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Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Transferring photocatalytic CO₂ reduction mediated by Cu(N^N)(P^P)⁺ complexes from organic solvents into ionic liquid media

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Photocatalytic carbon dioxide reduction utilizing metal complexes based on the earth-abundant transition metals iron and copper was transferred from organic solvents into ionic liquids with high selectivity and moderate turn-over numbers. Different classes of ionic liquids were evaluated to determinate the CO/H₂ selectivity of the process. High-purity conditions were utilized to validate that CO was a result of CO₂ reduction and not resulting from other carbon sources. In addition, a novel copper-based photosensitizer was synthesized and its photo- and electrochemical properties were investigated.

Introduction

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Carbon dioxide constitutes 81% of the total amount of Greenhouse gas (GHGs) emissions.¹ Utilization of CO₂ captured from emissions is, therefore, mandatory to mitigate its negative effects on the atmosphere envisioning it as a carbon source replacing fossil fuels.^{2, 3} The reduction of CO₂ to CO, generating an energy-rich commodity chemical, is one of the strategies for CO₂ valorization.³⁻⁶

Moreover, energy utilization plays a crucial role in the development of sustainable catalytic processes using solar power as energy source.⁷ Low-cost storage methodologies covering variable atmospheric conditions are required in order to use solar energy as the primary energy supply.⁸ A feasible approach in this direction is the development and optimization of thermodynamically uphill photocatalytic processes that enable chemical transformations by the use of photonic energy as the driving force.⁹

Consequently, a combination of renewable energy and CO_2 utilization towards sustainable catalytic processes such as photocatalytic systems that convert carbon dioxide to more valuable chemicals is an area of great interest. In this respect, transition metal complexes have been studied as photocatalysts where rhenium ¹⁰⁻¹³, iridium ¹⁴⁻¹⁶ and ruthenium ¹⁷⁻¹⁹ are known for being selective towards different reduction products. In general, selective processes towards the production of CO from CO_2 are challenging not only because they are thermodynamically uphill, but also numerous by-products may be generated.²⁰ In aqueous systems the reduction of CO_2 is also in competition with hydrogen

formation from water splitting, a process that usually requires less negative potentials, and therefore is difficult to avoid.^{21, 22} Nevertheless, several successful examples of dual catalytic systems typically involving ruthenium or iridium complexes as photosensitizers (PS) in combination with a transition metal catalyst (cat) have been developed.²³ More recently, examples based on earth-abundant metals as stated in recent reviews^{6,} 24 , such as Mn, $^{24\text{-}26}$ Ni, 27 Cu, $^{28,\ 29}$ Co, $^{30\text{-}32}$ and Fe $^{30,\ 31,\ 33}$ were reported, too. In this regard, some of us developed an efficient system for the reduction of CO₂ to CO based on (cyclopentadienone) iron-tricarbonyl complexes as catalysts (Scheme 1). Beneficial for this reaction is the ability of such complexes not only to possess a hydride-donor site via the metal center, but also a proton-donor site (via the ligand).³⁴ The chosen photosensitizer was [Ir(dF(CF₃)ppy)₂-(dtbbpy)]PF₆ (IrPS) (where dF(CF₃)ppy = cyclometalated 2-(2,4difluorophenyl)-5-trifluoromethyl-pyridine and dtbbpy = 4,4'di-*tert*-butyl-2-2'-bipyridine).³⁵ Triethanolamine (TEOA) as sacrificial electron donor and 1-methylpyrollidin-2-one (NMP) as solvent were used, irradiating the reaction mixture using a 2.5 W Hg-lamp (emission range: 400–700 nm) for 5 h at room temperature. Under these reaction conditions, a turnover number (TON) of 596 was obtained using 3.75×10^{-8} mol of catalyst, outperforming the structurally related [Fe(CO)₃(bpy)] that reached a TON of 129.36

The replacement of the iridium photosensitizer by the more economical copper (CuPS) resulted in a slightly lower TON of 487.³⁷ In this case 1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo[d]imidazole (BIH) was used as sacrificial electron donor and again a reductive quenching mechanism operating between CuPS* and BIH was proposed.

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Scheme 1: Fe-based CO₂ reduction catalysts and photosensitizers reported by Beller and co-workers ^{34, 37} and by the Sakai group.

More recently, another catalytic system based on the same CuPS in combination with a Fe(II) catalyst bearing a tetradentate macrocyclic nitrogen-donor ligand (Scheme 1) was reported by Yamauchi, Sakai and co-workers.³⁸ Under optimized conditions, a TON(CO) of 565 and a CO selectivity of 84% within 8 h were observed in *N*,*N*-dimethylformamide/TEOA (4:1, v:v) utilizing BIH as sacrificial reductant and visible light (>400 nm, 179 mW/cm²).

Notably, all the aforementioned photocatalytic systems function using organic solvents, but in the perspective of a environmentally-friendly process, more non-recyclable solvents should be replaced. In this respect, ionic liquids (ILs) have been explored as a promising alternative to conventional organic solvents because they possess advantages including negligible vapor pressure, high thermal stability, wide electrochemical stability window, tunable polarity, hydrophobicity and solvent miscibility behavior through variation of the cations and anions.³⁹ These properties make them the ideal reaction media for many applications, and replacing volatile solvents by ILs reduces solvent losses to the atmosphere.^{40, 41}

Indeed, Wang and co-workers reported the capture and activation of CO₂ to produce CO by ILs coupled with photoredox catalysis using [Ru(bpy)₃]Cl₂ as PS and CoCl₂·6H₂O as catalyst.⁴² In a [EMIM][Tf₂N]/H₂O/TEOA (3/1/1; [EMIM][Tf₂N]: 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide) mixture, reduction of CO₂ and proton reduction occurred with a total TON of 45.6 and a selectivity of 76.1% towards CO. The structures of the cations and anions of the imidazolium ILs showed considerable effects on the activation and reduction of CO₂. Better performances were obtained with [Tf₂N]⁻ and tetrafluoroborate ([BF₄]⁻) counterions compared to acetate, dicyanamide ([N(CN)₂⁻]), L-lactate and trifluoromethane-sulfonate ([OTf]⁻) attributed to a

lower viscosity and a stronger interaction between CO_2 and these ILs. In addition, an elongation of the alkyl chain in 1-position resulted in a significant decrease of catalytic activity.

Furthermore, a report by Grills described the photocatalytic CO_2 reduction in a biphasic IL/sc CO_2 system using the catalyst *fac*-ReCl(bpy)(CO)₃ and 1-butyl-1-methylpyrrolidinium tetracyanoborate ([Bmpyrr][TCB]) as ionic liquid and TEOA as electron donor. After 3 hours of irradiation at 400±25 nm, the activity was optimized by the use of a high-pressure biphasic system with TONs increasing from 0.7 to 5.⁴³

Since CO₂ is a thermodynamically highly stable molecule,⁴⁴ it is expected that many other carbon-containing molecules, i.e. impurities incidentally present in the reactor, will react faster under the selected experimental conditions. This has been reports.45-48 demonstrated previously in numerous Consequently, it is very important for CO₂ reduction experiments to verify that neither hydrocarbons nor CO are produced from the catalyst, reaction media or any other Ccontaining impurities that could be present in the reaction chamber. If such outcomes are not analyzed carefully, the photocatalytic efficiency of the tested sample can be overestimated leading to invalid conclusions.^{46, 49} Compared to photocatalytic measurements of purely inorganic systems (i.e. bare TiO_2 in water), proof of product formation from CO_2 is even more important when the catalyst itself, or the reaction medium, contains organic components such as ligands or solvents.

The formation of products from CO_2 as carbon source can be evidenced by the analysis of apparent product formation in a blank experiment in the absence of CO_2 gas. Under identical reaction conditions, CO_2 is replaced by an inert gas such as He or Ar and each collected chromatogram is analyzed in order to identify possible catalyst decomposition, solvent degradation, or any other impurities present in the reaction set-up.⁵⁰ The use of noble metal free cooperative photocatalytic processes represents *vide supra* a cost-effective and environmentally friendly alternative to traditional transition metal photocatalysis.^{51, 52} Copper and iron are ideal metals of choice as their crustal abundances are 27 ppm for the former and 52157 ppm for the later. Precious transition metals are significantly less abundant and therefore more expensive with the following crustal abundances: Rhenium 0.000188 ppm, ruthenium 0.000037 ppm and iridium 0.000037 ppm.^{53, 54}

In the present work we show the feasibility of photocatalytic reduction of CO_2 to CO in ionic liquid media by well-defined $[Cu(N^N)(P^P)][PF_6]$ and $[Fe(cyclopentadienone)(CO)_3]$ metal complexes under high purity conditions. More specifically, we showcase the performance of ionic complexes in ionic liquid media for photocatalytic applications. Using a high-purity photoreactor and with extensive blank batch cleaning experiments, we were able to further establish that the origin of CO is indeed the CO_2 of the feed stream that is reduced by our tested catalyst.

Results and discussion

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Synthesis and characterization of complexes Synthesis

Initially, copper(I) complexes $\mathbf{1}^{55}$ and $\mathbf{2}$ were obtained according to known protocols (Schemes 1 & 2). A more rigid and sterically demanding ligand was used to form complex $\mathbf{2}$ as the related complex bearing POP-thixantphos (**3**) has been reported to give remarkable performance in photocatalytic applications.^{7, 55} Complex $\mathbf{2}$ was successfully synthesized by reaction of 4,5-bis(2,8-dimethyl-10-phenoxaphosphano)-9,9dimethylxanthene (POP-xantphos) with tetrakis(acetonitrile)copper(I) hexafluorophosphate in CH₂Cl₂, followed by the addition of the 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (bathocuproine) ligand.



dimethylxanthene); POP: 2,8-dimethyl-10-phenoxaphosphano

substituent; POP-thixantphos: 4,5-bis(2,8-dimethyb ዝቢphenoxaphosphano)-2,7-dimethylphenoxቆthiֆ.^{1039/DOGC01627F}

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Electrochemical and photophysical characterization of complexes

Complex 1 has been characterized previously⁷ and shows similar absorption features in acetonitrile solution compared to our findings. The solution absorption spectra of 1 and 2 (Figure 1) show a broad absorption at around 395 nm arising from metal-to-ligand charge transfer (MLCT) and is characteristic for this type of heteroleptic [Cu(N^N)(P^P)]⁺ complex.7, 52, 56 Upon excitation in the MLCT band, both compounds exhibit a broad unstructured emission (Figure 2). Complex 2 shows an emission maximum at 539 nm, whereas the emission of 1 is red-shifted by around 15 nm. This is attributed to the higher steric demand of the phosphane ligand in 2. The lower flexibility of POP-xantphos in comparison to xantphos results in a lower degree of distortion of the distorted tetrahedral geometry upon excitation. This leads to a hypsochromic shift of the emission, as has been observed for related [Cu(N^N)(P^P)][PF₆] complexes.^{7, 57} The emission spectra reported previously are red shifted compared to our findings due to the different choice of solvent (580 nm in acetonitrile,⁵⁸ 568 nm in THF⁷ vs 555 nm in CH₂Cl₂ (Table 1)).



Figure 1: Solution absorption spectra of complexes 1 and 2 $(CH_2Cl_2, 2.5 \times 10^{-5} \text{ mol dm}^{-3}).$



Figure 2: Normalized emission spectra of copper(I) complexes 1 and 2 (λ_{exc} = 400 nm, degassed CH₂Cl₂, 2.5 x 10⁻⁵ mol dm⁻³).

Complexes **1** and **2** show high photoluminescence quantum yields (PLQY) in deaerated solution (40 and 38% respectively) and excited state lifetimes of 9.42 and 7.24 μ s^b, respectively.

The here reported solution quantum yield and excited state lifetime of **1** in CH₂Cl₂ are significantly higher than those reported in a previous study with a quantum yield of 8% and an excited state lifetime of 6.4 μ s in deaerated THF.⁷ Note that ⁻⁻ the higher excited state lifetime is not a result of a decreased – concentration, which has previously been shown to impact the value due to self-quenching (Table 1).⁵⁹

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Table 1: Photophysical properties of the complexes in CH_2Cl_2 solution at a concentration of 2.5 x 10^{-5} mol dm⁻³ (λ_{exc} = 365 nm).

Complex	UV-Vis	λ _{em} /nm	PLQY %	$\tau_{1/2} \mu s^c$
	MLCT			
	λ_{abs}/nm			
1	393	555	1.1 ^{<i>a</i>} /38 ^{<i>b</i>}	0.338 ^a /7.24 ^b
2	398	539	1.3 ^{<i>a</i>} /40 ^{<i>b</i>}	0.446 [°] /9.42 ^b

^aNon-degassed solution ^bDegassed solution by bubbling an argon stream through the solution for 20 min. ^cValues ±15% instrumental error.

The redox behaviour of complexes **1** and **2** was investigated using cyclic voltammetry and data are summarized in Table 2. Each compound exhibits a partially reversible oxidation at +0.86 or 0.83 V (vs. Fc/Fc⁺) which is assigned to a copper oxidation. Additionally, **1** and **2** both show partially reversible reduction processes at -2.11 or -2.10 V, respectively. The oxidation and reduction potentials for **1** in CH₂Cl₂ are slightly lower than previously observed values in acetonitrile and are discussed in depth in literature.⁷ It is noteworthy that the literature cyclic voltammogram in acetonitrile shows a reversible ligand reduction and irreversible copper oxidation, which is contrary to our findings in CH₂Cl₂.

Table 2: Cyclic voltammetry data for copper(I) complexes referenced to internal $Fc/Fc^{+} = 0 V$; degassed HPLC grade CH_2Cl_2 solution with [ⁿBu₄N][PF₆] as supporting electrolyte and a scan rate of 100 mV s⁻¹.

			- Indexes for the solid state structures of complexes 1 and			
Complex	$E_{1/2}^{ox}/V (E_{pc} - C_{pc})$	$E_{1/2}^{red}/V (E_{pa} - (m))$	Parameter	Complex 1 ⁶¹	Complex	
	E _{pa} /mv)	E _{pc} /mv)	N1-Cu1-N2	80.41(10)	80.65(10	
1	+0.86 (81)	-2.11 (154)	N1-Cu1-P1	102.63(8)	100.78(7	
2	+0.83 (72)	-2.10 (127)		110 /1(9)	120 51/7	
			NI-CUI-F2	119.41(8)	120.51(7	

Excited state redox potentials are estimated according to formulas (1) and (2) ⁶⁰ and the results are summarized in Table 3 where E_{00} is the (non-observable) energy difference between the lowest vibrational level of the electronic ground and electronic excited states. $E_{ox}^{1/2}$ and $E_{red}^{1/2}$ are the copper-based oxidation and ligand-based reduction potentials. E_{00} is estimated from the solution emission onset (5% emission intensity) at room temperature.

$$E_{ox}^{*} = E_{ox}^{1/2} - E_{00}$$
 (1)

$$E_{red}^{*} = E_{red}^{1/2} + E_{00}$$
 (2)

Table 3: Excited state redox potentials. $E_{00VieValues of the solution emission Donset Stateestimated from the solution emission Donset Stateintensity) at room temperature.$

Complex	E* _{ox} /V	E* _{red} /V	E ₀₀ /eV
1	-1.77	0.52	2.63
2	-1.84	0.57	2.67

X-ray crystallographic structure of 2

Crystals of **2** were obtained by slow diffusion of *n*-hexane in a saturated solution of the complex in CH_2Cl_2 . The single crystal structure of **1** has previously been reported.⁶¹ The coordination geometry of **2** in the solid state is similar to that of complex **1** (Figure 3, Table 4) and can be best described as distorted tetrahedral with a τ_{tet-sq}^{62} index value of 0.98 (with 1.00 being the value for an ideal tetrahedral geometry).



Figure 3. Molecular structure of **2.** Hydrogen atoms and the $[PF_6]^-$ anion are omitted for clarity. Thermal ellipsoids are set to 30% probability level.

Table 4: Selected bond lengths [Å],	angles [°], and geometry
indexes for the solid state structures	of complexes 1^{61} and 2 .

Complex 1 ⁶¹	Complex 2
80.41(10)	80.65(10)
102.63(8)	100.78(7)
119.41(8)	120.51(7)
97.34(8)	99.43(7)
128.84(8)	124.58(8)
119.68(4)	121.80(3)
2.065(3)	2.061(2)
2.099(3)	2.059(3)
2.2425(10)	2.2124(8)
2.3048(10)	2.2789(8)
0.94	0.98
	Complex 1 ⁶¹ 80.41(10) 102.63(8) 119.41(8) 97.34(8) 128.84(8) 119.68(4) 2.065(3) 2.099(3) 2.2425(10) 2.3048(10) 0.94

DFT Calculations: HOMO and LUMO characteristics

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Ground state DFT calculations were carried out for the $[Cu(bcp)(xantphos)]^{+}$ and $[Cu(bcp)(POP-xantphos)]^{+}$ cations in the gas phase and the compositions of the HOMO and LUMO – of each complex are shown in Figure 4. The orbital character is partitioned on the ligands with the LUMO being localized on the bcp ligand (Figures 4b and 4d), while the HOMO is centered largely on the copper in $[Cu(bcp)(xantphos)]^{+}$ (Figure 4a) and on the copper and bisphosphane ligand in the POP-xantphos containing complex (Figure 4d). Similar orbital distributions have been observed for heteroleptic $[Cu(N^N)(P^PP)]^{+}$ complexes.^{60, 63-65}



Figure 4. Orbital characteristics of the (a) HOMO and (b) LUMO of $[Cu(bcp)(xantphos)]^+$ and of the (c) HOMO and (d) LUMO of $[Cu(bcp)(POP-xantphos)]^+$.

Photocatalysis

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Our photocatalytic investigations started using the welldefined photosensitizers **1** and **2** in combination with the iron catalyst **I** and *N*-methyl-2-pyrrolidone (NMP) as molecular solvent (Table 5). Under these reaction conditions a TON (CO) of 427 was obtained with high selectivity toward CO (\ge 98%) when using the well-defined PS **1** (Table 5, entry 1).³⁷ A higher TON(CO) was observed when using **2**, despite a marginal decrease in selectivity (Table 5, entry 2).

Table 5. Iron photocatalyzed CO_2 reduction with $[Cu(N^N)(P^P)][PF_6]$ complexes as PS in molecular solvent systems.



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View Article Online DOI: 10.1039/D0GC01627F

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Entry	Complex	Solvent	TON	TON	Selectivity
			(CO)	(H ₂)	[%]
1 ³⁷	1	NMP/TEOA (5:1, v:v)	427	5	≥98
2	2	NMP/TEOA (5:1, v:v)	505	23	≥93

Reaction conditions: [Fe] $(1 \mu mol)$, $[Cu(N^N)(P^P)][PF_6]$ (5 μ mol), BIH (150 mg) and TEOA (1.25 mL) were illuminated at 400-700 nm (1.50 W) under 1 atm of CO₂ in 6.25 mL of NMP for 5 h. Results presented are the averages of reactions carried out in duplicate (single experiment results can be found in Table S2 in the ESI), TON values calculated based on the iron catalyst. Entry 1: TON for HCO₂H are not reported in the literature. Entry 2: TON of HCO₂H of 10 was observed by ¹H NMR spectroscopy using benzene as internal standard.

The CuPS/Fe systems were then tested using different ionic liquids as solvents (Table 6) in order to ascertain the impact of the latter on the catalytic performances. While the study conducted by Wang and co-workers mainly evaluated the influence of different anions on the catalytic performance, we were intrigued by the impact of different classes of ionic liquids. Hence, we compared an imidazolium-, a pyrrolidinium-, and a phosphonium-based IL under similar conditions. Interestingly, the activity and selectivity of the system was highly dependent on the ionic liquid used. A significant increase in selectivity was obtained using 1-butyl-1methylpyrrolidinium dicyanamide ([Bmpyrr][N(CN)₂]) (Table 6, entries 1 and 2) compared to 1-butyl-3-methylimidazolium triflate ([Bmim][OTf]) (Table 6, entries 4 and 5), independently from the CuPS used. In particular, almost equal TON(CO) and TON(H₂) were observed for **2** in [Bmim][OTf] as solvent (Table 6, entry 4) and a significant overproduction of hydrogen was observed when 1 in [Bmim][OTf] was used (Table 6, entry 5). This undesired selectivity towards hydrogen formation was even more pronounced when using **1** in [Tbmp][NTf₂] (tributyImethylphosphonium

bis(trifluoromethylsulfonyl)imide) (Table 6, entry 6). Interestingly, similar selectivity towards H₂ production was found when [Bmpyrr][NTf₂] was utilized (Table 6, entry 3). This result contrasts with the high CO selectivity obtained when utilizing the dicyanamide analogue of [Bmpyrr]. While we cannot fully exclude an impact of the potentially coordinating $N(CN)_2$ on the catalysts, the difference in selectivity could result from the biphasic reaction system resulting from nonmiscibility of the NTf2-based ILs and TEOA. In summary, [Bmpyrr][N(CN)₂] was found to be the most suitable IL to selectively produce CO and 1 was identified as the best photosensitizer both in terms of activity (TON(CO) = 77) and selectivity (≥92%, Table 6, entry 2). Importantly, the in-situ formation of the CuPS is ineffective when using ILs as solvents (Table 6, entry 7), in contrast to the outcome noticed in

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organic solvents. Finally, the production of CO varies only marginally by addition of a second equivalent of CuPS **1**, which shows that the catalyst deactivates over longer reaction times as it has been stated previously³⁷ (Table 6, entry 8).

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Catalyst deactivation impacts the long term stability and recyclability of our reaction system. To achieve a fully recyclable system the stabilities of catalyst and CuPS require further enhancement. For Cu(N^N)(P^P)⁺, better interlocking caused by ligand-ligand interactions and/or supported complexes could enhance the stability of the catalytic system in ILs. Deactivation, specifically of the CuPS remains a significant challenge in this research area. Recently, Lin and coworkers have tackled the stability drawbacks of copper(I) photosensitizers by integration of the Cu(N^N)(P^P)⁺ complex into a metal-organic framework.⁶⁶ Further investigations on the applicability of these Cu-modified MOFs might eventually enable a recyclable IL-based system for photocatalytic reduction reactions.

Table 6. Iron photocatalyzed CO_2 reduction with $[Cu(N^N)(P^P)][PF_6]$ complexes as PS in different ionic liquids.

X [−]		N+ N −otf				
X ⁻ = N(C	$(N)_{2}^{T}$ NTf ₂				$\$	
[Bmp	oyrr][X]	[Bmim][OTf]		[Т]	bmp][NTf ₂]	
Entry	Complex	Solvent	TON	TON	Sel. ^e	
,			(CO)	(H ₂)	[%]	
1	2	[Bmpyrr][N(CN) ₂]	29	≤3	≥82	
		/TEOA(4:1, v:v)				
2	1	[Bmpyrr][N(CN) ₂]	77	≤3	≥92	
		/TEOA(4:1, v:v)				
3 ^{<i>a</i>}	1	[Bmpyrr][NTf ₂]	60	338	15	
		/TEOA (1:1, v:v)				
4	2	[Bmim][OTf]	171	171	49	
		/TEOA (4:1, v:v)				
5 ^{<i>b</i>}	1	[Bmim][OTf]	60	124	30	
		/TEOA (4:1, v:v)				
6 ^{<i>a</i>}	1	[Tbmp][NTf ₂]	60	274	17	
		/TEOA (4:1, v:v)				
7 ^{<i>b,c</i>}	1	[Bmpyrr][N(CN) ₂]	1	≤3	14	
		/TEOA (4:1, v:v)				
8 ^{<i>d</i>}	1	[Bmpyrr][N(CN) ₂]	79	≤3	≥92	
		/TEOA (4:1, v:v)				

Reaction conditions: [Fe] $(1 \mu mol)$, $[Cu(N^N)(P^P)][PF_6]$ (5.0 μmol), BIH (150 mg) and TEOA (1.5 mL) were illuminated at 400-700 nm (1.50 W) under 1 atm of CO₂ in 6.0 mL of solvent for 5 h. Unless stated otherwise results presented are the averages of reactions carried out in duplicate (results of single experiments can be found in Table S2 in the ESI to TONS of HCO₂H: Entry 3 = 5, entry 4 = 6, entry SQ: 11.1478/entry 65279 were observed by ¹H NMR spectroscopy using benzene as internal standard. ^aNote: The IL was not miscible with TEOA resulting in a biphasic reaction mixture. ^bResult of a single reaction. ^cAn *in situ* CuPS system consisting of [Cu(CH₃CN)₄][PF₆] (5.0 µmol), bathocuproine (5.1 µmol), and xantphos (15 µmol) has been utilized. ^dA second equivalent of CuPS **1** (5.0 µmol) in [Bmpyrr][N(CN)₂] (1.0 mL) was added after 5.5 h and the reaction illuminated for a total 23 h. ^eSelectivity towards CO.

The only system described in the literature that reduces CO₂ to CO in pure ionic liquid is based on fac-[ReCl(bpy)(CO)₃]and 1butyl-1-methylpyrrolidinium tetracyanoborate ([Bmpyrr][TCB]), using supercritical scCO₂ where CO₂ acts both as solvent and reactant in order to avoid substrate solubility problems.⁴³ This system showed dramatically lower TON's between 0.7 and 5 when compared with our respective values. Moreover, the use of an ionic liquid in combination with an organic solvent was reported to enhance the intrinsic activity of a photocatalytic system based on [Ru(bpy)₃Cl₂] as the photosensitizer and CoCl₂.6H₂O as the catalyst. The chosen ionic liquid was 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Emim][NTf₂]), obtaining a TON(CO) of 34.7 and a selectivity of 76%, using water in the reaction mixture.⁴² Both values are lower than the ones achieved with our system. Unfortunately, the authors did not report the activity in pure ionic liquid. Nevertheless, besides the higher catalytic activity of the system reported herein, the sole utilization of earth-abundant copper and iron render this system interesting. Notably, these results indicate the possibility of transferring established photocatalytic CO2 reduction protocols from organic solvents into ionic liquids.

Control experiments were performed in order to confirm the necessity of all the components used in the aforementioned protocol (Table 7). First, irradiating the ionic liquid in combination with the sacrificial reductant and the base (BIH and TEOA) in the presence of CO_2 produced only traces of CO and H₂ (Table 7, entries 1 and 2). Similar results were obtained using either only I (Table 7, entry 3) or CuPS (Table 7, entry 4). Therefore, all the components need to be present in order to effectively convert CO_2 , which does not proceed in the absence of light, confirming its photochemical nature (Table 7, entry 5). Finally, replacing CO_2 with argon atmosphere did not yield CO at the end of the reaction (Table 7, entry 6) confirming that this methodology forms CO from CO_2 and not from decomposition of the catalyst or other components of the reaction system.

Table 7. Blank reactions for evaluation of the necessity of thecomponents of the catalytic system.

Entry	[Fe]	[CuPS]	TON	TON	TON
	[µmol]	[µmol]	(CO)	(H ₂)	(HCO ₂ H)
1 ^{<i>a</i>}	-	-	≤1	≤3	≤3
2	-	-	≤1	≤3	≤3

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3	1	-	≤1	≤3	≤3
4	-	5	≤1	≤3	≤3
5 ^{<i>b</i>}	1	5	≤1	≤3	≤3
6 ^{<i>c</i>}	1	5	≤1	≤3	≤3

Reaction conditions: [Fe] and 2 [Cu(N^N)(P^P)]PF₆ as stated in the table, BIH (150 mg) and TEOA (1.5 mL) were illuminated at 400-700 nm (1.50 W) in 6.0 mL of 1-butyl-1methylpyrrolidinium dicyanamide for 5 h. Results presented were obtained from single experiments. ^a1-Butyl-3methylimidazolium triflate (6.0 mL) was applied as the solvent. ^{*p}Reaction* conducted in the absence of light. 'Reaction</sup> performed under an atmosphere of argon.

To further confirm that the CO produced originated from CO_2 , the sample, containing Fe complex I (0.13 mM), CuPS 1 (0.72 mM), BIH (30 mg), and TEOA (0.30 mL) in 0.90 mL of 1butyl-1-methylpyrrolidinium dicyanamide, was introduced to a high-purity photocatalytic reactor and tested for CO₂ reduction in batch mode. This setup is predominantly used to test samples in powder form (immobilized or not), but for the first time a liquid sample was successfully tested in such reactor. To ensure that the sample remains intact under the selected reaction conditions and that no products are formed without the presence of CO_2 (i.e., from potential degradation of the catalyst system), reference measurements took place under pure (6.0) helium atmosphere (Figure 5).



Figure 5: Iron photocatalyzed CO₂ reduction with [Cu(N^N)(P^P)][PF₆] complex 1 as PS: Production of CO over 6 hours (CO production in µmol). Comparison of a reaction run with CO_2 in the reaction atmosphere (black) and a blank experiment in pure helium (red).

A 420 nm cut-off filter was used to remove the UV part of the irradiation spectrum. Furthermore, in the latter measurement in pure helium and with visible light only, hardly any CO or other carbon-containing molecules were detected in the effluent gas (Figure 5, red curve). When replacing pure He with CO2 and under similar irradiation conditions with the application of the cut-off filter, a clear production of CO was observed, not present when CO₂ was absent (Figure 5, black curve). No other products (e.g. CH₄, H₂) were detected in the gaseous reaction mixture.

Conclusions

DOI: 10.1039/D0GC01627F Ionic liquids proved to be a suitable reaction media for the photocatalytic CO₂ reduction to CO using a copper(I) photosensitizer and an iron catalyst. High selectivity for CO and moderate turnover numbers were achieved. Overall our results show that the presented system is competitive compared to previously reported ones with rhenium⁴³ or ruthenium and cobalt⁴² in ionic liquid media for the reduction of CO₂ to CO. Moreover, this work indicates the possibility of transferring photocatalytic processes mediated by earthabundant metals from an organic solvent to an ionic liquid. Using high-purity conditions, the origin of produced CO was proven to be directly related to the presence of CO₂ in the reaction mixture. In reference measurements under visible light irradiation in inert gas, the components of the reaction mixture appeared to be stable, and no carbon-containing compounds were detected in the gas phase. In addition, a new CuPS 2 was synthesized and its electrochemical and photophysical properties were examined. Albeit showing promising properties, the well-known CuPS 1 proved to be more selective for the given process. Further investigations regarding the applicability of CuPS 2 are part of on-going research in our laboratories.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

P.A.F.-C. would like to thank the Marie Skłodowska-Curie Actions for funding; Prof. Paul C. J. Kamer for funding and valuable discussions. M.M. is grateful to the Fonds der Chemischen Industrie for a Kekulé fellowship. Part of this work was funded by the German Federal Ministry of Education and Research (BMBF, Grant No. 033RC003A, PROPHECY). P.A.F.-C., M.M, N.G.M., F.B., C.H., E.C., H.J., M.B. and J.S. thank Dr. Anke Spannenberg for X-ray analysis of compound 2 and Hilario D. Huerta for preparing one batch of complex I.

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