CO + H$_2$O

Fischer-Tropsch process

Earth-abundant photocatalytic CO$_2$ reduction

CO$_2$

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A fully earth-abundant photocatalytic system for the visible-light-driven reduction of CO$_2$ to CO

A highly active noble metal-free catalytic system for light-driven CO$_2$ reduction was developed. The combination of an iron cyclopentadienone catalyst with an *in situ* generated copper photosensitizer allowed for a CO$_2$-to-CO transformation with a selectivity of 99%. Based on luminescence quenching experiments, a reductive quenching mechanism between the excited state of the photosensitizer and the electron donor was proposed.

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Earth-abundant photocatalytic systems for the visible-light-driven reduction of CO_2 to CO†

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Herein, we report a highly selective photocatalytic system, based on an *in situ* copper photosensitizer and an iron catalyst, for the reduction of CO_2 to CO. Turnover numbers (TON) up to 487 (5 h) with selectivities up to 99% and $\Phi_{CO} = 13.3\%$ were observed. Stern–Volmer analysis allowed us to establish a reductive quenching mechanism between the Cu PS and electron donor.

Over the last 50 years, the use of fossil fuels has increased the concentration of greenhouse gas carbon dioxide in the atmosphere.[1] Technologies to control CO_2 production and reduce its accumulation in the atmosphere are highly desired. In this context, photochemical reduction of CO_2 provides a pathway to convert a waste product into more valuable molecules whereby the energy from sunlight is stored.[2] Thus, not only carbon dioxide can be used as C_1-feedstock but also this approach allows to harvest the energy from sunlight, helping the transition towards a more sustainable energy source.

Inspired by the seminal work of Lehn and co-workers,[3] several molecularly defined systems have been developed to mediate the photochemical reduction of CO_2.[2a] In these works usually a multicomponent system is used employing a photosensitizer (PS) and a catalyst (Cat) which is responsible for CO_2-coordination and its subsequent reduction. Ru(II) polypyridyl and cyclometalated Ir(III) complexes are often used as PS due to their strong oxidation and reduction power and extended lifetimes of their excited states.[4] In addition, transition metal complexes based on Ru,[5] Re,[6] and Ir[7] have been successfully applied as Cat. Due to the obvious advantages, the use of more earth-abundant metals for both PS and Cat is desired in these materials.

Recently, several complexes based on non-precious transition metals have been described as Cat in the photoreduc-tion of CO_2.[8] For instance, Bonin, Robert *et al.* reported the use of an iron tetraphenylporphyrin complex together with an iridium-based PS to reduce CO_2 selectively to CO with a turnover number (TON) of 140.[8g] The substitution of the Ir PS by an organic dye decreased the activity of the catalytic system by half. A Co^{II} complex supported by a cyclic pentadentate ligand has been also used as Cat in the presence of an Ir PS, driving a selective CO_2-to-CO conversion with a TON of 270.[8e] A photocatalytic system comprising a quaterpyridine Co^{II} or Fe^{II} complex as Cat and a ruthenium-based PS led to CO_2 reduction into CO with high selectivity (98%) and TONs between 497 and 2660.[8a] When an organic dye is used instead of the Ru PS, the system converted CO_2 to CO with a TON of 1365 (based on Cat, $c = 0.005$ mM) and a quantum yield $\Phi_{CO} = 1.1\%$. In addition, Ishitani and co-workers recently reported the use of a dimeric Cu^I complex, supported by a tetradentate ligand, as PS for the CO_2 reduction to CO with a selectivity of 78% over H_2 production.[9] The catalytic process was performed in the presence of an Fe^{II} complex as Cat and 1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo[*d*]imidazole (BIH) as sacrificial electron donor (SD). The efficiency and durability for CO formation were high, with $\Phi_{CO} = 6.7\%$ and $TON_{CO} = 270$. Apart from all these interesting developments, the use of abundant-metal complexes for efficient and durable photocatalytic systems for selective CO_2 reduction with visible light still remains rare.

In our research group, several heteroleptic Cu^I complexes were developed in the last years and used as PS in photocatalytic water reduction.[10] To render an operationally simpler process, we also established a photocatalytic system where the synthesis and isolation of the corresponding Cu PS is bypassed.[11] Accordingly, the heteroleptic emissive Cu complex is formed *in situ*, allowing a facile screening of a broad range of ligands in order to easily correlate the structural features of the PS with the observed catalytic activity.

Here, we describe for the first time the application of this process to the photochemical reduction of CO_2. More specifically, we employed cyclopentadienone iron complexes as Cat,[12] generating a fully earth-abundant catalytic system.

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We started our investigations using iron cyclopentadienone complex **1** as CO_2-reduction catalyst. *In situ* generation of the Cu PS was performed with equimolar quantities of a simple copper salt ([Cu(MeCN)$_4$]PF$_6$), a bidentate phosphine ligand (xantphos), and a phenantroline derivate (bathocuproine, **5**); see Scheme 1. We observed that upon dissolution of all components in a 5 : 1 (v/v) mixture of *N*-methyl-2-pyrrolidone (NMP) and triethanolamine (TEOA), with the addition of a SD (1-benzyl-1,4-dihydrinicotinamide, BNAH) and subsequent visible light irradiation for 5 h, CO_2 was reduced to CO with a TON of 245 and a selectivity of 86% over H_2 production (Table S3,† entry 1). This result suggests that the copper-based PS is easily formed *in situ* and it is able to mediate a photo-induced electron transfer from the SD to the CO_2-reduction catalyst **1** (*vide infra*).

It is worthy to point out that an amine (BNAH) has been employed as sacrificial electron donor. In a large-scale use of this technology, photochemical reduction of CO_2 needs to be coupled with water oxidation reaction. So water can be used as an electron source, just as in the case of photosynthesis. Since the oxidation of water is also a challenging reaction by itself,[13] it is a common practice to optimize both reactions separately. Thus, sacrificial donors such as amines are used to explore the activity of potential catalysts in CO_2 photoreduction.

Notably, when dissolving a heteroleptic Cu^I complex with both diimine and diphosphine ligands an equilibrium with the homoleptic Cu^I(N–N)$_2$ complex (N–N = diimine ligand) is established.[10d] Evidently, this equilibrium can be affected by the ratio between the diimine and diphosphine ligand in the *in situ* formation of the Cu PS, thus influencing the catalytic activity of the system as well. In fact, when the reaction was performed in the absence of a source of diphosphine ligand, the generation of CO dropped dramatically (Table S2,† entry 2). In this case, only a homoleptic Cu^I(N–N)$_2$ complex can be formed, suggesting that the photophysical properties of such copper complex are not adequate to drive the photochemical reduction of CO_2.[14] Accordingly, when an excess of diphosphine ligand was used (*i.e.* 2 or 3 equiv.) the catalytic activity of the system was improved (TON$_{CO}$ = 271 and 270 and selectivity = 95% and 97%, respectively; Table S2,† entries 5

and 6). Under these experimental conditions, the presence of the heteroleptic Cu PS is favoured over the inactive homoleptic species.

Considering the limitations of BNAH as SD (*i.e.* inner-filter effect and rapid back-electron transfer from oxidized products),[15] we turned our attention to BIH, a suitable electron donor recently used in photocatalytic reactions.[8a,9] In fact, applying BIH, the photocatalytic activity of the system raised up to a TON$_{CO}$ = 487 with a selectivity of 99% (Table 1, entry 1). Thus, BIH was used as SD in the following photocatalytic investigations.

Notably, using an isolated sample of Cu complex **5** instead of the *in situ* generated PS, the catalytic activity was slightly lower (Table S4,† entry 2), which proves that the heteroleptic Cu PS is effectively assembled *in situ*.

Excited state lifetimes of heteroleptic Cu^I PS are heavily influenced by exciplex quenching of the resulted flattened Cu^{II} complex upon light irradiation.[14] Commonly, steric effects of the diimine ligand influence the degree of excited state distortion. Thus, aiming to increase the excited state lifetime of the Cu PS and the catalytic activity of the system as well, we tested several sterically demanding 1,10-phenantroline derivates as ligands (Table 1, entries 1–6). However, when diimine **7** – containing ^{i}Bu groups in the 2 and 9 positions of the phenantroline moiety – was used instead of bathocuproine **5**, the activity of CO_2 photoreduction was diminished (entry 1 *vs.* entry 4, Table 1). Interestingly, when applying ligand **9** instead of bathocuproine, the catalytic activity is almost similar (Table 1, entry 6). We assume that not only the steric effects of the substituents in position 2 and 9 of the phenantroline play a major role, but also the electronic properties of the various substituents in the remaining positions.

Table 1 Photochemical reduction of CO_2 with visible light, iron-based Cat and *in situ* Cu PS[a]

$$CO_2 \xrightarrow[\substack{\text{NMP/TEOA (5:1 v/v), BIH (0.1 M)} \\ h\nu \text{ (400-700 nm), 5 h, 25 °C}}]{\substack{\text{[Cu]/[Fe]} \\ \text{N–N/P–P}}} CO$$

Entry	N–N ligand	[Fe] complex	TON[b] (CO)	TON[b] (H_2)	Selec. (CO)
1	**5**	**1**	487	7	99%
2[c]	**5**	**1**	64	15	81%
3	**6**	**1**	360	17	95%
4	**7**	**1**	310	8	97%
5	**8**	**1**	404	26	94%
6	**9**	**1**	467	31	94%
7	**5**	**2**	254	9	97%
8	**5**	**3**	260	16	94%
9	**5**	**4**	80	11	88%

[a] Reaction conditions: NMP/TEOA (5 : 1, v/v) 7.5 mL; 5 μmol [Cu(MeCN)$_4$]PF$_6$; 15 μmol xantphos P–P ligand; 5 μmol N–N ligand; 1 μmol Fe catalyst; BIH 0.1 M; Hg-lamp (light output 1.5 W) equipped with a 400–700 nm filter. [b] Determined using calibrated GC; TON = n(CO)/n(catalyst). [c] Reaction performed using MeCN/TEOA (5 : 1, v/v) as solvent mixture.
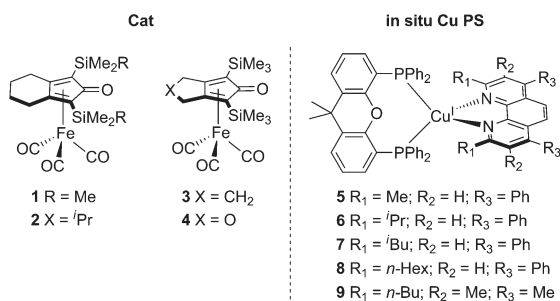
Scheme 1 Molecular structure of the cyclopentadienone iron complexes used as Cat and the *in situ* formed Cu PS.

Cat — in situ Cu PS

1 R = Me
2 X = ^{i}Pr
3 X = CH$_2$
4 X = O

5 R$_1$ = Me; R$_2$ = H; R$_3$ = Ph
6 R$_1$ = ^{i}Pr; R$_2$ = H; R$_3$ = Ph
7 R$_1$ = ^{i}Bu; R$_2$ = H; R$_3$ = Ph
8 R$_1$ = n-Hex; R$_2$ = H; R$_3$ = Ph
9 R$_1$ = n-Bu; R$_2$ = Me; R$_3$ = Me

Steric effects caused by bidentate phosphine ligands also influence the degree of excited state distortion as well as the equilibrium between homoleptic and heteroleptic species.[10d,11] For instance, if the flexible diphosphine ligand DPEPhos **11** was used instead of xantphos (Table S1,† entry 1), the catalytic activity of the system decreased (TON_{CO} = 340). On the other hand, applying the sterically demanding thixantphos **10** led to catalytic activities comparable to xantphos (Table S1,† entry 2). Since it has been previously reported that the ratio between homoleptic and heteroleptic species is comparable for all three diphosphines,[11] the observed differences in activity are mainly due to the restrictions imposed by such ligands during the flattening distortion of the copper complexes. Obviously, the lower catalytic activity displayed by **11** is due to the less steric hindrance of the substituents on the phosphorous atom and the smaller bite angle (102°), which both are responsible for preventing flattening distortion and exciplex quenching by nucleophilic attack of a solvent molecule.

Notably, we observed that the activity of the photocatalytic system is strongly influenced by the structure of the cyclopentadienone iron catalyst. Comparing the activities of complexes **1** and **2** (Table 1, entries 1 and 7), it becomes evident that increasing the steric hindrance of the substituents at the silicon atom has a negative influence on the activity of the system. In addition, when a heteroatom (oxygen) is present in the saturated cycle of the ligand (Table 1, entry 9), the catalytic performance decreased dramatically. Specifically, the TON is reduced from 487 to 80. Attempts to increase the catalyst productivities (TON) by elongation of irradiation time failed, suggesting that the photocatalytic system is no longer active after 5 h.

In order to get insights into the mechanism of the photochemical CO_2 reduction catalyzed by iron complex **1** in the presence of *in situ* Cu PS **5**, the quantum yield of the overall catalytic photoredox cycle reduction was determined by using the following equation:

$$\Phi_{CO}(\%) = \frac{\text{produced CO molecules}}{\text{incident photons}} \times 100\%.$$

The number of incident photons was determined using an iron actinometer (see ESI† for details). After 2 h of irradiation using monochromatic light (415 nm), 2.5×10^{-4} mol of CO were quantified. Hence, the calculated quantum yield for this molecular system is 13.3%, which is twice as high as the previously reported catalytic system for CO_2 photoreduction based on a dimeric Cu PS and an Fe phenanthroline catalyst.[8]

To probe the mechanism of photoinduced electron transfer in this catalytic system, we further carried out quenching experiments of the *in situ* Cu PS **5** excited state by the iron catalyst **1** and by the electron donor (BIH) using Stern–Volmer analysis (see ESI† for details). At an excitation wavelength of 450 nm, the luminescence at 550 nm of the Cu PS was effectively quenched by BIH with an apparent quenching rate constant of 1.1×10^8 M^{-1} s^{-1} (Fig. 1a). For comparison, typical quenching constants for Ru PS are in the order of
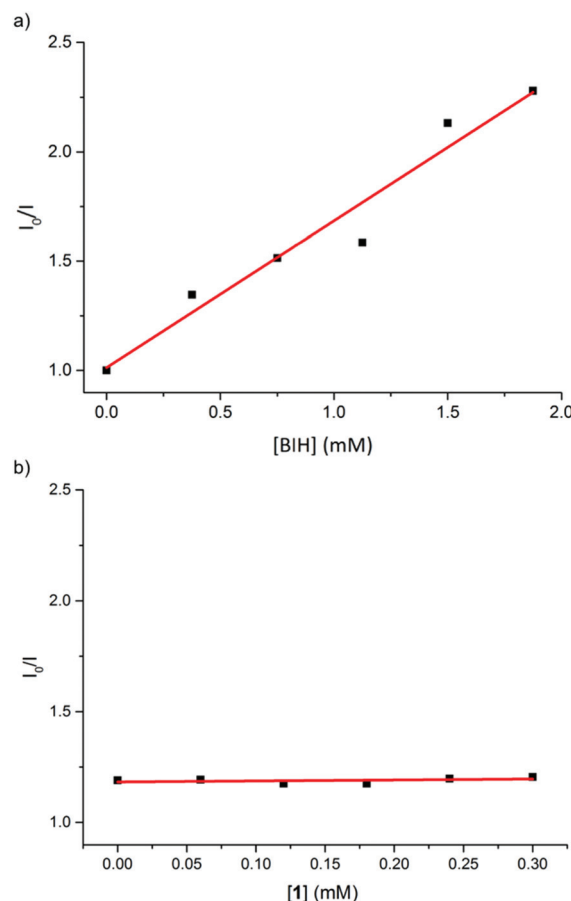
Fig. 1 Linear plots of ratio of fluorescence intensities of *in situ* Cu PS **5** in the absence and presence of (a) BIH ($y = 0.672x + 1.013$, $R^2 = 0.94$) and (b) **1**, according to the Stern–Volmer equation.

10^7–10^{10} M^{-1} s^{-1}, suggesting that reductive quenching of Cu PS with the electron donor BIH can reasonably operate in this photocatalytic system. On the other hand, the fluorescence of Cu PS **5** was not attenuated by iron catalyst **1**. That excludes the possibility of an oxidative quenching mechanism (Fig. 1b) by the catalyst itself. These observations are in agreement with the reported redox potentials of the involved species. For instance, whereas an electron transfer from BIH (E^{ox} = 0.33 V *vs.* SCE)[15] to the excited state of the PS (Cu PS$^-$/Cu PS*, E^0 = 1.03 V)[10b] is thermodynamically feasible, an electron transfer from the excited state of the PS (Cu PS*/Cu PS$^+$, E^0 = −1.35 V *vs.* SCE)[10b] to the iron complex **1** (E^{red} = −1.65 V *vs.* SCE) is not possible.

Clearly, a reductive quenching mechanism operates in the photocatalytic CO_2 reduction mediate by complex **1** and Cu PS **5**. Accordingly, a photoinduced electron transfer between the Cu PS and BIH takes place first, resulting in the generation of the reduced state of PS (Cu PS$^-$). Subsequent reduction of the iron catalyst by Cu PS$^-$, generates the active catalyst species that mediates the photoreduction of CO_2 to CO, as previously observed when an Ir PS was used.[12]

Conclusions

In summary, we have described a novel selective photocatalytic system for CO_2 reduction based on earth-abundant elements, combining a copper-based photosensitizer and a molecularly-defined iron catalyst. The Cu PS was easily generated *in situ* using a copper salt, bidentate phosphines, and easily available diimine ligands. When such a luminescent Cu complex was combined with an iron cyclopentadienone catalyst in the presence of light and a suitable electron donor, carbon dioxide is selectively reduced to CO with a TON up to 487 and a Φ_{CO} = 13.3%. According to mechanistic investigations, the photocatalytic reduction of CO_2 proceeded *via* reductive quenching of the excited Cu PS with BIH and further electron transfer from the resulting reduced species of Cu PS to the iron catalyst.

Acknowledgements

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