catalysts

Review

Conversion of CO₂ via Visible Light Promoted Homogeneous Redox Catalysis

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Abstract: This review gives an overview on the principles of light-promoted homogeneous redox catalysis in terms of applications in CO_2 conversion. Various chromophores and the advantages of different structures and metal centers as well as optimization strategies are discussed. All aspects of the reduction catalyst site are restricted to CO_2 conversion. An important focus of this review is the question of a replacement of the sacrificial donor which is found in most of the current publications. Furthermore, electronic parameters of supramolecular systems are reviewed with reference to the requisite of chromophores, oxidation and reduction sites.

Keywords: CO_2; photoreduction; photocatalysis; photooxidation; sacrificial amines

1. Introduction

The hunger for energy is unbroken and will not even stagnate in the face of a growing human population. The amount of CO_2 emitted in human activities was recently estimated to be about 5.5 Gt carbon per year [1]. With a growing CO_2 concentration, the effects of greenhouse gases to nature enforce recurring discussions on how to handle this interference with effects on the climate that are already noticeable and will even rise. Beside direct heat emission (e.g., via combustion gases) these greenhouse gases are responsible for the greenhouse effect and, according to reports of the Intergovermental Panel on Climate Change (IPCC), cause a slow but increasing global warming [2]. In

the context of climate aspects, the discussions are not so much about the existence of global warming, but more about the influence of CO_2 on this process. In 1990, Lindzen *et al.* reported that 98% of the greenhouse effect is due to water vapor and stratiform clouds with CO_2 contributing less than 2% [3]. However, these studies do not differentiate between condensing and noncondensing greenhouse gases. Unlike water, gases like CO_2, N_2O, CH_4 and chlorofluorocarbons do not condense and precipitate at current climate temperatures. Therefore, those gases provide the stable temperature structure that sustains the current levels of atmospheric water vapor and clouds. The direct influence of water is, in current studies, still estimated to be 75% on the climate but without the radiative forcing supplied by noncondensing gases like CO_2 the earth temperature would be strongly reduced [4].

Even for CO_2, as a noncondensing gas, measurements and reconstructions of the atmospheric CO_2 history reveals that less than half of these emissions remain in the atmosphere. The anthropogenic CO_2 that did not accumulate in the atmosphere has been taken up by the ocean, by the land biosphere, or by a combination of both [5]. This leads to a measurable acidification of the oceans and changes the saturation state of the oceans with respect to calcium carbonate ($CaCO_3$) particles [6], with a huge negative impact on especially corals and plankton [7–9]. On the other hand, the amount of fossil carbon sources are limited. Due to rising oil prices, CO_2 gains more and more interest as cheap and abundant C1 feedstock, although CO_2 is the lowest in energy of all carbon-containing binary neutral species. Reactions that generate reduced forms of CO_2 (e.g., CO, formates) require energy [1]. However, routes towards organic base chemicals have the potential of high volume CO_2 conversions, although the energy problem of these uphill reactions need to be solved. In terms of sustainability the photocatalytic reduction of CO_2 is a very interesting pathway, in which the activation energy originates from sunlight. Within one hour the irradiation power of sunlight on the earth would be sufficient for the human energy consumption of a complete year. However, the intensity of sunlight strongly depends on the wavelength with a maximum at 550 nm. Thus, with sunlight as the energy source, a visible light absorbing photosensitizer is required. These requirements for an effective chromophore, as well as the general principles of light promoted homogeneous redox catalysis in terms of applications in CO_2 conversions, are summarized in this review. Mechanistic aspects, as well as the products, are discussed in the face of possible applications. Especially the question about a replacement of the sacrificial donor which is found in most of the current publications is an important focus of this review.

2. Principle of Homogeneous Redox Photocatalysts and Their Building Units

Homogenous redox photocatalysts, in principle, consist of a light harvesting unit (photosensitizer) and two catalytic sites [10]. One site is for the oxidation process, where a donor provides the electrons, and the other is the reduction site, where the electrons are transferred to an acceptor. For clarity, this review covers only processes where CO_2 acts as acceptor (Figure 1). In many cases the photosensitizer has dual activity, e.g., as photosensitizer and reduction site, as will be discussed later on (especially in rhenium(I) catalysts).

Figure 1. Building principle of homogeneous photoredox catalysts.
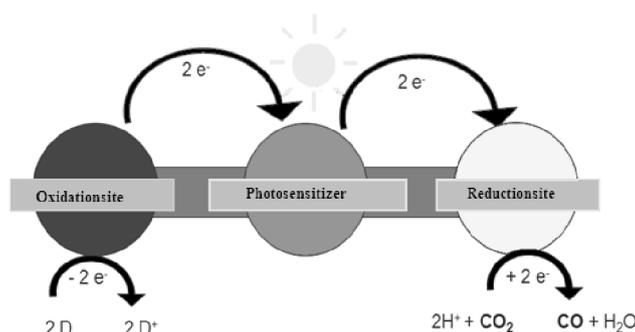
Figure 2. Formation of the ^{3}MLCT state via photon absorption.
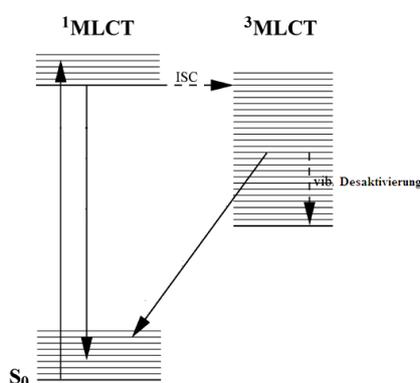
Visible light absorption by the photosensitizer unit leads to the excited state. Concerning CO_2 reduction, the most commonly used photosensitizers are ruthenium (polypyridyl)- and (bipyridyl)-rhenium(I) complexes (2.1 Chromophores). In this case, the light absorption gives rise to a singlet metal to ligand charge transfer (^{1}MLCT) which produces a triplet excited state (^{3}MLCT) by inter system crossing (Figure 2). This ^{3}MLCT state has different redox properties than the ground state. Due to the reducing properties of this state, direct interaction with an acceptor can lead to the one-electron oxidized ground state of the photosensitizer via oxidative quenching, as it was reported for the interaction of *Ru(bpy)$_3$$^{2+}$ with methylviologen (Scheme 1) [11,12].

Scheme 1. Reduction of methylviologen with *Ru(bpy)$_3$$^{2+}$.

$$MV^{2+} \ + \ ^*Ru(bpy)_3^{2+} \longrightarrow \ MV^+ \ + \ Ru(bpy)_3^{3+}$$

However, in terms of CO_2 reduction, reductive quenching is the more important process. With an electron that is provided from the oxidation site, a ground state of the one-electron reduced species is formed, which is capable of transferring one electron to the reduction site to recover the d^6 neutral ground state of the photosensitizer (Figure 3) [13–15].

Figure 3. Schematic representation of the electronic aspects of the electron transfer during oxidation of the donor and the reduction of the acceptor site.
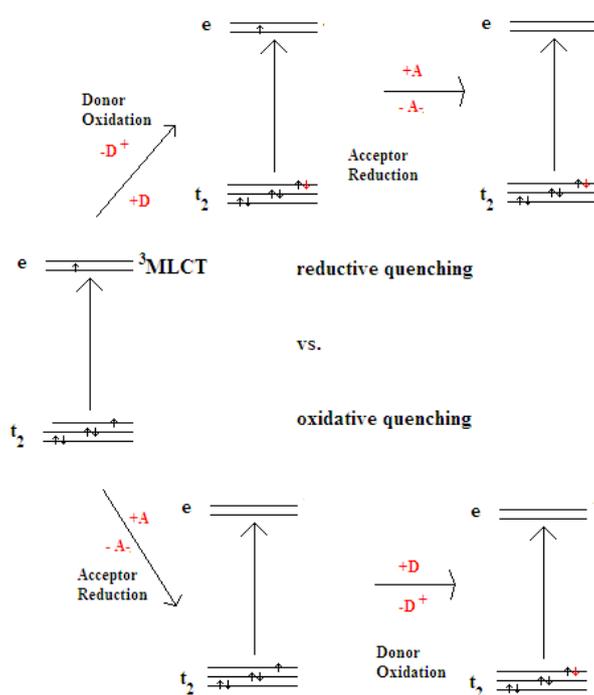
2.1. Chromophores

As already discussed, the intensity of sunlight strongly depends on the light wavelength with a maximum at 550 nm and, therefore, a visible light-absorbing photosensitizer is required. The most frequently used and thoroughly investigated photosensitizers are *tris*(bipyridyl)ruthenium(II) chloride and its analogs. The photophysics and photochemistry of these types of complexes with their powerful photosensitization capacity for electron transfer processes have already been summarized in several comprehensive reviews [16–18]. The excited state of *tris*(bipyridyl)ruthenium(II) chloride is sufficiently long lived (*ca.* 800 ns in water at room temperature), so that this excited state can act as both a reducing agent [19–23] and an oxidizing agent [24–26]. Great attention has also been paid to *bis*(terpyridine)ruthenium(II) complexes, due to the easy accessibility of stereopure polynuclear complexes with this motif [27]. However, the excited lifetime of $Ru(tpy)_2^{2+}$ is only 0.25 ns at room temperature [28], which is far too short for any long range electron transfer [29].

The excited state lifetime is dependent on the radiative and nonradiative rate constants of the relaxation process. In the weakly emitting Ru(II) polypyridine complexes the nonradiative decay constant is the more important factor [30]. Beside direct contributions from the ground state, this nonradiative decay can be reached via a thermally accessible metal-centered state (^{3}MC). Lowering the energy of the ^{3}MLCT state reduces the accessibility of this ^{3}MC state, but increases the direct contribution of the ground state according to the energy gap law [31,32]. Synthetic strategies to prolong this lifetime have already been discussed. [29,33]. For example, by introduction of electron withdrawing substituents (e.g., SO_2Me) [34], or acetylene groups [35], lifetimes of the ^{3}MLCT state up to 580 ns were found, due to the lowering of the ^{3}MLCT energy which reduces the population of the

^{3}MC state. However, the most successful strategy to extend the lifetime of the excited state is to equilibrate the emissive ^{3}MLCT state with a nonemissive triplet state [36]. The ruthenium(II) complex bearing a terpyridine-pyrimidyl-anthranyl ligand reached two lifetimes for the decay of the excited states of 9 ns and 1806 ns [37]. Utilizing similar strategies the lifetime of Ru(II) bipyridine complexes can also be extended reaching lifetimes of up to 58.4 μs in CH_3CN (Figure 4).

Comparing Ru(tpy)$_2^{2+}$ with its higher homolog Os(tpy)$_2^{2+}$, a relatively long-lived ^{3}MLCT (269 ns in acetonitrile) is found. The absorption wavelength of the MLCT transfer and its first reduction potential are nearly identical to the analogous ruthenium complex [27]. A comprehensive list of the excited state behavior of further metal terpyridine complexes is detailed in Table 1.

Beside ruthenium(II) complexes and their higher homologs, another well-established category of photosensitizers are rhenium(I) complexes. One important aspect to note for this type of complex is that they can act as both photosensitizers and catalytic site for the selective reduction of CO_2 to CO.

Figure 4. Representation of Ru(II)terpyridine and Ru(II)bipyridine complexes with elongated lifetime of the activated state [33,38].

λ_{em}=698 nm, τ = 580 ns

λ_{em}=675 nm, τ = 1806 ns

λ_{em}=667 nm, τ = 58.4 μs
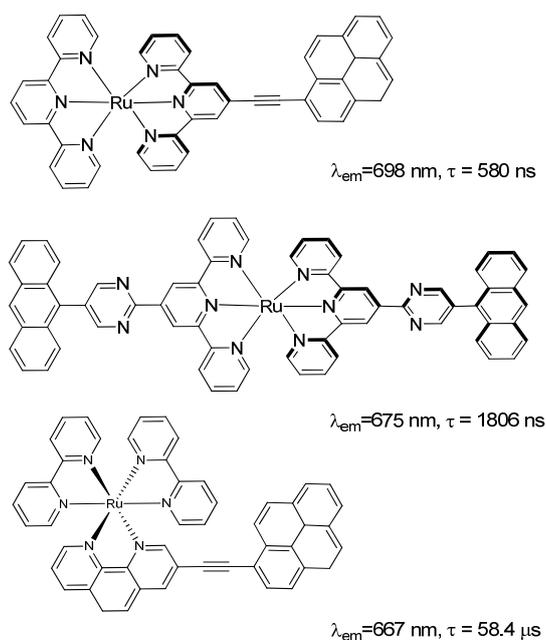
The absorption of visible light by (bipyridyl)Re(I) complexes is much weaker than the previously discussed *tris*(bipyridyl)ruthenium(II) complexes (Table 1), however, Re(I) complexes are found in many reports on photocatalysis. Even in terms of photocatalytic hydrogen formation, where Re(I) cannot act as a catalytic reduction site but only as photosensitizer, this type of complex is found [39]. This is likely because in the excited state, these complexes undergo faster reductive quenching by tertiary amines as compared to ruthenium polypyridine dyes [40,41]. In terms of photocatalytic formation of hydrogen, further reports can be found with Pt(II) [42,43], Ir(III) [44–46], and Os(II) [47]-based chromophores.

**Table 1.** Absorption, Luminescence and Electrochemical Data.

Complex	λ_{max} absorption [nm] $(10^3 M^{-1} cm^{-1}])$	Emission			Electrochemistry E [V]		ref
		[nm]		[ns]	ox	red	
$Ru(bpy)_3^{2+}$	452 * (4.16)	607 *	0.073 *	800 *	1.29	−1.33, −0.81 [a]	[48,49]
$Ru(dmb)_3^{2+}$	459 (14.9)	630	0.089	840	+0.80	−2.22, −1.96, −1.77 [b]	[17,50–54]
$Ru(tpy)_2^{2+}$	476 (17.7)	-	-	0.250	+1.30	−1.24 [a]	[28,55]
$Os(tpy)_2^{2+}$	657 (3.65), 477 (13.75)	718	0.014	296	+0.97	−1.23 [a]	[56–58]
$Cr(tpy)_2^{3+}$	473	775		50	+1.43	−0.17 [c]	[59,60]
$Fe(tpy)_2^{2+}$	522	-	-	2.5	+1.05	−1.17 [c]	[61]
$Ir(tpy)_2^{3+}$	355 (13.8)	455		70			[62]
$(bpy)Re(CO)_3Cl$	370 (3.42)	637		30		−1.61 [b]	[63,64]
$(bpy)Re(CO)_3NCS$	375	635		25		−1.67 [b]	[63,65]
$(dmb)Re(CO)_3Cl$	366 (3.7)	601	0.0016		+1.36, 1.85	−1.43, −1.95 [a]	[66]

[a] *vs.* SSCE, [b] *vs.* AgNO₃ [c] *vs.* NHE–measured in acetonitrile unless otherwise noted, * measured in H₂O.

2.2. Design of the Reduction Site

In the first report about homogeneous catalyst systems for the photoreduction of CO_2 by Lehn and co-workers, $CoCl_2$ was used as the catalytic site with $[Ru(bpy)_3]Cl_2$ as photosensitizer [67,68]. However, $CoCl_2$ has only very low selectivity towards the reduction of CO_2 and hydrogen, resulting from the reduction of water in the aqueous media that is the main product in this system. In alternative catalyst systems such as $RhCl_3$, $NiCl_2$, $CuCl_2$ or K_2PtCl_4, the selectivity towards CO_2 reduction was found to be further reduced. Cobalt macrocycles such as $CoHMD^{2+}$ with *p*-terphenyl as a photosensitizer and a tertiary amine as a sacrificial electron led to formation of both CO and formate with a reduced hydrogen yield (Figure 5) [69–71].

Figure 5. *N-rac*-CoHMD^{2+} (left) and Ni(II)-cyclam (right) complex.
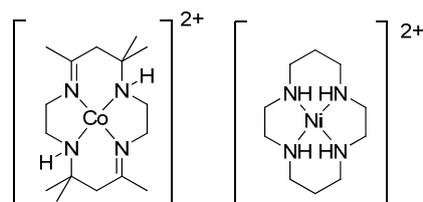
Grant *et al.* reported a Ni(II)-cyclam reduction site for the photoreduction of CO_2 to CO with $Ru(bpy)_3^{2+}$ as photosensitizer (Figure 5) [72,73]. These Ni-cyclam catalysts were modified by Kimura *et al.* for the photocatalytic CO_2 reduction by synthesis of supramolecular Ru-Ni catalysts with covalent linkage of the Ru-based chromophores to the reduction site (Figure 6). However, due to the lack of

selectivity for production of CO over H_2 and other unidentified competing processes in the catalytic cycle, these complexes exhibit very low yields. The amount of CO, produced by this type of investigated Ni-cyclam catalyst is less than stoichiometric [74–76].

**Figure 6.** Bimetallic Ru-Ni catalysts for CO_2 reduction.
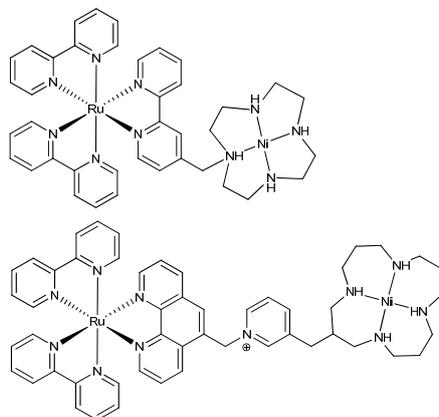
To date, the most selective catalytic reduction site for the photoreduction of CO_2 are rhenium(I) systems. These selectively form CO from CO_2 with only small amounts of hydrogen as a by-product [63]. The first reported Re(I)-type complexes were [Re(bpy)(CO)$_3$X] (X = Cl, Br), affording quantum yields of up to 0.14 [77,78]. Mechanistic aspects are summarized and discussed in recently published reviews [13–15]. A central role in reduction half-cell reaction with Re(I) complexes is ascribed to the one-electron reduced species (OER). The reduction site is capable of transferring the electron that is provided from the electron donating site to the CO_2 molecule. In reports on mechanistic investigations of this half-cell reaction, this OER is simply formed by one-electron reduction of the ^{3}MLCT state of the Re(I) complex via TEOA (triethanolamine), which forms the ground state of the OER. This gives an unstable 19 electron species in which a coordination site becomes available by dissociation of the ligand X [78]. Subsequently, a CO_2 adduct can be formed via nucleophilic attack of the rhenium center on the electrophilic carbon atom of the CO_2 molecule (Scheme 2). The intermediates of the catalytic cycle cannot be unambiguously labeled, but at least several carboxylato-metal complexes of rhenium have been isolated, characterized, and their reactivity towards decarboxylation studied [79,80].

Due to the high reduction potential of the one-electron reduction (−1.9 V *vs.* normal hydrogen electrode), multielectron reduction processes are more favorable [81]. Therefore, the reduction of CO_2 to CO at moderate potentials requires the concerted transfer of two electrons. Ishitani and co-workers postulated a bimetallic reaction sequence where the second electron originates from another OER [65]. This bimetallic mechanism and the special role of the OER was confirmed by the direct comparison of the activity of Re-NCS and Re-Cl complexes in the photocatalytic formation of CO in the presence of a sacrificial donor (TEOA). The photophysical properties (especially absorption and emission properties) of both complexes do not differ remarkably, but the Re-NCS complex with the longer-lived OER is the more active catalyst. With the cationic complex [Re(bpy)(CO)$_3${P(OEt)$_3$}]$^+$, a quantum yield of up to 0.38 was reached, strongly depending on the light intensity [82]. This again can be ascribed to the long-lived OER due to the strong π-accepting ability of the P(OEt)$_3$ ligand. With further modifications, Ishitani *et al.* reached the highest known quantum yield for the photocatalytic formation

of CO of 0.59 with the cationic $[Re(bpy)(CO)_3(MeCN)]^+$ complex [65]. The weakly bound MeCN ligand can be easily dissociated to generate a free coordination site for CO_2 and the strongly bound $P(OEt)_3$ in $[Re\{4,4'-(MeO)2bpy\}(CO)_3(POEt)_3)]^+$ results in a long-lived OER that can provide a second electron.

Scheme 2. Catalytic cycle for the photoreduction of CO_2 with (bipyridyl)Re(CO)$_3$X complexes [78].
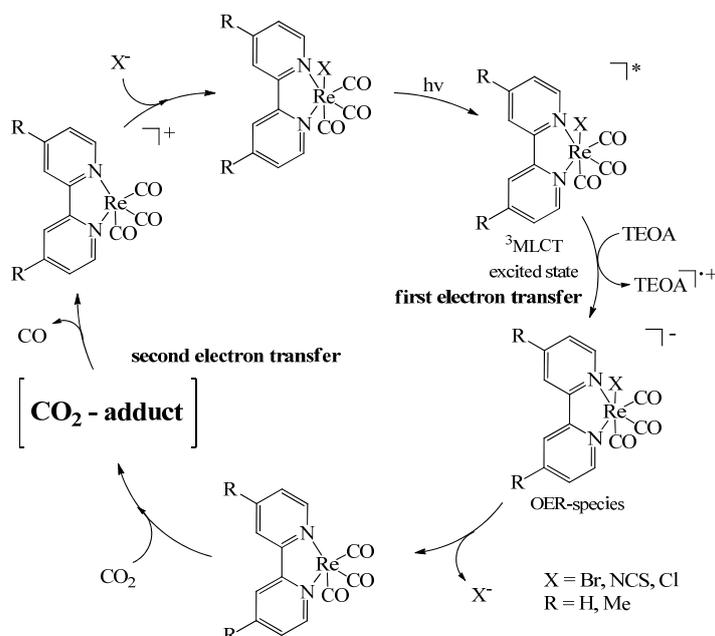
The nature of the bimetallic intermediate that enables the transfer of two electrons is not fully clarified. However, Fujita and co-workers identified a CO_2 bridged dimer $[(CO)_3(dmb)Re-CO(O)-Re(dmb)(CO)_3]$ as an intermediate in the photocatalytic reduction of CO_2 [83]. This key product was isolated previously by Gibson *et al.* via thermolysis of $[(dmb)Re(CO)_3(COOH)]$ in dimethyl formamide [84,85].

Figure 7. Binuclear Re(I)-catalyst.
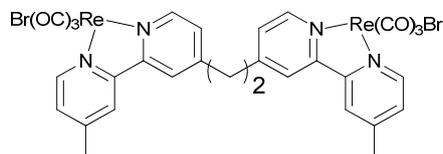
The binuclearity of this reduction reaction was recently investigated with binuclear rhenium complexes (Figure 7) [86]. Usually Re-Br type complexes with their short-lived OER clearly show a mononuclear overall reaction rate for the photocatalytic reduction of CO_2, with no indication of any binuclear aspects. However, with a covalently linked binary Re(I) complex (Figure 7) the catalytic activity was increased due to the presence of a second Re center in proximity to the first. According to this it was concluded that a binuclear mechanism predominates if the proximity of centers is adjusted according to the lifetime of the OER. In case of Re-NCS-type complexes, with long-lived OERs, the bimetallic mechanism can be realized by simply increasing the concentration of the catalyst. Therefore,

Re-NCS-type complexes were often reported to be the most active rhenium(I) photocatalysts for the reduction of CO_2 [65]. However, in case of the binuclear complexes, it was shown that Re-Br type complexes are more active, if the proximity of centers is precisely adjusted by covalent linkage. In the case of bimetallic rhenium(I) complexes, the Re-Br type complexes act in a bimetallic fashion, which results in unexpectedly high activity.

Another well-established category of reduction sites are catalysts of the type $[Ru(bpy)_2(CO)X]^{n+}$ (X = CO, Cl, H) and $[Ru(bpy)_2(CO)_2X_2]^{n+}$ (X = Cl, CH_3CN). They are known to produce formate and CO by photocatalytic and electrocatalytic processes. In these systems, the open cluster polymeric $[\{Ru^0(bpy)(CO)_2\}_n]$ species was identified as the catalytically active product that is formed by two-electron reduction and loss of ligand. These polymeric precipitates selectively form CO from the reduction of CO_2 [87–97].

2.3. Oxidation Site

In most of the reports on the photocatalytic reduction of CO_2 the oxidation site is circumvented with the help of a sacrificial donor that reduces the activated ^{3}MLCT state of the photosensitizer. This generates the one-electron reduced species of the photosensitizer which is important for the further reduction process (reductive quenching). In case of rhenium(I) complexes TEOA (triethanolamine) is most frequently used as donor (E_0[TEOA/TEOA$^+$] = 0.82 V) (Scheme 3) [12].

Scheme 3. Reductive quenching of the activated rhenium(I) complex with TEOA [12].

$$(bpy)Re(CO)_3Br^* + TEOA \longrightarrow (bpy)Re(CO)_3Br^- + TEOA^+$$

Scheme 4. Reaction sequence for the oxidation of TEOA [98].
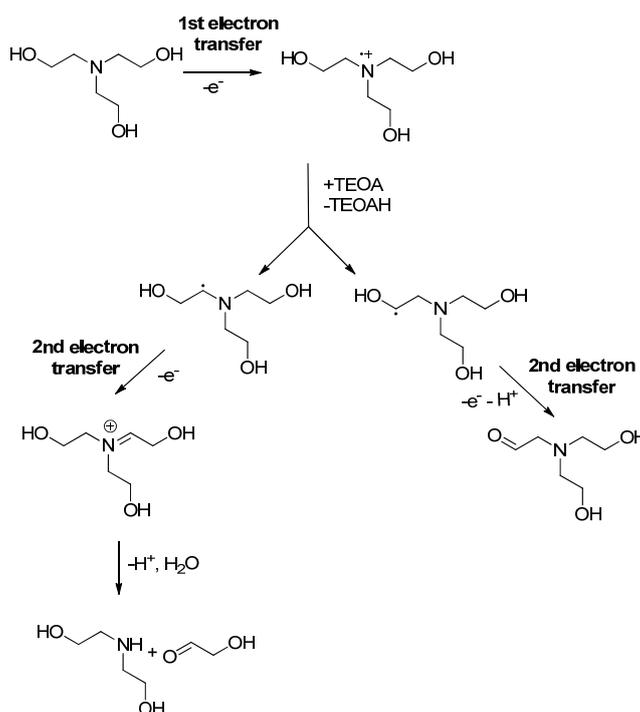
Reductive quenching of the activated photosensitizer with TEOA generates the nitrogen-centered radical cation of TEOA. Abstraction of a proton at this TEOA radical by a further TEOA molecule yields the carbon-centered radicals (Scheme 4) [12,99–102]. Unlike the aminyl radical TEOA·, these carbon-centered radicals are strong reducing agents that prevent back electron transfer from the OER and are capable of donating a second electron [12,99–104].

Table 2. Properties of various organic donors in face of reductive quenching of $Ru(bpy)_3^{2+}$.

| Donor	k_q [10^7 $M^{-1} s^{-1}$]	E_0[V]	Lit
N,N,N',N'-Tetramethylbenzidine	740	0.69	[98]
Phenothiazine	560	0.73	[98]
Dimethyl-Dibenzothiofulvalene	400	0.78	[98]
N-Methylpheno-thiazine	130		[98]
1-Benzyl-1,4-dihydronicotinamide	15	*0.52* [a]	[105,106]
Diphenylamine	2.50	0.80	[98]
Triethanolamine	0.65	0.82	[12]

[a] calculated value from original measurements *vs.* Ag/AgNO$_3$ reference electrode.

For *tris*(2,2'-bipyridine)-ruthenium(II) chloride, the photoreduction with various organic donors was investigated by Maestri *et al.* [107]. The rate constants obtained for the reductive quenching of *$Ru(bpy)_3^{2+}$ are given in Table 2. The electrochemical transfer coefficient and therefore the quenching rate constants depend on the electrochemical potential in agreement with the Marcus theory [108,109]. When the potentials of donor and acceptor become approximately equal a sharp decrease of the rate constant is obtained according to the parabolic free energy relation of Marcus. Therefore, the reduction potential of *$Ru(bpy)_3^{2+}$ was estimated to be close to the thermodynamic limit of $E_0 = 0.85$ V [98].

For complexes of the type $Ru(dmb)_3^{2+}$ and its multinuclear analogs, the most frequently used sacrificial donor is BNAH (1-benzyl-1,4-dihydronicotinamide) as the emissive ^{3}MLCT state cannot be quenched effectively with tertiary amines in this case [110] However, deprotonation of the BNAH$^{+\bullet}$ radical is accelerated in the presence of TEOA and therefore inhibits the back electron transfer (Scheme 5). Further dimerization products of the one-electron oxidized BNAH$^{\bullet}$ radical are known [105].
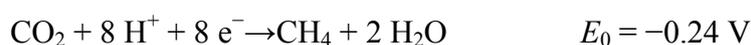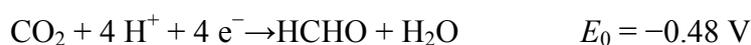
Scheme 5. Reaction sequence for the oxidation of BNAH [111].
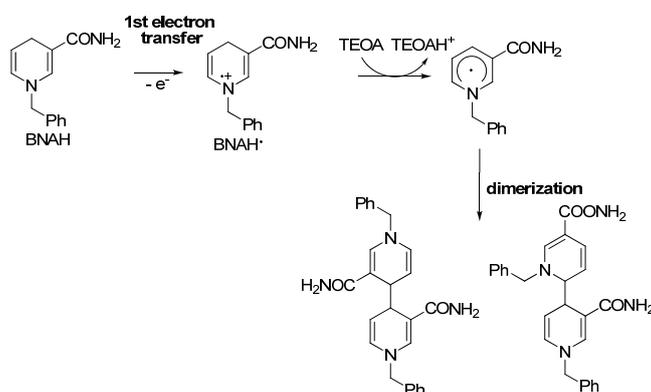
3. Reduction Products of CO_2

Due to the high reduction potential of the one-electron reduction (−1.9 V *vs.* normal hydrogen electrode), multielectron reduction processes are more favorable [81]. Scheme 6 shows potential multielectron reduction products of CO_2. From the beginning of homogeneous photocatalytic reduction of CO_2, this topic was associated with the formation of CO.

Scheme 6. Multielectron reduction products of CO_2 [81].

$$CO_2 + 2\,H^+ + 2\,e^- \rightarrow HCOOH \qquad\qquad E_0 = -0.61\ V$$

$$CO_2 + 2\,H^+ + 2\,e^- \rightarrow CO + H_2O \qquad\qquad E_0 = -0.53\ V$$

$$CO_2 + 4\,H^+ + 4\,e^- \rightarrow HCHO + H_2O \qquad\qquad E_0 = -0.48\ V$$

$$CO_2 + 6\,H^+ + 6\,e^- \rightarrow CH_3OH + H_2O \qquad\qquad E_0 = -0.38\ V$$

$$CO_2 + 8\,H^+ + 8\,e^- \rightarrow CH_4 + 2\,H_2O \qquad\qquad E_0 = -0.24\ V$$

CO is the feedstock for several synthetic processes, such as d-metal catalyzed Fischer Tropsch (production of hydrocarbons), Monsanato and Cativa (both acetic acid) processes [112]. Carbon monoxide also has a significant fuel value ($\Delta H_c^0 = -283$ kJ/mol) and can readily be converted into methanol (e.g., by the $CuO/ZnO/Al_2O_3$-catalyzed ICI process) for use as a liquid fuel [113]. The most active and selective catalysts for the photoreduction of CO_2 to CO are Re(I) type catalysts, but as already mentioned in section 2.2, formic acid can also be obtained via homogeneous photocatalytic CO_2 reduction [13–15]. Formic acid has been used as a preservative and an insecticide, as well as a reducing agent and a source of carbon in synthetic chemical industry. However, only a few photocatalysts for selective formation of formic acid from CO_2 have been reported. Yanagida *et al.* published systems based on oligo(*p*-phenylenes) with quantum yields of formic acid formation up to 0.084. Another system developed by the same group involves phenazine as photosensitizer, Co^{III}-cyclam (cyclam = 1,4,8,-11–tetraazacyclotetradecan) as an electron mediator and triethylamine as electron donor. In this case, quantum yields reach values up to 0.07. Both systems require UV-light activation [70,114]. In contrast, Tanaka *et al.* were able to selectively produce $HCOO^-$ via visible light irradiation using $[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)_2(CO)_2]^{2+}$ in a CO_2-saturated TEOA/DMF solution (1:4). The maximum quantum yield in this case is 14% [95,115,116].

According to Scheme 6, the reduction potential for the proton-assisted formation of methane is even smaller than in case of CO formation. Therefore, from a thermodynamic perspective, these photoreduction catalysts should also be capable of producing methane. The reduction of CO_2 to methane, commonly known as the sabatier process, is of substantial industrial importance. This reaction proceeds at high temperatures and hydrogen pressures and is catalyzed by metal catalysts such as Ru, Mo and Ni [117–120]. However, to date, through strictly homogeneous photocatalysis, this process has never been realized, which is probably due to the requirement of eight electrons that need to be transferred. The only report of photocatalytic reduction of CO_2 to methane employed *tris*(bipyrazine)ruthenium(II) as the photosensitizer and a Ru metal colloid as the reduction catalyst. In

aqueous solution in the presence of TEOA, this system selectively formed methane (no CO formation) in a quantum yield of 0.04% [121].

4. Alternatives to Sacrificial Amines

As amine sacrificial donors react to undesirable site products during the catalytic cycle, one of the most challenging goals is to develop catalytic systems which are able to quench the excited state (^{3}MLCT) without sacrificial agents. In this context, Neumann *et al.* published an organometallic-polyoxometalate hybrid complex that is capable of replacing sacrificial amines in the photoreduction of CO_2 by hydrogen (Figure 8) [122]. A first important reaction step is the oxidation of hydrogen forming two protons and two electrons, which has been realized by using the Keggin-type polyoxometalate $H_3PW_{12}O_{40}$ as oxidizing agent. This polyoxometalate was linked to a photocatalyst by coordination of 5,6-(15-crown-5)-1,10-phenanthroline (L) and thus proton and electron transfer between the H_2 oxidative site and the CO_2 reductive site is supported. However, quantum yields and turnover frequencies in the reduction of CO_2 in this system are lower than in some previous rhenium and ruthenium catalyzed photoreductions using amines as sacrificial electron donors.

Figure 8. Photoreduction of CO_2 with H_2 [122].
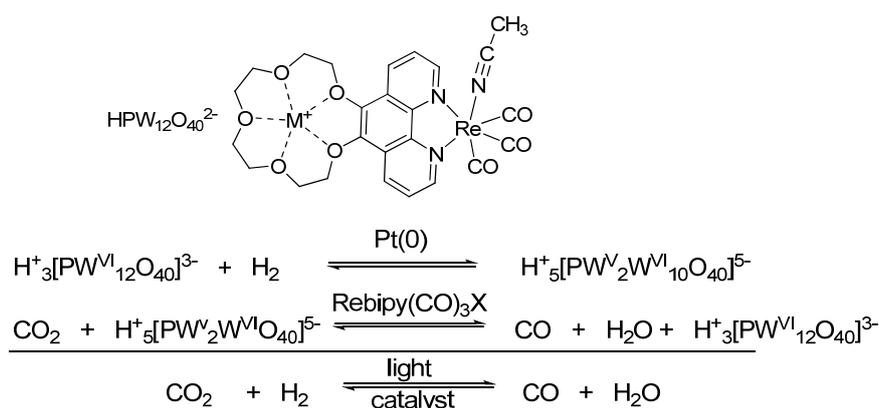
Another possible method to circumvent the use of sacrificial agents has been described by Carpenter *et al.* [123]. Instead of replacing an external reductant, the idea was to recycle the sacrificial agent by hydrogenation. To realize this approach it was necessary to find amine structures which do not form typical reactive species such as amino radicals, enamines and iminium ions from the radical cation, but an alkene product [124]. One suggested structure, with complaints about these requirements, is shown in Figure 9. The tricyclic structure blocks the formation of undesired reactive intermediates and reacts to the corresponding olefinic compound, which can then be converted back to the starting material with a Pd/C catalyst in EtOAc. It has to be mentioned that there is a counterion- and solvent-dependent side reaction of the olefin, as well, which is shown in Figure 10.

One of the most desired reactions in the field of photocatalytic CO_2 reduction is the coupling to water oxidation. There are some reports of photocatalytic water oxidation in homogeneous systems such as molecular ruthenium complexes [125–135], as well as earth abundant metal complexes [136–138] in the presence of sacrificial electron acceptors. In this case, a recently published mononuclear ruthenium

complex shows TOF values up to 0.32 s^{-1} [139]. The main structure motif is a ruthenium center with a tridentate ligand and three picoline ligands (Figure 11).

Figure 9. Tricyclic amine structure as recyclable electron donor [123].

Figure 10. Recycling of the amine donor (**left**) and side reaction (**right**) [123].

Figure 11. Mononuclear ruthenium water oxidation catalyst (WOC) [139].

By varying the tridentate ligand site, Tong *et al.* could show that anionic tridentate ligands compared to neutral ligands demonstrate an increased picoline/water substitution rate which results in higher activity of the catalysts. These results demonstrate a correlation between the activity of WOCs and ligand properties, providing important information for future catalyst design. However, water oxidation in the absence of sacrificial acceptors to date was only realized in heterogeneous systems. For example Kudo *et al.* developed an Ag cocatalyst-loaded ALa$_4$Ti$_4$O$_{15}$ (A = Ca, Sr, Ba) photocatalyst, which reduces CO_2 to CO and HCOOH in aqueous suspension without any additional sacrificial reagents [140]. Furthermore Kajino *et al.* have been able to combine reduction of CO_2 to HCOO$^-$ and water oxidation with a *p*-type InP/Ru-complex polymer hybrid photocatalyst connected to

TiO$_2$. In this case, water is the donor of electrons, as well as the source of protons. The conversion efficiency (solar energy to chemical energy) of this catalytic process is 0.03–0.04%. Therefore, an electrical bias-free reaction approaching photosynthesis was found. Further optimization in selectivity, as well as efficiency, can be achieved by configuration of the energy band, variation of catalyst structure, as well as conjugation conformation [141]. An alternative heterogeneous approach was developed by Yoneyama *et al.* in 1992 (Scheme 7) [142,143]. In this case, malic acid was synthesized from lactic acid and CO$_2$ using a multicomponent system containing a cadmium sulfide suspension as photocatalyst, methylviologen (MV) as electron relay, and malic enzyme (ME) and ferredoxin-NADP$^+$ reductase (FNR). Firstly, photogenerated electrons are transferred from the cadmium sulfide photocatalyst to MV^{2+} and the reduced MV provides the electrons to reduce NADP$^+$ and H$^+$. The resulting hole in the conduction band of the semiconductor particles leads to a potential which is adequate to regenerate the photocatalyst and to oxidize lactic acid. The resulting pyruvic acid is then converted to malic acid by reaction with CO$_2$ and NADPH in a ME-catalyzed process. This catalytic cycle therefore consists of two coupled photoredox reactions. First, the reduction of MV^{2+}, and, second, the oxidation of lactic acid. The C-C bond formation between CO$_2$ and pyruvic acid takes place in the absence of light with the quantum efficiency of this system being around 2.5% [142,143].

Scheme 7. Photocatalytic conversion of lactic acid to malic acid via pyruvic acid [142,143].
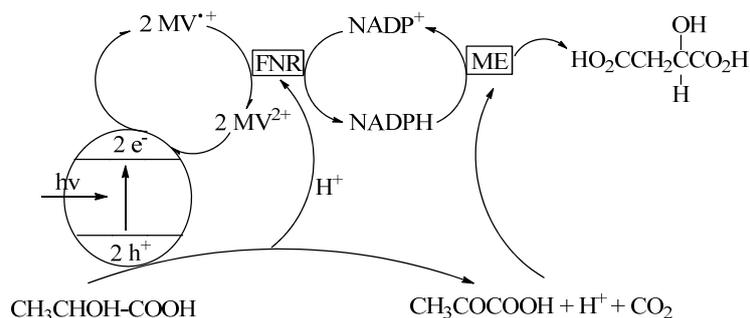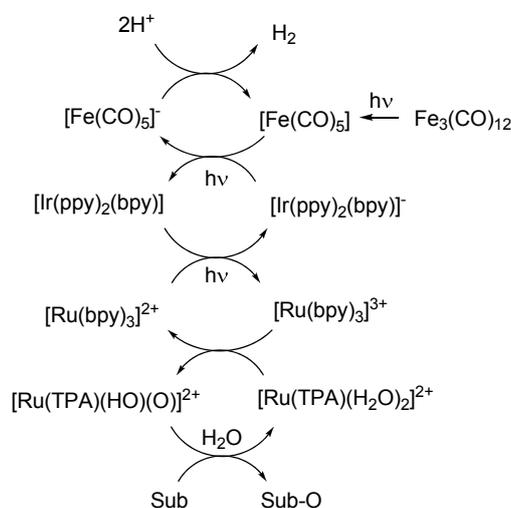

Figure 12. Mechanistic aspects of the hydrogen production coupled to hydrocarbon oxygenation [144].

In 2011, Zhao *et al.* published a light-induced hydrocarbon oxygenation coupled to H$_2$ formation from water splitting (Figure 12) [144]. Starting from the photocatalytic oxidation of hydrocarbons

using $[Co(NH_3)_5Cl]^{2+}$ as sacrificial electron acceptor, Zhao's group has been able to develop a complex system containing a $[Ru(TPA)(H_2O)_2]^{2+}$ photocatalyst, Ru- and Ir photosensitizers as well as the proton reduction catalyst $Fe_3(CO)_{12}$ for water splitting in a one-pot reaction without sacrificial agents (Figure 13). This kind of electron transfer cascade is believed to be a good initial point for photocatalytic CO_2 reduction combined with desirable oxidation processes.

Figure 13. Hydrocarbon oxygenation as electron donor in photocatalysis [144].
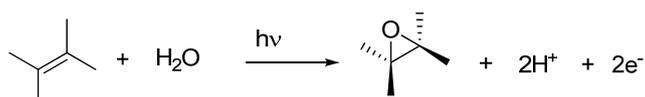
## 5. Structural Parameters for Supramolecular Catalyst Design

The bridging ligand in multinuclear tethered complexes affects the properties of the assemblies, such as photoinduced energy transfer [145–149], and intervalence transition [150,151]. There are many examples of multifunctional CO_2 reduction photocatalysts with visible light absorbing antenna (e.g., $[Ru(dmb)_3]^{2+}$ derivatives) and CO_2 catalytic reduction centers (e.g., $[Re(dmb)(CO)_3Cl]$, where the catalytic activity strongly depends on the efficiency of electron transfer from reduced photosensitizers to catalytic centers [74,75,110,152,153]. By direct comparison of the photocatalytic activity of the two Ru(II)–Re(I) binuclear complexes of Figure 14, one comprising a saturated linker and one with a conjugated linker, it was found that the saturated covalently bridged photocatalyst shows higher activity for the photoreduction of CO_2 compared with its conjugated analogue [154]. The nature of the ligand has an impact on the electrochemical properties of the supramolecular systems, which strongly affects the photoreduction activity [155]. In the case of the conjugated ligand with strong electronic communication across the bridging ligand, the reducing power of the OER species is insufficient for efficient reduction of CO_2. Therefore, strong electronic communication between the photosensitizer moiety and the reduction site lessens the photocatalytic activity even though it accelerates the electron transfer between them. [53].

**Figure 14.** Structures of hetero binuclear Ru(II)–Re(I) complexes.
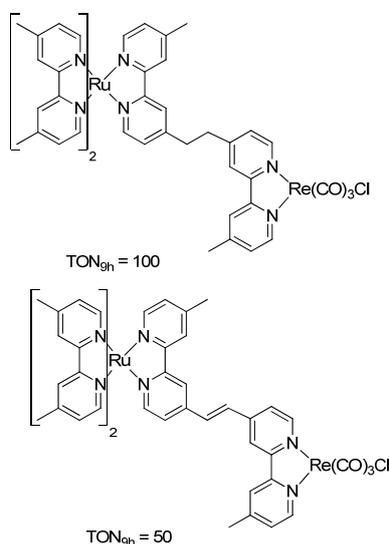
Another consideration for supramolecular systems is adjustment of the distance between the covalently tethered metal centers. Koike *et al.* investigated a series of covalently linked Ru-Re complexes with a saturated alkyl linker of various lengths and compared their activity in the photoreduction of CO_2 (Figure 15). The most efficient catalyst was that comprising of the shortest alkyl chain in the bridging position. According to the photophysical properties of these complexes, the most obvious difference is found in the luminescence quenching with BNAH. According to Stern-Volmer plot measurements, the quenching of the emissive state to form the OER was most effective for the complex with *n* = 2. The quenching fraction affects the efficiency of the photocatalysis of the diad as this reductive quenching is the first process of the photocatalytic reaction [156]. The electron transfer rate from the Ru site to the Re site may be another factor, but it could play only a minor role because it is assumed not to be a rate-determining process in the photocatalytic reaction.

Figure 15. Covalently linked Ru-Re complexes with tethers of different lengths.
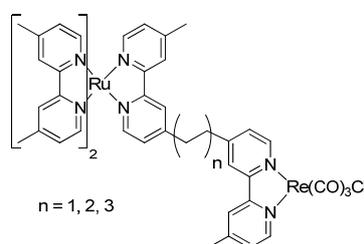
In a recent review [111], the photocatalytic ability of these supramolecular Ru-Re catalysts was further modified by phosphorus ligands on the rhenium site, resulting in one of the most active photocatalysts for CO_2 reduction (TOF_{CO} = 281 h^{-1}). Especially for R = p-FPh, the selectivity towards CO formation and the durability of the catalysts was optimized by the phosphorus ligands (Figure 16).

Figure 16. Modified Ru-Re complexes with phosphorus ligands.
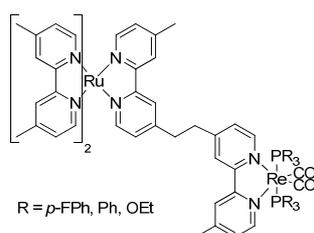
6. Conclusions

In contrast to thermal reactions, photocatalytic systems have the potential to conduct uphill transformations, which cannot be realized by thermal reactions. The central building unit of each visible light photocatalyst is the photosensitizer. The most widely investigated systems are Ru(II) catalysts which are known for their high absorption of visible light and their long-lived ^{3}MLCT state. With regards to the reduction site rhenium(I) catalysts with their high efficiencies and high selectivities towards CO formation have been subject to most study. However, other products such as formates can be obtained via photoreduction of CO_2 with special optimized reduction sites. One major task for prospective investigations is the search for alternatives to the sacrificial donors which are used in most

cases. To date, there are a limited number of reports on alcohol or olefin oxidation that give defined oxidation products, but they are barely used in photoredox reactions with CO_2. The search for supramolecular catalysts that combine both an effective oxidation and reduction site must continue. Many important parameters (e.g., saturated bridging linkers) for the building principle of supramolecular systems have already been identified and will help to find optimized systems.

Acknowledgments

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