Highly Efficient and Selective Photocatalytic CO_2 Reduction by Iron and Cobalt Quaterpyridine Complexes

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S *Supporting Information*

ABSTRACT: The design of highly efficient and selective photocatalytic systems for CO_2 reduction that are based on nonexpensive materials is a great challenge for chemists. The photocatalytic reduction of CO_2 by $[Co(qpy)(OH_2)_2]^{2+}$ (**1**) (qpy = 2,2′:6′,2″:6″,2‴-quaterpyridine) and $[Fe(qpy)(OH_2)_2]^{2+}$ (**2**) have been investigated. With $Ru(bpy)_3^{2+}$ as the photosensitizer and 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole as the sacrificial reductant in CH_3CN/triethanolamine solution under visible-light excitation (blue light-emitting diode), a turnover number (TON) for CO as high as 2660 with 98% selectivity can be achieved for the cobalt catalyst. In the case of the iron catalyst, the TON was >3000 with up to 95% selectivity. More significantly, when $Ru(bpy)_3^{2+}$ was replaced by the organic dye sensitizer purpurin, TONs of 790 and 1365 were achieved in N,N-dimethylformamide for the cobalt and iron catalysts, respectively.

Artificial photosynthesis using solar energy and abundant resources such as H_2O and CO_2 to produce renewable fuels has emerged as the most viable strategy to solve the energy crises and pollution problems associated with the use of fossil fuels. The photocatalytic reduction of CO_2 to products such as CO and CH_3OH is an attractive way to generate renewable fuels and at the same time reduce the amount of CO_2 in the environment.[1,2] CO can be further converted to liquid fuels by the Fischer−Tropsch process.[3,4] Since the reduction of CO_2 is an uphill process with a high energy barrier, appropriate catalysts are required in order for this process to occur at a reasonable rate. A homogeneous photocatalytic system for CO_2 reduction typically consists of a photosensitizer, a sacrificial reductant, and a molecular catalyst. There are many systems employing noble metals such as Re[5−13] and Ru[14−20] as catalysts because of their high activity and stability; however, to make the process economically viable, it is desirable to design catalytic systems that are based on earth-abundant materials. Although there have been a number of reports on catalytic CO_2 reduction by complexes of Co,[21−34] Ni,[23,35−37] Fe,[38−41] and

Mn,[42−45] the efficiency and selectivity of most of these systems need to be improved.

We previously reported that the complex $[Co(qpy)(OH_2)_2]^{2+}$ (**1**) (qpy = 2,2′:6′,2″:6″,2‴-quaterpyridine) is an efficient catalyst for both water oxidation and reduction.[46] We report herein that **1** (Scheme 1) as well as $[Fe(qpy)(OH_2)_2]^{2+}$ (**2**) are also highly efficient and selective catalysts for CO_2 reduction.

Scheme 1. Structures of the Catalysts (1, 2), Photosensitizers ($Ru(bpy)_3^{2+}$, Purpurin), and Sacrificial Reductant (BIH)
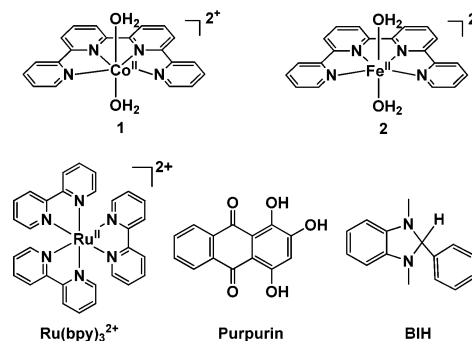
Electrocatalytic CO_2 reduction by **1** was first studied by Wong and Che in 1995, and they reported that controlled-potential electrolysis of **1** at −1.7 V vs SCE in CO_2-saturated MeCN produced CO with a Faradaic efficiency of 80%.[47] In this work, we found that addition of a weak Brønsted acid such as phenol greatly enhances the catalysis by **1** in terms of efficiency and overpotential. In the presence of 1 M phenol, a high Faradaic efficiency of 94% for CO formation was obtained at a lower potential of −1.4 V vs SCE in MeCN after electrolysis for 3 h (Figures S1 and S2), with only 1% H_2 detected. We also investigated electrocatalytic CO_2 reduction by the iron analogue **2**; in this case, the Faradaic efficiency for CO production was found to be only 37% at −1.4 V vs SCE in MeCN, but the selectivity was 100% (Figures S3 and S4).

Encouraged by these preliminary results, we discovered that **1** and **2** are highly efficient catalysts for visible-light-induced CO_2 reduction using $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) as the photosensitizer and 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole (BIH) as sacrificial reductant (Scheme 1). BIH can be easily prepared on a multigram scale and is also commercially available. It has been shown by Ishitani and co-workers that BIH is a highly efficient quencher for the excited state of $Ru(bpy)_3^{2+}$ while triethanolamine (TEOA) functions as a proton acceptor for BIH[+•].[10,20] As shown in Figure 1 and
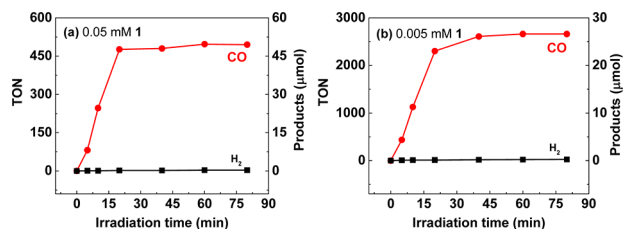

Figure 1. CO (●) and H_2 (■) TONs as functions of time during irradiation (blue LED centered at 460 nm) of a CO_2-saturated MeCN solution containing (a) 0.05 mM or (b) 0.005 mM **1**, 0.3 mM $Ru(bpy)_3^{2+}$, 0.1 M BIH, and 0.5 M TEOA. TON = number of moles of product/number of moles of catalyst.

Table S1, irradiation of a mixture of **1** (0.05 mM), $Ru(bpy)_3^{2+}$ (0.3 mM), BIH (0.1 M), and TEOA (0.5 M) in CO_2-saturated MeCN with a blue light-emitting diode (LED) for 80 min led to the production of CO, formate, and H_2 with turnover numbers (TONs) of 497, 5, and 3, respectively; this gives a selectivity of 98% for CO production. The TON was found to increase when [**1**] was decreased, and at [**1**] = 0.005 mM, the TON for CO was 2660 after irradiation for 80 min with a turnover frequency (TOF) of 117 min^{−1} for the first 20 min. This phenomenon that the TON increases as the concentration of catalyst decreases has also been observed in other systems[32,37] and probably occurs because only a fraction of the catalyst molecules reduce CO_2 while the remainder act a reservoir when the catalyst is progressively deactivated over time. The TONs were much lower when either BIH (114) or TEOA (182) was omitted. Increasing the concentration of $Ru(bpy)_3^{2+}$ from 0.3 to 0.5 mM led to a slight increase in CO (TON increased from 497 to 521), but the selectivity decreased from 98% to 90%. In the absence of **1**, only trace amounts of formate and H_2 were produced, and no CO could be detected (Table S1). Experiments carried out under Ar with no CO_2 gave only a trace amount of H_2.

Dynamic light scattering (DLS) measurements did not reveal the presence of any particles in solution even after irradiation for 4 h, indicating that the catalytic reaction is homogeneous (Figure S5). Experiments were also carried out using $Co(ClO_4)_2$ instead of **1** as the catalyst; in this case, very low TONs of CO (33), formate (11), and H_2 (7) were detected after irradiation for 60 min, indicating that the catalytic activity does not arise from demetalation of the cobalt catalyst (Table S1). Experiments carried out in the presence of Hg(0) gave 24% lower TON (375 vs 497 after 80 min of irradiation; Figure S6). Hg(0) is known to quench the catalytic activity of bulk or colloidal metal(0) by amalgamation, while molecular catalysts are usually less affected.[48] These results suggest that **1** is predominantly a homogeneous molecular catalyst.

Complex **2** was also found to be a highly active catalyst for visible-light-induced CO_2 reduction. In a CO_2-saturated

CH_3CN/TEOA (4:1 v/v) solution containing 0.05 mM **2**, 0.2 mM $Ru(bpy)_3^{2+}$, and 0.1 M BIH, a TON of 1879 for CO and a TOF of 16 min^{−1} (first 90 min) were obtained after irradiation for 3 h (Figure 2a). Formate and H_2 were also
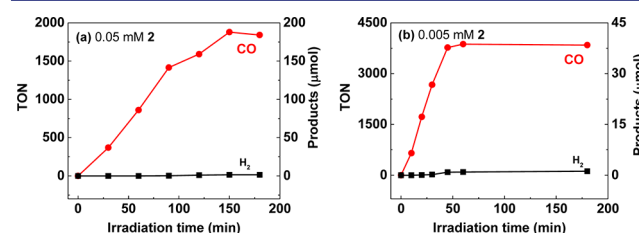

Figure 2. CO (●) and H_2 (■) TONs as functions of time during irradiation of a CO_2-saturated CH_3CN/TEOA (4:1 v/v) solution containing (a) 0.05 mM or (b) 0.005 mM **2**, 0.2 mM $Ru(bpy)_3^{2+}$, and 0.1 M BIH.

produced with TONs of 48 and 15, respectively, giving a selectivity of 97% for CO. When the concentration of **2** was reduced to 0.005 mM, the TON and TOF for CO production increased to 3844 and 87 min^{−1} (first 45 min), respectively (Figure 2b). In this case, the TONs for formate and H_2 were also increased to 534 and 118, respectively; hence, the selectivity for CO was 85%. Reducing the concentration of $Ru(bpy)_3^{2+}$ from 0.2 to 0.05 mM led to lower CO production (TON decreased from 1879 to 1440), probably because of a decrease in the amount of light absorbed (Table S2). As expected, little or no products could be observed in the absence of **2** or CO_2. In the absence of BIH, CO could still be obtained with a TON of 160 and a selectivity of 84% after irradiation for 3 h (Table S2), which are comparable to or even better than those using other iron catalysts.[39,41] Isotopic labeling experiments using [13]CO_2 showed that the product formed was predominantly [13]CO, indicating that CO was generated from CO_2 reduction (Figure S7).

Similar to that of **1**, the catalytic system involving **2** is also homogeneous since DLS measurements revealed the absence of particle formation during 3 h of irradiation (Figure S5). Moreover, experiments in the presence of Hg(0) gave only 23% lower TON (1440 vs 1879 after 4 h of irradiation; Figure S8).

Although catalysts **1** and **2** are based on earth-abundant metals, the sensitizer used for CO_2 reduction, $Ru(bpy)_3^{2+}$, is a noble-metal complex. To make the process economically viable, it is desirable to use an earth-abundant metal complex or an organic compound as the photosensitizer. Fujita and co-workers reported the use of *p*-terphenyl as a photosensitizer,[24−27] but in that case the system only works under UV light (λ < 400 nm). Recently, Bonin and Robert used 9-cyanoanthracene as the photosensitizer for CO_2 reduction by an iron porphyrin catalyst and obtained a TON of 60 and a selectivity of 100% for CO.[39] On the other hand, Ishitani reported the use of $[Cu^I(dmp)(P)_2]^+$ (dmp = 2,9-dimethyl-1,10-phenthroline; P = phosphine ligand) as the photosensitizer and $[Fe^{II}(dmp)(NCS)_2]$ as the catalyst for photocatalytic CO_2 reduction, which gave a TON of 273 and a selectivity of 78% for CO (at 0.05 mM catalyst concentration).[40] In this work, we found that **1** and **2** can also function as highly active catalysts for photocatalytic CO_2 reduction using the cheap and commercially available organic dye purpurin as the photosensitizer. The negative reduction potential, strong absorption in the visible region, and relatively intense emission of purpurin (Figure S9) suggest that it can function as a

photosensitizer for photocatalytic CO_2 reduction. N,N-Dimethylformamide (DMF) was used as the solvent instead of MeCN because purpurin has poor solubility in MeCN. With 0.05 mM **1**, 2 mM purpurin, and 0.1 M BIH in CO_2-saturated DMF, TONs of 197, 9, and 1 were obtained for production of CO, formate, and H_2, respectively, corresponding to 95% selectivity for CO (Figure 3a). When the concentration of **1**
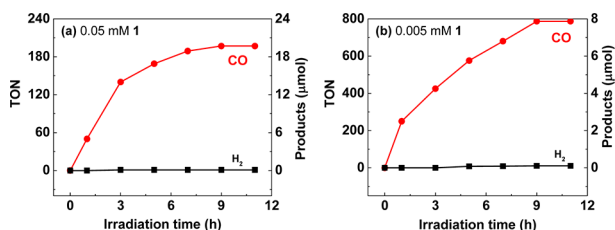

Figure 3. CO (●) and H_2 (■) TONs as functions of time during irradiation of a CO_2-saturated DMF solution containing (a) 0.05 mM or (b) 0.005 mM **1**, 2 mM purpurin, and 0.1 M BIH.

was reduced to 0.005 mM, the TON for CO production increased to 790 (Figure 3b). More impressively, when **2** was used as the catalyst, a TON of 520 was achieved for CO (97% selectivity) using 0.05 mM **2**, 0.02 mM purpurin, and 0.1 M BIH (Figure 4a). The TON further increased to 1365 (92%
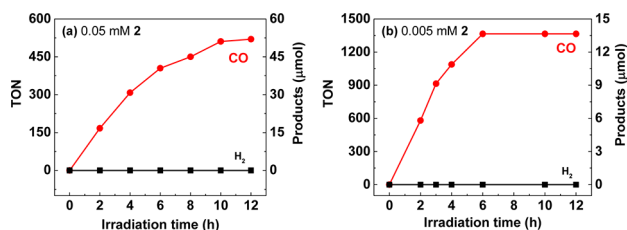

Figure 4. CO (●) and H_2 (■) TONs as functions of time during irradiation of a CO_2-saturated DMF solution containing (a) 0.05 mM or (b) 0.005 mM **2**, 0.02 mM purpurin, and 0.1 M BIH.

selectivity of CO) when the concentration of **2** was reduced to 0.005 mM (Figure 4b). No H_2 was detected and the amount of formate was less than that that under Ar or without **2**, so the selectivity for CO was 100% (Table S4). Isotopic labeling experiments using $^{13}CO_2$ demonstrated that CO was generated from CO_2 reduction (Figure S10).

The purpurin catalytic systems are also likely to be homogeneous, since DLS measurements showed no particle formation during 10 h of irradiation (Figure S11). Moreover, experiments in the presence of Hg(0) gave only 21% and 24% lower TON for **1** and **2**, respectively (154 vs 196 for **1** after 11 h of irradiation and 395 vs 520 for **2** after 12 h of irradiation; Figure S12).

Experiments were carried out to better understand the factors that cause the catalysis to stop (Figure S13−S17). The loss of catalytic activity is mainly due to the decomposition of the catalyst and photosensitizer as well as consumption of BIH.

Quantum yields for CO production (Φ_{CO}) were determined by ferrioxalate actinometry. When $Ru(bpy)_3^{2+}$ was used as the sensitizer, the quantum yields for the overall photocatalytic reduction of CO_2 to CO were 2.8% for **1** and 8.8% for **2** after irradiation for 12 h at 458 nm (see the Supporting Information for details). These values are the highest reported for homogeneous systems using earth-abundant metal catalysts, matched only by very recent results obtained by Ishitani and

co-workers with an iron-based catalyst.[40] When purpurin was used as the sensitizer, good CO quantum yields of 0.8% for **1** and 1.1% for **2** were also obtained after irradiation for 24 h at 458 nm.

Quenching of the excited state of $Ru(bpy)_3^{2+}$ by BIH and catalyst was also investigated. The bimolecular quenching rate constants for BIH, **1**, and **2** obtained from Stern−Volmer plots are 4.0×10^9, 2.1×10^8, and 8.3×10^7 $M^{-1} \cdot s^{-1}$, respectively (Figure S18). These results suggest that for the two catalytic systems, the excited state of $Ru(bpy)_3^{2+}$ is reductively quenched by BIH as a result of its higher quenching rate and much higher concentration compared with the catalyst. Transient absorption spectroscopy showed the formation of $Ru(bpy)_3^+$ upon laser excitation of a solution of $Ru(bpy)_3^{2+}$ and BIH in $CH_3CN/$TEOA, which is similar to Ishitani's system using $[Ru(dmb)_3]^{2+}$ (dmb = 4,4′-dimethyl-2,2′-bipyridine) as the photosensitizer (Figure S19).[10,49]

A plausible mechanism for photocatalytic reduction of CO_2 to CO by the M^{II} qpy complexes is shown in Scheme 2. With

Scheme 2. Proposed Mechanism for the Photocatalytic Reduction of CO_2 to CO for the 1 (M = Co) or 2 (M = Fe)/$Ru(bpy)_3^{2+}$/BIH/TEOA Systems
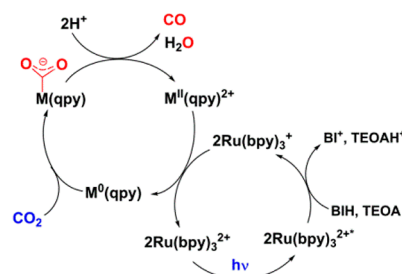
both metals, the M^{II} catalyst is first doubly reduced to the active species (formally M^0, as shown by Wong and Che for the electrochemical reduction of CO_2 with the Co complex[47]) by $[Ru(bpy)_3]^+$, which is generated by the reductive quenching of $[Ru(bpy)_3]^{2+*}$ with BIH. CO_2 then binds to the reduced metal through the carbon atom to form a M−CO_2 adduct, after which protonation gives CO and regenerates the catalyst. A similar mechanism is postulated for catalysis using purpurin as the photosensitizer. Further spectroscopic and density functional theory studies will shed more light on the mechanisms and will be reported in due course.

In conclusion, we have reported highly efficient and selective photocatalytic CO_2 reduction by cobalt(II) and iron(II) complexes bearing a quaterpyridine ligand. The TONs and TOFs obtained from these catalysts are among the highest reported to date for homogeneous photocatalytic CO_2 reduction. More significantly, these complexes are also highly active and selective catalysts when using the cheap and commercially available organic dye purpurin as the photosensitizer, with the highest TONs and TOFs for CO formation reported to date for systems using all earth-abundant materials. Our results represent a significant step toward the development of practical catalysts for CO_2 reduction.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b06002.

Experimental details (synthesis, photocatalytic and electrochemical studies, quantum yield determination, fluorescence quenching, transient absorption, dynamic light scattering) and additional data (PDF)

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The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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