Electronic Supplementary Information (ESI)

Molecular Quaterpyridine-based Metal Complexes for Small Molecules Activation: Water Splitting and CO_2 Reduction

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Table S1 Summary of electrocatalytic reduction of CO_2 catalysed by quaterpyridine-based catalysts and selected catalysts reported in the literatures.

Catalyst	Reaction conditions	Electrode	Applied potential (V)	Current density (mA cm^{-2})	Products (selectivity)	Turnover number (vs. total amount of Cat.)	Turnover frequency (vs. total amount of Cat.) (s^{-1})	Faradaic efficiency	Reference
$[Co(qpy)(H_2O)_2]^{2+}$	MeCN, 0.1 M $^nBu_4NPF_6$, 0.2~0.4 mM of Coqpy	Glassy carbon	-1.70 vs. SCE	-	CO (80%)	20 (based on total amount of Cat.)	0.0056	80%	*J. Chem. Soc., Dalton Trans.*, 1995, 1103-1107. [1]
	MeCN, 0.1 M $^nBu_4NPF_6$, 1 M phenol, 0.5 mM of Coqpy	Glassy carbon	−1.4 vs. SCE	-	CO (99%)	-	-	94%	*J. Am. Chem. Soc.* 2016, **138**, 9413-9416. [2]
	MeCN, 0.1 M $^nBu_4NPF_6$, 3 M phenol+10% H_2O, 0.5 mM of Coqpy	Glassy carbon	−1.1 vs. SCE	-	CO (96%)	17 (based on total amount of Cat.)	0.0016	94%	*ACS Catal.*, 2018, **8**, 3411-3417. [3]
	MeCN, 0.1 M $^nBu_4NPF_6$, 0.1 M phenol, 0.5 mM of Coqpy	Glassy carbon	−1.6 vs. SCE	-	CO (77%)	-	-	72%	*Organometallics* 2019, **38**, 1280-1285. [4]
$[Co(qpy)]^{2+}$@MWCNTs	H_2O, 0.5 M $NaHCO_3$ (pH 7.3), 8.5 nmolcm^{-2} Coqpy	Carbon paper	-0.35 vs. RHE	0.94	CO (100%)	4700	0.59	100%	*Angew. Chem. Int. Ed.* 2018, **57**, 7769 –7773. [5]
	H_2O, 0.5 M $NaHCO_3$ (pH 7.3), 20.5 nmolcm^{-2} Coqpy	Carbon paper	-0.48 vs. RHE	6.3	CO (100%)	42960	3.4	100%	
	H_2O, 0.5 M $NaHCO_3$ (pH 7.3), 8.5 nmolcm^{-2} Coqpy	Carbon paper	-0.48 vs. RHE	10	CO (100%)	29360	5.9	100%	
	H_2O, 0.5 M $NaHCO_3$ (pH 7.3), 8.5 nmolcm^{-2} Coqpy	Carbon paper	-0.53 vs. RHE	11.9	CO (100%)	35875	7.2	100%	
	H_2O, 0.5 M $NaHCO_3$ (pH 7.3), 8.5 nmolcm^{-}	Carbon paper	-0.58 vs. RHE	19.9	CO (99%)	59910	12.0	100%	

	[2] Coqpy								
Co-qPyH|m-TiO2	H_2O, 0.1 M $KHCO_3$ (pH 6.8), 29 nmolcm^{-2} Co-qPyH	FTO	-0.51 vs. RHE	1.2	CO (80%)	1002	0.14	63%	Nat. Commun., 2020, **11**, 3499. [6]
CoPc/carbon [Co phthalocyanine]	Membrane flow reactor, 1 M KOH, 1 M phenol	Gas diffusion electrode (carbon paper)	-	150	>95%	129	0.215	>95%	*Science*, 2019, **365**, 367-369. [7]
CoTPP-CNT [Co tetraphenyl porphyrin]	H_2O, 0.5 M $KHCO_3$, 170 nmolcm^{-2} CoTPP	Glassy carbon	-1.35 V vs. SCE	0.59	CO (>90%)	1118	0.069	83%	*Angew. Chem. Int. Ed.*, 2017, **56**, 6468-6472. [8]
CoPc/CNT (2.5%)	H_2O, 0.1 M $KHCO_3$ (pH 6.8)	Glassy carbon	-0.63 V vs. RHE	~10.0	CO (92%)	162	2.7	92%	*Nat. Commun.*, 2017, **8**, 14675. [9]
CoPc-CN/CNT (3.5%)	H_2O, 0.1 M $KHCO_3$ (pH 6.8)	Glassy carbon	-0.63 V vs. RHE	~15.0	CO (98%)	-	4.1	98%	
$[Co(tpyH_2PhCl)_2](PF_6)_2$ [tpy: terpyridine]	DMF/H_2O (95 : 5), 0.1M $^nBu_4NPF_6$, 1 mM catalyst	Hg pool	-	0.17	CO (31%)	-	-	31%	*Chem. Sci.*, 2015, **6**, 2522-2531. [10]
Cobalt macrocyclic aminopyridine	DMF, 0.1M $^nBu_4NPF_6$, 1.2 M TFE, 0.5 mM catalyst	Glassy carbon plate	−2.8 V vs. Fc	0.17	CO (98%)	6.2 (based on total amount of Cat.)	0.00086	98%	*J. Am. Chem. Soc.*, 2016, **138**, 5765-5768. [11]
FeTPP-CNT [iron tetraphenyl porphyrin]	H_2O, 0.5 M $KHCO_3$ (pH 7.3), 170 nmolcm^{-2} FeTPP	Glassy carbon	-1.35 V vs. SCE	1.9	CO (>90%)	-	0.069	97%	*Angew. Chem. Int. Ed.*, 2017, **56**, 6468-6472. [8]
$[Fe(qpy)(H_2O)_2]^{2+}$	MeCN, 0.1 M $^nBu_4NPF_6$, 1 M phenol	Glassy carbon plate	−1.4 vs. SCE	-	CO (100%)	-	-	37%	*J. Am. Chem. Soc.* 2016, **138**, 9413-9416. [2]
CATpyr [iron porphyrin modified with OH groups]	H_2O, 0.5 M $NaHCO_3$ (pH 7.3), 24 nmolcm^{-2} FeTPP	Carbon plate	-1.03 V vs. NHE	0.186	CO (96%)	432 (based on total amount of Cat.)	0.04	97%	*J. Am. Chem. Soc.*, 2016, **138**, 2492-2495. [12]
FeTPP	DMF, 0.1 M PhOH, 1mM FeTPP	Hg pool	-1.46 V vs. NHE	-	CO (100%)	-	-	100%	*J. Am. Chem. Soc.*, 2013, **135**, 9023-9031. [13]
FeTDHPP [iron porphyrin modified with OH groups]	DMF, 2 M PhOH, 1mM FeTPP	Hg pool	-1.16 V vs. NHE	0.31	CO (95%)	-	-	95%	*Science*, 2012, **338**, 90-94. [14]
FeP [iron porphyrin modified with $^+N(Me)_3$	H_2O, 0,1 M KCl (pH 6.7)	Glassy carbon	-0.86 V vs. NHE	0.05	CO (98%)	-	-	98%	*Proc. Natl Acad. Sci.*

groups]		crucible							*USA,* 2015, **112**, 6882-6886. [15]
FeP [iron porphyrin modified with $^{+}$N(Me)$_3$ groups]	Flow cell, H_2O, 0,1 M KOH (pH 14)	Gas diffusion electrode (carbon paper)	-0.59 V vs. RHE	152	CO (98%)	-	-	98%	*Chem. Eur. J*, 2020, **26**, 3034-3038. [16]
Fe-o-TMA [iron porphyrin modified with $^{+}$N(Me)$_3$ groups]	DMF, 0.1 M H_2O, 3 M PhOH, 0.5 mM FeTPP	Glassy carbon crucible	-0.96 V vs. NHE	0.05	CO (100%)	-	-	100%	*J. Am. Chem. Soc.*, 2016, **138**, 16639-16644. [17]
NiPc-OMe-MDE/CNT	DMF, 0.5 $KHCO_3$, 0.03 mg cm^{-2} NiPc	Carbon fibre paper	-0.64 V vs. NHE	14.5	CO (100%)	-	2.9	100%	*Nature Energy*, 2020, DOI: 10.1038/s41560-020-0667-9. [18]
[Ni(HTIM)]$^{2+}$ [nickel cyclam]	H_2O, 0.1 M NaClO4, (pH 5), 0.05 mM [Ni(HTIM)]$^{2+}$	Hg pool	-0.96 V vs. NHE	-	CO (100%)	-	-	88%	*Energy Environ. Sci.*, 2012, 5, 9502-9510. [19]
[Ni(tpy)]$^{2+}$	DMF/H_2O (95 : 5), 0.1M $^{n}Bu_4NPF_6$, 2 mM [Ni(tpy)]$^{2+}$	Hg pool	-1.72 V vs. NHE	-	CO (100%)	-	-	18%	*Phys. Chem. Chem. Phys.*, 2014, **16**, 13635-13644. [20]

Table S2 Summary of photocatalytic reduction of CO_2 catalysed by quaterpyridine-based catalysts and selected catalysts reported in the literatures.

Catalyst	**Photosensitizer**	**[Catalyst]/ [Photosensitizer]**	**TON of products (selectivity%) based on catalyst**			**Φ_{CO}**	**Reaction conditions**	**Reference**
			CO	**H_2**	**HCOOH**			
[Fe(qpy)(OH$_2$)$_2$]$^{2+}$	[Ru(bpy)$_3$]$^{2+}$	50 µM / 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. [2]
		5 µM / 0.2 mM	3844(85)	534(12)	118(3)	-		
	Purpurin	50 µM / 0.02 mM	520(97)	0(0)	14(3)	1.1%	0.1 M BIH in DMF, blue LED (460 nm), 11 h	
		5 µM/0.02 mM	1365(92)	0(0)	115(8)	-		
	mpg-C_3N_4	20 µM / 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. [21]

$[Co(qpy)(H_2O)_2]^{2+}$	$[Ru(bpy)_3]^{2+}$	50 µM / 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. [2]
		5 µM / 0.3 mM	2660(98)	23(1)	35(1)	-		
$[Cu(qpy)]^{2+}$	$[Ru(bpy)_3]^{2+}$	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. [22]
Coqpy@mpg-C_3N_4	Coqpy@mpg-C_3N_4	3 µM /6 mg catalyst	254 (97%)	8 (3%)	-	0.25%	0.05 M BIH and 0.03 M PhOH in 3 mL MeCN, 100 W Xenon lamp	*J. Am. Chem. Soc.*, 2020, **142**, 6188-6195. [23]
$BiqpyCo_2$	$Ru(phen)_3Cl_2$	50 µM/0.2 mM	829(96)	22(2.5%)	12(1.5%)	-	0.1 M BIH and 1 M PhOH MeCN, blue LED	*Nat. Catal.*, 2019, **2**, 801-808. [24]
	$Ru(phen)_3Cl_2$	50 µM/0.2 mM	8 (2%)	6 (1.5%)	386(96.5%)	2.6%	0.025 M BIH MeCN/TEA (4:1 v/v), blue LED	
	g-C_3N_4	20 µM/2.5 mg	0(0%)	48(8.9%)	493(91.1%)	1.7%	0.05 M BIH MeCN/TEOA (4:1 v/v), Xe-Hg lamp	
	Pheno [phenoxazine based organic sensitizer]	15 µM/0.4 mM	518(89.3%)	62(10.7%)	0(0%)	-	0.05 M BIH and 1 M PhOH MeCN, solar simulator	
$[Fe(qnpy)(H_2O)_2]^{2+}$	$[Ru(phen)_3]^{2+}$	50 µM / 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	*Chem. Commun.*, 2020, **56**, 6249-6252. [25]
		5 µM / 0.2 mM	14095(98)	360(2)	0(0)	-		
$[Fe(phen)_2(C_2H_5OH)Cl]^{+}$	$[Ru(bpy)_3]^{2+}$	30 µM / 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. [26]
		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	50 µM / 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. [27]
Fe tetraphenyl 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. [28]
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. [29]
	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	*ChemSusChem,* 2017, **10**, 4447-4450. [30]

							> 420 nm, 94 h	
	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. [31]
$Fe(CO)_3bpy$	$[Ru(bpy)_3]^{2+}$	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. [32]
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.*, 2018, **57**, 16480-16485. [33]
CoCo cryptate	$[Ru(phen)_3]^{2+}$	0.025 µM / 0.4 mM	17000(98)	368(2)	0(0)	0.04%		
$[Ni(^{Pr}bimiq1)]^{2+}$	$Ir(ppy)_3$	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**, 14413-14424. [34]
		0.2 µM / 0.2 mM	1500(100)	0(0)	0(0)	-		
$[Ni(bpet)(MeCN)_2]^{2+}$	$[Ru(bpy)_3]^{2+}$	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. [35]
$[Ni(bpet\text{-}py_2)(H_2O)_2]^{2+}$	$[Ru(bpy)_3]^{2+}$	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. [36]
$[Cu(pyN_2^{Me2})(HCO_2)]^-$	$[Ru(phen)_3]^{2+}$	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. [37]
$[Mn(pyrox)(CO)_3Br]$	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. [38]
[Mn(4OMe)]	$[Cu_2(P_2bph)_2]^{2+}$	50 µM / 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. [39]

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