosensitizer.[a]

Entry	**1**	Purpurin	Sacrificial	Proton	Solvent	TON(selectivity %)	
	mM	mM	reductant	source		CO	H_2
1	0.05	0.05	0.1 M BIH	-	DMF	280(98.6)	4(1.4)
2	0.05	0.05	0.1 M BIH	-	NMP	196(99.5)	1(0.5)
3	0.05	0.05	0.1 M BIH	-	MeCN	30(99.3)	0.2(0.7)
4	0.05	0.05	0.1 M BIH	-	THF	121(97.6)	3(2.4)
5	0.05	0.05	0.1 M BIH	3% TFE	DMF	530(99.2)	4(0.8)
6	0.05	0.05	0.1 M BIH	5% TFE	DMF	544(99.3)	4(0.7)
7	0.05	0.05	0.1 M BIH	8% TFE	DMF	408(99.3)	3(0.7)
8	0.05	0.05	0.1 M BIH	5% H_2O	DMF	274(96.1)	11(3.9)
9	0.05	0.1	0.1 M BIH	5% TFE	DMF	628(99.7)	2(0.3)
10	0.02	0.1	0.1 M BIH	5% TFE	DMF	843(99.5)	4(0.5)

[a] In a typical run, a CO_2-saturated DMF solution containing **1** (0.05 mM), purpurin (0.05 mM), BIH (0.1 M) and 5% TFE was irradiated for 15 h using blue LED (460 nm) under a CO_2 atmosphere.

Table S7 Comparison of the photocatalytic performances for CO_2 reduction with molecular complexes in noble-metal-free systems.

Catalyst	Photosensitizer	[Catalyst]/ [Photosensitizer]	TON(selectivity %) based on catalyst			Quantum yield	Reaction conditions	Reference
			CO	H_2	$HCOO^-$			
$[Fe(dqtpy)(H_2O)]^{2+}$	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	**this work**
Fe(0) porphyrin	9CNA	2 μM / 0.2 mM	60(100)	0(0)	0(0)	0.0008%	0.05 M TEA and 0.2 mM 9CNA in MECN, λ>400 nm, 45 h	*J. Am. Chem. Soc.* **2014**, *136*, 16768-16771.[1]
Fe-*p*-TMA	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 in MeCN/H_2O (1:9 v/v), λ>420 nm, 94 h	*ChemSusChem* **2017**, *10*, 4447-4450.[2]
Fe-*p*-TMA	Non-sensitized	2 μM / 0.2 mM	101(100)	0(0)	0(0)	-	0.02 M BIH in MeCN, λ>420 nm, 102 h	*Chem. Commun.* **2017**, *53,* 2830-2833.[3]
$[Co(qpy)(OH_2)_2]^{2+}$	Purpurin	0.05 mM / 2 mM	197(95)	1(1)	9(4)	0.8%	0.1 M BIH in DMF, blue LED (460 nm), 11 h	*J. Am. Chem. Soc.* **2016**, *138*, 9413-9416.[4]
		0.005 mM / 2 mM	790(90)	11(1)	78(9)	-		
$[Fe(qpy)(OH_2)_2]^{2+}$	Purpurin	0.05 mM / 0.02 mM	520(97)	0(0)	14(3)	1.1%		
		0.005 mM / 0.02 mM	1365(92)	0(0)	115(8)	-		
$[Fe(qpy)(OH_2)_2]^{2+}$	mpg-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.[5]
$Fe(dmp)_2(NCS)_2$	$Cu(dmp)(P)_2^+$	0.05 mM / 0.25 mM	273(78)	75(22)	0(0)	6.7%	0.05 M BIH in CH_3CN-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.[6]
Cyclopentadienone iron complex	In situ Cu PS	0.13 mM / 0.67 mM	487(99)	7(1)	0(0)	13.3%	1 μmol Fe catalyst, 5 μmol $[Cu(MeCN)_4]PF_6$, 15 μmol xantphos P–P ligand, 5 μmol N–N ligand, 0.1 M BIH in 7.5 mL NMP/TEOA (5 : 1, v/v), Hg-lamp (1.5 W, 400–700	*Green Chem.* **2017**, *19,* 2356-2360.[7]

							nm), 5 h	
$[Ni(terpyS)_2]^{2+}$	CdS	100 μM / 1 μM	20(62)	12(38)	0(0)	0.28%	0.1 M aq. TEOA, pH 6.7 in H_2O; 22 h irradiation, 100 mW cm^{-2}, AM1.5G, λ>400 nm, 25°C	*J. Am. Chem. Soc.* **2017**, *139,* 7217-7223.[8]
NiCycP	ZnSe–BF_4/MEDA	10 mM / 0.5 mM	283(34)	549(66)	0(0)	3.4%	25 mM MEDA, 0.1 M AA in H_2O, pH 5.5, λ>400 nm (AM 1.5G), 20 h	*Chem. Sci.* **2018**, *9*, 2501-2509.[9]
Dinuclear cobalt complex Co_2L	CdS-MPA	1 μM / 4 μM	1380(95)	32(2)	0(0)	n,d,	25 mL aqueous solution of 0.1 M $NaHCO_3$, 120 h, 300 W Xe lamp (λ > 420 nm).	*ACS Catal.*, **2018**, *8,* 11815-11821.[10]
[Mn(4OMe)]	$[Cu_2(P_2bph)_2]^{2+}$	0.05 mM / 0.25 mM	1314(CO+HCOOH)			57%	BIH (0.1 M), DMA−TEOA (4:1, v/v) solution, λ_{ex} = 436 nm, 36 h, 25 °C	*J. Am. Chem. Soc.,* **2018,** *140,* 17241-17254.[11]

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