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Article

Selective photocatalytic reduction of CO₂ to CO mediated by a [FeFe]-hydrogenase model with a 1,2-phenylene S-to-S bridge

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ABSTRACT

Photocatalytic reduction of CO₂ to CO is a promising approach for storing solar energy in chemicals and mitigating the greenhouse effect of CO₂. Our recent studies revealed that [(μ-bdt)Fe₂(CO)₆] (**1**, bdt = benzene-1,2-dithiolato), a [FeFe]-hydrogenase model with a rigid and conjugate S-to-S bridge, was catalytically active for the selective photochemical reduction of CO₂ to CO, while its analogous complex [(μ-edt)Fe₂(CO)₆] (**2**, edt = ethane-1,2-dithiolato) was inactive. In this study, it was found that the turnover number of **1** for CO evolution reached 710 for the **1**/[Ru(bpy)₃]²⁺/BIH (BIH = 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]-imidazole) system under optimal conditions over 4.5 h of visible-light irradiation, with a turnover frequency of 7.12 min⁻¹ in the first hour, a high selectivity of 97% for CO, and an internal quantum yield of 2.8%. Interestingly, the catalytic selectivity of **1** can be adjusted and even completely switched in a facile manner between the photochemical reductions of CO₂ to CO and of protons to H₂ simply by adding different amounts of triethanolamine to the catalytic system. The electron transfer in the photocatalytic system was studied by steady-state fluorescence and transient absorption spectroscopy, and a plausible mechanism for the photocatalytic reaction was proposed.

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1. Introduction

Photocatalytic reduction of CO₂ has become one of the most attractive topics in the fields of catalysis and sustainable chemistry since the first pioneering work on this topic [1,2]. The photosynthetic processes in photocatalytic CO₂ reduction can not only store solar energy in chemical forms, but also alleviate the greenhouse effect of CO₂ on the climate. Photocatalytic CO₂ reduction is an ideal approach for converting waste CO₂ to value-added low carbon products that can be employed either as alternative energy sources for the limited fossil fuel resources or as industrial feedstocks for the synthesis of a variety of valuable hydrocarbon products. The development of highly active, selective, stable, and inexpensive catalysts for photochemical

CO₂ reduction reaction (CRR) is the key scientific problem that must be solved in order to achieve this highly attractive but challenging goal.

In recent years, increasing attention has been directed to first-row transition metal-based molecular CO₂-reduction catalysts (MCRs) in order to provide economically viable technologies for practical applications [3–6]. Although a number of MCRs based on Mn [7–10], Fe [11–23], Co [20–33], Ni [34–38], and Cu [39] were reported over the past several decades, most of the investigated earth-abundant catalysts display low reaction rate and/or low selectivity for light-driven CRR. Many MCRs afforded a mixture of C₁ products, predominantly CO and formic acid [10,15,24], together with large amounts of H₂ derived from proton reduction [9,11,20,23,39]. To date, only

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a few non-precious metal-based MCRCs displayed high rates ($> 100 \text{ h}^{-1}$) with high selectivity for the photochemical CO_2 -to-CO conversion [20,31–35,40,41]. Hence, the development of earth-abundant MCRCs with both high activity and selectivity for visible-light-driven CRR is still a great challenge for the researchers in the catalysis community.

The [NiFe] carbon monoxide dehydrogenase (CODH) with a dinuclear active site found in nature displays high activity and perfect selectivity for the reduction of CO_2 to CO due to the synergistic effect of the adjacent Ni and Fe ions in the CODH cofactor [42]. However, the reported MCRCs for the photochemical CO_2 reduction are mostly mononuclear complexes except for the following few examples of dinuclear complexes: $[\{\text{Re}(\text{CO})_3\text{X}\}_2(\text{L}1)]$ ($\text{L}1 = 1,2\text{-bis}(4,4'\text{-methyl-[2,2']bipyridyl})\text{ethane}$; $\text{X} = \text{Br}, \text{NCS}$) [43], $[\{\text{Ir}(\text{tpy})\text{X}\}_2(\text{L}2)]^{2+}$ ($\text{L}2 = 1,2\text{-bis}(2\text{-phenylpyridin-4-yl})\text{ethane}$; $\text{tpy} = \text{terpyridine}$; $\text{X} = \text{Cl}, \text{I}$) [44], and $[\text{Ni}_2(\text{L}3)]^{4+}$ ($\text{L}3 = 6,6'\text{-bi}(5,7\text{-dimethyl-1,4,8,11-tetraazacyclotetradecane})$) [45]. In these dinuclear MCRCs, the two metal sites of the catalyst molecule are located too far away from each other to exert a substantial synergistic effect on photocatalytic CRR. Recently, Lu and co-workers reported that $[\text{CoM}(\text{OH})(\text{L}4)]^{3+}$ ($\text{M} = \text{Co}, \text{Zn}$; $\text{L}4 = \text{N}[(\text{CH}_2)_2\text{NHCH}_2(m\text{-C}_6\text{H}_4)\text{CH}_2\text{NH}(\text{CH}_2)_2\text{N}]$) dinuclear complexes displayed significantly higher activity and selectivity for the reduction of CO_2 to CO than the corresponding mononuclear complexes due to the synergistic catalytic effect between the adjacent metal ions of the catalyst molecule [32,33]. These appealing results show that earth-abundant dinuclear complexes with two metal ions located in close proximity to each other are highly promising for application in selective CO_2 reduction.

Recently, we demonstrated the high catalytic activity of the $[(\mu\text{-bdt})\text{Fe}_2(\text{CO})_6]$ (**1**, $\text{bdt} = \text{benzene-1,2-dithiolato}$) diiron dithiolate complex containing a rigid and conjugate S-to-S bridge for the electrochemical CO_2 reduction in $\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$, affording formic acid as the major product (81%) together with small amounts of CO and H_2 [46]. In continuous studies, we examined the catalytic performance characteristics of **1** and a reference complex, $[(\mu\text{-edt})\text{Fe}_2(\text{CO})_6]$ (**2**, $\text{edt} = \text{ethane-1,2-dithiolato}$, Fig. 1), for the photochemical CO_2 reduction, using $[\text{Ru}(\text{bpy})_3]^{2+}$ as the photosensitizer and 1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo[*d*]-imidazole (BIH) as the sacrificial electron donor in acetonitrile. Here, we report that **1** exhibits a high catalytic activity (7.12 min^{-1}) for CO evolution in the first hour of visible-light-driven CO_2 reduction, with a superior selectivity for CO (97%). Most interestingly, we find that the catalytic selectivity of **1** can be adjusted and even completely switched between the photochemical CRR and the hydrogen evolution reaction (HER) through the addition of a controlled amount of triethanolamine (TEOA) to the system.

Fig. 1. Structures of the diiron dithiolate complexes **1** and **2** used in the present work.

In sharp contrast, the analogous diiron complex **2** was inactive for the photochemical CO_2 reduction under the same conditions. To the best of our knowledge, the present work is the first demonstration of the catalytic activity of a hydrogenase model complex for photochemical CRR that expands the catalytic versatility of the [FeFe]-hydrogenase ([FeFe]-H₂ase) models to reactions beyond proton reduction.

2. Experimental

2.1. Materials

Anhydrous acetonitrile (Energy Chemical, 99.9%, water $\leq 50 \text{ ppm}$, packaged under argon in a resealable ChemSeal bottle) was used as received. 1,3-Dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo[*d*]-imidazole (BIH) was purchased from local suppliers, and $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ from Energy Chemical. Triethanolamine (TEOA) and mercury with the purity of 99.999% were purchased from Aladdin, and $n\text{Bu}_4\text{NPF}_6$ was obtained from J&K Chemical. Gaseous CO_2 (99.999 %) and argon (99.999 %) were purchased from local suppliers, and $^{13}\text{CO}_2$ (^{13}C 99%) was obtained from Cambridge Isotope Laboratories, Inc. The $[\text{Fe}_2(\mu\text{-bdt})(\text{CO})_6]$ (**1**) and $[\text{Fe}_2(\mu\text{-edt})(\text{CO})_6]$ (**2**) diiron complexes were prepared according to the procedures reported in the literatures [47,48]. All other chemicals were reagent grade and were used as received.

2.2. Photocatalytic experiments

The photocatalytic reaction was carried out in a 10 mL Schlenk bottle equipped with a large spherical glass vessel (volume of 150 mL) to reduce the concentration of CO in the gaseous phase of the reaction system for accurate GC analysis with an FID detector. A lightproof plate with a $1 \times 1 \text{ cm}^2$ square hole was placed in front of the lower part of the Schlenk bottle. The typical photocatalytic experiment was carried out with diiron catalyst (20 μM), $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ (0.2 mM), and BIH (20 mM) in CH_3CN (5 mL) or $\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$ at 298 K. The solution was purged with CO_2 for 30 min prior to irradiation using a Xe lamp (CEL-HXF 300, 100 mW cm^{-2}) equipped with a 420 nm long-pass filter. To cut off infrared light, a 3-cm-long glass cell filled with deionized water was placed between the Xe lamp and the Schlenk bottle.

The gaseous products of the photocatalytic reaction in the headspace of the bottle were analyzed using a gas chromatograph (GC-2014, Shimadzu, Japan) equipped with TCD and FID detectors. The FID detector was fitted with a methanizer to detect CO at the detection limit of 0.5 ppm. The TCD detector was used to detect H_2 at the detection limit of 1 ppm. The amounts of the evolved CO and H_2 were calculated on the basis of the GC analysis. The product ^{13}CO obtained from $^{13}\text{CO}_2$ reduction was confirmed by GC-MS spectra measured using an Agilent 7890A GC instrument (Agilent, USA) equipped with a HP-PLOT (30 m $\times$ 320 μm) capillary column that was connected to an Agilent 5975C MS spectrometer (Agilent, USA) with a triple-axis detector. The liquid product (HCOOH) in the resulting electrolyte was detected using an ion chromatograph

(ThermoFisher DIONEX ICS-5000) equipped with an electrical conductivity detector and an ionic exchange column. The liquid product was also detected by NMR spectroscopy carried out using a Bruker Avance III 500 spectrometer.

2.3. Determination of internal quantum yield (IQY_{CO})

In a typical experiment, the system containing **1** (20 μM), [Ru(bpy)₃](PF₆)₂ (0.4 mM), and BIH (20 mM) in CH₃CN (5 mL)/CH₃OH (1.5 M) was used as the sample for quantum yield evaluation. The light source was a 300 W Xe lamp (CEL-HXF 300) equipped with a 420 nm band pass filter. The light intensity was measured with a CEL-NP 2000 laser power meter, and was 55 and 13 mW cm⁻², respectively, at the front and back point of the reactor (irradiation area of approximately 1.0 cm²). The absorbed power was calculated as follows:

$$(55 \text{ mW cm}^{-2} - 13 \text{ mW cm}^{-2}) \times 1.0 \text{ cm}^2 = 42 \text{ mW}.$$

The photoreaction was carried out for 2 h at 298 K and released approximately 14.86 μmol CO. The number of moles of photons (n_p) absorbed by the photosensitizer was determined using Eq. (1):

$$n_p = Pt\lambda/N_Ahc \quad (1)$$

where n_p is the number of the moles of the photons absorbed by the photosensitizer, P is the absorbed power of the light, t is the irradiation time, λ is the irradiation wavelength number, N_A is the Avogadro constant ($6.02 \times 10^{23} \text{ mol}^{-1}$), h is the Planck constant ($6.63 \times 10^{-34} \text{ J s}$), and c is the speed of the light ($3.0 \times 10^8 \text{ m s}^{-1}$).

The internal quantum yield (IQY_{CO}) was evaluated for two-electron reduction of CO₂ using Eq. (2).

$$\text{IQY}_{\text{CO}} = 2n_{\text{CO}}/n_p \quad (2)$$

An IQY_{CO} of 2.8% was calculated on the basis of the measured n_{CO} (14.86 μmol) and n_p (1.06 mmol) during 2 h of irradiation.

2.4. Steady-state fluorescence and transient absorption measurements

Photoluminescence spectra were recorded using a Fluoro-Max-4 fluorimeter (Horiba Jobin Yvon, Inc.). The quenching rate constant (k_q) of electron transfer from BIH to *[Ru(bpy)₃]²⁺ in CH₃CN was calculated using the Stern-Volmer equation:

$$I_0/I = 1 + k_q\tau_0[Q] \quad (3)$$

Table 1

Photochemical CO₂ reduction in the presence of **1** and **2** under different conditions.

Catalyst	Additive	CO (μmol)	H ₂ (μmol)	TON CO / H ₂	CO selectivity (%)
1	—	25.6	0.07	256/0.7	> 99
2	—	0.06	0.03	0.6/0.3	—
1	0.5 M CH ₃ OH	25.3	0.2	253/2	> 99
1	1.5 M CH ₃ OH	38.9	2.5	389/25	94
1	2% TEOA	9.8	12.4	98/124	44
1	20% TEOA	0.9	102	9/1020	< 2

^a Reaction conditions: complex **1** or **2** (20 μM), [Ru(bpy)₃]²⁺ (0.2 mM), and BIH (20 mM) in CO₂-saturated CH₃CN (5 mL), without and with addition of CH₃OH or TEOA, and under irradiation.

where I_0 and I are the emission intensities of *[Ru(bpy)₃]²⁺ in the absence and presence of BIH, and τ_0 is the lifetime of *[Ru(bpy)₃]²⁺ in CH₃CN ($\tau_0 = 1.10 \text{ μs}$ at 293 K) [49].

Transient absorption spectra and kinetics traces were measured using a laser flash photolysis spectrometer (Edinburgh Instrument, LP920) in combination with a probe xenon light (Edinburgh Instrument, Xe920). The transient absorption spectra and kinetic data were measured using a Nd:YAG laser pulse excited at 355 nm, and the lifetimes were calculated from the kinetic data by single exponential fitting.

3. Results and discussion

3.1. Photocatalytic CO₂ reduction by complexes **1** and **2**

Initially, the photocatalytic CO₂ reduction was carried out with **1** as the catalyst in dry CH₃CN under irradiation by a Xe lamp ($\lambda > 420 \text{ nm}$, 100 mW cm⁻²). Based on the GC analysis of the gaseous products in the headspace of the catalytic system, 25.6 μmol CO and a negligible amount of H₂ (Table 1) were released from the catalytic system during 1.5 h of irradiation (Fig. 2), corresponding to a turnover number (TON_{CO}) of 256. To examine the liquid products obtained from CO₂ reduction, we conducted the reaction in CO₂-saturated CD₃CN. After 2 h of irradiation, formic acid was not detected in the resulting solution by ¹H NMR spectroscopy and ion chromatographic analysis. Moreover, no signal for formic acid was observed in the ¹³C NMR spectrum of the solution obtained from the ¹³CO₂-labeling experiment. Therefore, the photochemical CRR catalyzed by **1** demonstrated an almost quantitative selectivity (> 99%) for CO.

By contrast, when CRR was carried out with **2** as the catalyst, only a trace amount of CO was detected after 1.5 h of irradiation (Table 1), which was similar to the amount of CO evolved from the control reaction in the absence of a catalyst under otherwise identical conditions. This observation indicated that **2** was inactive for photochemical CO₂ reduction, even though its Fe₂S₂-butterfly framework is analogous to that of **1**. The distinctly different catalytic behaviors of **1** and **2** can be explained based on the difference in their redox properties.

Fig. 2. Time-dependent evolution of CO and H₂ during photocatalytic CO₂ reduction with the system of **1** (20 μM), [Ru(bpy)₃](PF₆)₂ (0.2 mM), and BIH (20 mM), in dry CH₃CN or CH₃CN/CH₃OH (1.5 M); the solution was saturated with CO₂ and irradiated by visible light ($\lambda > 420 \text{ nm}$).

Table 2

Control experiments under different conditions.

Entry	[1] (μM)	[Ru(bpy) ₃] ²⁺ (mM)	[BIH] (mM)	TON _{CO}	TON _{H₂}
1	20	0.2	20	255	0.7
2	0	0.2	20	0.7	1.2
3	20	0.2	0	1.5	0
4	20	0	20	0	0
5 ^a	20	0.2	20	0	0
6 ^b	20	0.2	20	0.3	0.8

Reaction conditions: in CO₂-saturated CH₃CN (5 mL) under 1.5 h of irradiation.^a In the dark.^b Under Ar (without CO₂).

Complex **1** with a reversible two-electron reductive potential ($E_{1/2}(\text{FeFe})$) at -1.33 V vs $\text{Fc}^{+/0}$ [46] is readily reduced to **1**²⁻ by [Ru(bpy)₃]⁺ ($E_{1/2}(\text{Ru}) = -1.73$ V vs $\text{Fc}^{+/0}$) [50] with a large driving force. Meanwhile, for **2**, the first reduction potential (E_{red1}) is found at -1.69 V vs $\text{Fc}^{+/0}$ and the second reduction potential (E_{red2}) is found at -2.11 V [46], which is more negative than $E_{1/2}(\text{Ru})$ of the [Ru(bpy)₃]²⁺/[Ru(bpy)₃]⁺ couple. Therefore, although **2** can be reduced to **2**⁻ by [Ru(bpy)₃]⁺ with a very small driving force, the further electron transfer from [Ru(bpy)₃]⁺ to **2**⁻ is not thermodynamically feasible. Therefore, the photocatalytic CRR cannot be triggered in the **2**/[Ru(bpy)₃]²⁺/BIH system. The rigid and conjugate S-to-S bridge endows complex **1** with unique redox properties that endow it with catalytic characteristics different from those of the other [FeFe]-H₂ase models.

Control experiments were performed to understand the role of each component of the photocatalytic system for the selective photocatalytic CO₂ reduction. In the absence of **1**, only a trace amount of CO (ca. 0.07 μmol) was detected (Table 2, entry 2), showing that **1** acted as the catalyst in the photochemical CO₂ reduction. Notably, similar amounts of H₂ were evolved in the absence and presence of **1**, implying that H₂ evolution was at least in part not caused by catalysis by **1** under test conditions. In the absence of BIH, a very small amount of CO (0.15

μmol) was detected (Table 2, entry 3), while no H₂ was found. These observations suggested that (i) a small fraction of coordinated-COs was dissociated from the all-CO diiron catalyst **1** under irradiation in the absence of BIH and (ii) BIH may act as a proton source for H₂ generation in the photocatalytic system. Moreover, neither CO nor H₂ were detected when the reaction was carried out in the absence of [Ru(bpy)₃]²⁺ or in the dark (Table 2, entries 4 and 5), indicating that both CO₂ and proton reductions were indeed driven by visible light. Under Ar, only 0.03 μmol CO was detected together with 0.08 μmol H₂ after 1.5 h of photolysis (Table 2, entry 6). Here, the trace amount of CO detected from the reaction under Ar in the absence of CO₂ may originate from the slight degradation of catalyst **1**. Importantly, the ¹³CO/CO ratio of approximately 99:1 in the gaseous phase of the ¹³CO₂-labeling experiment after 2 h of irradiation was estimated by a GC-MS assay with a method of total ion current (TIC) detection and extracted ion current (EIC) chromatogram (Fig. 3(a)), confirming that the carbon source of CO originated from CO₂. To verify that the photochemical CRR was homogeneous, we conducted the commonly used Hg poison test. The amount of CO generated in the presence of Hg was nearly equal to that produced in the absence of Hg (Fig. 3(b)). All the results of the control experiments demonstrated that **1** acted as an efficient and selective molecular catalyst in photochemical CRR.

3.2. Influences of CH₃OH and TEOA on the photocatalytic CO₂ reduction by **1**

Our previous studies demonstrated that the addition of CH₃OH significantly enhanced the catalytic activity of **1** for the electrochemical CO₂ reduction in CH₃CN [46]. Therefore, we studied the photocatalytic CRR in CH₃CN/CH₃OH with other conditions kept the same as those for the experiments described above. We found that the addition of 0.5 M CH₃OH to the CO₂-saturated CH₃CN did not have a noticeable effect on the activity and selectivity of photocatalytic CRR by **1** (Table 1). Upon the increase in the concentration of CH₃OH in the reaction solution to 1.5 M, the TON_{CO} was enhanced to 389 over 2.5

Fig. 3. (a) Mass spectrum of CO obtained from the system of **1** (20 μM), [Ru(bpy)₃]²⁺ (0.2 mM), and BIH (20 mM) in ¹³CO₂-saturated MeCN solution after 2 h of irradiation. (b) Time-dependent evolution of CO and H₂ during the photocatalytic CO₂ reduction with the systems of **1** (20 μM), [Ru(bpy)₃]²⁺ (0.2 mM), and BIH (20 mM) in dry MeCN in the absence and presence of Hg (20 μL); the solutions were saturated with CO₂ and irradiated by visible light.

Fig. 4. Time-dependent evolution of CO and H₂ detected in the photocatalytic CO₂ reduction carried out by the irradiation of the CO₂-saturated CH₃CN solution of **1** (20 μM), [Ru(bpy)₃](PF₆)₂ (0.2 mM), and BIH (20 mM) containing 2% (v/v) (a) and 20% (v/v) (b) TEOA.

h of irradiation with a slight decrease in the selectivity for CO (~94%, Fig. 2), while the turnover frequency (TOF) for CO evolution in the first hour was 3.89 min⁻¹. In all cases, formic acid was not detected in the resulting solutions by either ¹H NMR spectroscopy or ion chromatography. We observed that the selectivity of photochemical CRR is different from that observed for the electrochemical CRR catalyzed by **1** in CH₃CN/CH₃OH. The calculated internal quantum yield (IQY) of CO evolution from the photocatalytic CO₂ reduction by **1** is 2.8% under irradiation at 420 nm.

Several reports in the literature suggested that TEOA acts as a proton acceptor in the photocatalytic systems with BIH acting as an electron donor, facilitating the conversion of BIH^{•+} to BI[•] and promoting the CRR activity [12,20,51]. Interestingly, we found that the selectivity of the photocatalytic reaction can be adjusted by the addition of TEOA to the **1**/[Ru(bpy)₃]²⁺/BIH system in CO₂-saturated CH₃CN. With the addition of 2% (v/v) TEOA, the H₂ production was increased significantly with the CO/H₂ ratio changing from 99:1 to 44:56 (Fig. 4(a)); furthermore, with the addition of 20% (v/v) TEOA, the selectivity of the products was completely switched from CO to H₂ (selectivity for H₂ > 98%), with a TON_{H₂} of 1020 over 1.5 h of irradiation (Fig. 4(b), Table 1). The reason for the switch of the reaction

selectivity in the presence of TEOA will be discussed below in the mechanism section.

3.3. Optimization of the concentration of the components in photocatalytic CRR

Subsequently, the influences of the concentrations of **1**, [Ru(bpy)₃]²⁺, and BIH on the CO₂ reduction performance of the photocatalytic system were explored. Fig. 5(a) shows that the amount of CO evolved from the system is proportional to the concentration of **1** and ranges from 5 to 20 μM. The output of CO increases linearly with reaction time during the initial 90 min of irradiation, and the plot of *k*_{obs(CO)} versus [**1**] shows a linear dependence of the CO-evolution rate on [**1**] (Fig. 5(b)), suggesting first-order kinetics of the catalyst.

As shown in Fig. 6(a), the concentration of the photosensitizer has a significant influence on the CO-evolution rate. When the concentration of [Ru(bpy)₃]²⁺ was increased from 0.2 to 0.6 mM, the TON_{CO} was enhanced from 392 to 556 over 4 h of irradiation (Table 3), with the TOF_{CO} rising to 6.73 min⁻¹ in the first 60 min. It is important to note that the CO-evolution activity in the initial 1.5 h of irradiation was considerably enhanced with increase in the concentration of [Ru(bpy)₃]²⁺ from 0.4 to 0.6

Fig. 5. (a) Time evolution of CO evolved from the system of [Ru(bpy)₃]²⁺ (0.4 mM) and BIH (20 mM) with varied concentrations of **1** in CO₂-saturated CH₃CN/CH₃OH (1.5 M) under irradiation (λ > 420 nm) over 3.5 h; (b) Plot of the CO evolution rate (*k*_{obs(CO)}) versus [**1**] in the first 90 min of irradiation.

Fig. 6. Time-dependent evolution of CO and H₂ from different photocatalytic systems. (a) **1** (20 μM) and BIH (20 mM) with varied concentration of [Ru(bpy)₃]²⁺; (b) **1** (20 μM) and [Ru(bpy)₃]²⁺ (0.6 mM) with varied concentration of BIH in CO₂-saturated CH₃CN/CH₃OH (1.5 M) under irradiation.

mM, while the same limiting TON_{CO} was attained that was caused by the low concentration of BIH remaining in the solution after 1.5 h of photolysis. When the initial concentration of BIH was increased from 20 to 40 mM, the TON_{CO} increased to 710 with a TOF_{CO} of 7.12 min⁻¹ in the initial 60 min (Table 3, Fig. 6(b)). In fact, the TOF_{CO} of **1** is higher than the reported values of most Fe-based molecular catalysts for photochemical CO₂ reduction [12,16–19,22], with the exception of the benchmark TOF_{CO} (16 min⁻¹ in the first 90 min) reported for [Fe(qpy)(OH₂)₂]²⁺ (qpy = 2,2':6',2'':6'',2''':6'''-quaterpyridine) [20]. In particular, the H₂ evolution did not show considerable changes with the variation in the concentrations of **1**, [Ru(bpy)₃]²⁺, and BIH within the tested ranges, indicating that the high selectivity of CO for photocatalytic CRR was maintained under these conditions (Table 3).

3.4. Stability of the **1**/[Ru(bpy)₃]²⁺/BIH three-component system for photocatalytic CRR

For the system containing **1** (20 μM), [Ru(bpy)₃]²⁺ (0.2 mM), and BIH (20 mM) in CO₂-saturated CH₃CN/CH₃OH (1.5 M), CO evolution gradually slowed down after approximately 90 min of irradiation and almost ceased after 150 min of irradiation (Fig. 7). To understand the origin of this deactivation of the system, two individual experiments were carried out with the re-addition of **1** or [Ru(bpy)₃]²⁺ to the catalytic system after

150 min of irradiation. The catalytic activity for CO evolution was apparently recovered when [Ru(bpy)₃]²⁺ was re-added to the deactivated system, while the re-addition of **1** led to only a slight recovery of the CO-evolution activity. These results suggested that the cessation of CO evolution was mainly due to the deactivation of the photosensitizer while the catalyst degradation played only a minor role.

3.5. Possible mechanism for the photocatalytic CRR by **1**

To obtain insights into the mechanism of the photoinduced electron transfer in the **1**/[Ru(bpy)₃]²⁺/BIH system, we studied luminescence quenching of the excited state of [Ru(bpy)₃]²⁺ by **1** and BIH, respectively. The results showed that the luminescence of [Ru(bpy)₃]²⁺ cannot be quenched by the addition of 0.1–1.3 equiv of **1** to the CH₃CN solution of [Ru(bpy)₃]²⁺ (Fig. 8(a)), while it was apparently quenched by the addition of 12–100 equiv of BIH (Fig. 8(b)). In fact, in the photocatalytic CRR, the **1**/[Ru(bpy)₃]²⁺ ratio was in the range of 0.01–0.2, and the BIH concentration was 25–200 times greater than that of [Ru(bpy)₃]²⁺. Therefore, the excited state *[Ru(bpy)₃]²⁺ was reductively quenched by BIH in the initial period of the photo-

Table 3
Results for the photocatalytic CO₂ reduction with different concentrations of **1**, [Ru(bpy)₃]²⁺, and BIH.

Entry	[1] (μM)	[Ru(bpy) ₃] ²⁺ (mM)	[BIH] (mM)	TON CO / H ₂	TOF _{CO} ^a (min ⁻¹)	CO selec- tivity (%)
1	5	0.4	20	464/9	5.16	98
2	10	0.4	20	549/42	5.16	93
3	20	0.4	20	557/36	4.63	94
4	20	0.2	20	395/27	3.54	94
5	20	0.6	20	556/23	6.73	96
6	20	0.6	40	710/21	7.12	97

Reaction conditions: in CO₂-saturated CH₃CN/CH₃OH (1.5 M) over 4 h of irradiation.

^a First 60 min.

Fig. 7. Plot of TON_{CO} versus time for the photocatalytic system containing **1** (20 μM), [Ru(bpy)₃]²⁺ (0.2 mM), and BIH (20 mM) in CO₂-saturated CH₃CN/CH₃OH (1.5 M); after 150 min of irradiation when CO evolution ceased, **1** or [Ru(bpy)₃]²⁺ equal to the initial quantity was added to the catalytic system.

Fig. 8. Phosphorescence spectra of $[\text{Ru}(\text{bpy})_3]^{2+}$ (10 μM) in CH_3CN containing different concentrations of **1** (a) or BIH (b), excited by monochromatic light at 450 nm. Kinetic traces of (c) transient bleaching recovery monitored at 450 nm for $[\text{Ru}(\text{bpy})_3]^{2+}$ (5.0×10^{-5} M) only, $[\text{Ru}(\text{bpy})_3]^{2+}$ /**1** (2.5×10^{-5} M), and $[\text{Ru}(\text{bpy})_3]^{2+}$ /BIH (2.0×10^{-4} M) and (d) transient decay monitored at 520 nm for $[\text{Ru}(\text{bpy})_3]^{2+}$ /BIH and $[\text{Ru}(\text{bpy})_3]^{2+}$ /BIH/**1** in deoxygenated CH_3CN solutions.

catalytic CRR. The calculated quenching rate constant (k_q) for electron transfer from BIH to $^*[\text{Ru}(\text{bpy})_3]^{2+}$ in CH_3CN was $2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, which is similar to the previous reports [20,36,53].

Further evidence of the electron transfer in the photocatalytic system was obtained from the transient absorption spectroscopic studies. The emission lifetime of $[\text{Ru}(\text{bpy})_3]^{2+}$ (0.87 μs) in the presence of **1** was almost the same as that measured for $[\text{Ru}(\text{bpy})_3]^{2+}$ only (0.85 μs) in CH_3CN , while in the presence of BIH, the emission lifetime of $[\text{Ru}(\text{bpy})_3]^{2+}$ was shortened to 0.44 μs (Fig. 8(c)). These observations further demonstrated that the excited state $^*[\text{Ru}(\text{bpy})_3]^{2+}$ cannot be oxidatively quenched by **1**; instead, it was reductively quenched by BIH [51]. This is consistent with the thermodynamic analysis of the redox potentials of $^*[\text{Ru}(\text{bpy})_3]^{2+}$ [50], BIH [52], and **1** [46]. In the presence of BIH, the transient absorption spectrum (Fig. 9) of $[\text{Ru}(\text{bpy})_3]^{2+}$ displayed a new absorption band at approximately 520 nm accompanied by an apparent bleaching of the $[\text{Ru}(\text{bpy})_3]^{2+}$ absorption. The new absorption band was assigned to $[\text{Ru}(\text{bpy})_3]^+$ that exhibited a decay lifetime of 35 μs in the $[\text{Ru}(\text{bpy})_3]^{2+}$ /BIH system. Upon the addition of **1**, the intensity of the absorption at 520 nm was substantially reduced (Fig. 9), and the decay lifetime of $[\text{Ru}(\text{bpy})_3]^+$ was shortened to approximately 16 μs (Fig. 8(d)), implying the presence of electron transfer from $[\text{Ru}(\text{bpy})_3]^+$ to **1**.

A plausible mechanism for the photocatalytic CO_2 reduction

by the system of **1**/ $[\text{Ru}(\text{bpy})_3]^{2+}$ /BIH is proposed in Scheme 1 on the basis of the above-mentioned spectroscopic evidences and the previous density functional theory (DFT) calculations for the pathway of the electrochemical CRR catalyzed by **1** [46], as well as based on the mechanisms reported for other molecular catalyst-based CRR systems containing $[\text{Ru}(\text{bpy})_3]^{2+}$ and BIH [20,36]. In the photo-initiation step, the excited state $^*[\text{Ru}(\text{bpy})_3]^{2+}$ is reductively quenched by BIH to form $[\text{Ru}(\text{bpy})_3]^+$ and $\text{BIH}^{\bullet+}$. The deprotonation of $\text{BIH}^{\bullet+}$ affords a

Fig. 9. Microsecond transient absorption spectra of $[\text{Ru}(\text{bpy})_3]^{2+}$ (5.0×10^{-5} M), $[\text{Ru}(\text{bpy})_3]^{2+}$ with BIH (2.0×10^{-4} M), and $[\text{Ru}(\text{bpy})_3]^{2+}$ with BIH and **1** (2.5×10^{-5} M) in deoxygenated CH_3CN solution.

Scheme 1. Proposed mechanism for the photocatalytic reduction of CO₂ to CO by the **1**/[Ru(bpy)₃]²⁺/BIH system.

strong reductant, namely a BI[•] radical that can reduce [Ru(bpy)₃]²⁺ in the dark [36]. Therefore the consumption of a BIH unit can produce two [Ru(bpy)₃]⁺ molecules together with a proton in the photo-initiation step of the catalytic cycle, and the protons released from BIH^{•+} are then catalytically reduced by **1** to evolve H₂ as a by-product. The successive electron transfer from two [Ru(bpy)₃]⁺ molecules to **1** generates the active catalyst **A** (**1**²⁻). The structure of the two-electron reduced species, **1**²⁻, featuring a dangling thiolate (κ¹-S) and a bridging CO (μ-CO) has been suggested by previous DFT calculations and experimental studies [52,54]. Importantly, the κ¹-S unit of **1**²⁻ can act as a pendant Lewis base to become protonated by the H⁺ from the oxidized BIH, and the intramolecular interaction between κ¹-S-H and the coordinated CO₂ facilitates C–O bond cleavage in the process of CO₂ reduction [46]. This is similar to the function of the methoxy group and thiourea tether in the second coordination sphere of Mn(I) and Re(I) bi-

pyridyl tricarbonyl CRR catalysts [55,56]. In fact, the protonation at the κ¹-S site of a diiron complex, [(μ,κ²-bdt)(μ-PPh₂)Fe₂(CO)₅]⁻ that is an analog to **1**²⁻ has been corroborated by ¹H NMR spectra and the X-ray diffraction analysis [57]. When the actual catalyst **1**²⁻ was formed in the photo-initiation step, the further catalytic cycle for reduction of CO₂ is similar to the one proposed for the electrochemical reduction of CO₂ to CO catalyzed by **1**²⁻ [46], albeit with a different electron supplier.

Upon an addition of a large amount of TEOA to the catalytic system, TEOA captures the H⁺ released by BIH^{•+}, and thus inhibits the protonation of the dangling κ¹-S in the reduced Fe₂S₂ intermediate. As mentioned above, the κ¹-S-protonated intermediates were crucial for the effective catalysis of CRR by **1** that allowed an intramolecular proton transfer that lowers the energy barrier for the cleavage of the C–O bond to form H₂O and CO. Moreover, the accumulation of [HTEOA]⁺, a strong acid (pK_a = 7.5) [58], in the solution could boost the hydrogen evolution reaction, as evidenced by the rapidly rising H₂-evolution curve after a ~15 min induction period (Fig. 4). Therefore, the addition of TEOA to the **1**/[Ru(bpy)₃]²⁺/BIH system can adjust or even completely switch the selectivity of the photocatalytic reaction from CO₂ reduction to proton reduction.

4. Conclusions

In summary, a unique [FeFe]-H₂ase model (**1**) bearing a 1,2-phenylene bridge between two S atoms was demonstrated to be a highly active and selective catalyst for the visible-light-driven reduction of CO₂ to CO in acetonitrile. The TON_{CO} and TOF_{CO} of **1** reached 710 and 7.12 min⁻¹ (first 60 min), respectively, under optimized test conditions, with 97% selectivity for CO. By contrast, a similar complex **2** with a

Graphical Abstract

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Selective photocatalytic reduction of CO₂ to CO mediated by a [FeFe]-hydrogenase model with a 1,2-phenylene S-to-S bridge

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An [FeFe]-hydrogenase model was demonstrated to be highly active for the photochemical reduction of CO₂ with a TOF of 7.12 min⁻¹ and CO selectivity of 97%. The CO/H₂ ratio can be adjusted by the addition of TEOA.

1,2-ethylene bridge between the two S atoms was inactive for the photocatalytic CO₂ reduction under the same conditions, revealing that the structural difference in the S-to-S bridge significantly affects the catalytic behavior of diiron dithiolate complexes. It is of interest to note that the selectivity of the photochemical reaction catalyzed by **1** can be simply adjusted and even completely switched between the reduction of CO₂ and proton by adding different amount of TEOA to the **1**/[Ru(bpy)₃]²⁺/BIH system, showing a possible route for the production of syngas with controlled CO/H₂ ratios. These findings pave the way for the application of bioinspired diiron complexes in photocatalytic CO₂ conversion.

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1,2-亚苯基二硫桥[FeFe]-氢化酶模拟物选择性光催化还原CO₂至CO

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摘要: 利用基于非贵金属的分子催化剂通过光驱动催化CO₂还原生成CO是将太阳能储存为化学能和缓解CO₂温室效应的有效途径之一, 具有重要的科学意义和潜在的应用前景. 已报道的非贵金属分子催化剂, 大多数对于光驱动CO₂还原表现出缓慢的催化反应速率和/或对CO产物的低选择性, 反应常常伴随着质子还原产氢反应, 只有很少几种非贵金属分子催化剂对光催化CO₂还原生成CO表现出高催化反应速率(> 100 h⁻¹)和高选择性. 研究表明, 双核过渡金属配合物由于分子中邻近的两个金属中心的协同催化作用, 对于CO₂还原生成CO的催化活性明显高于相应的单核配合物. 因此, 具有两个邻近的金属离子的非贵金属双核配合物有望作为CO₂选择性还原的高效分子催化剂.

我们最近的研究发现, 具有刚性、共轭亚苯基二硫桥结构的[FeFe]-氢化酶模拟物[(μ-bdt)Fe₂(CO)₆] (**1**, bdt = 苯-1,2-二巯基)能够高活性、高选择性地光化学还原CO₂至CO, 而与其类似的模拟物[(μ-edt)Fe₂(CO)₆] (**2**, edt = 乙烷-1,2-二巯基)则不具有光催化还原CO₂活性, 表明铁铁氢化酶模拟物中硫-硫桥的结构是影响模拟物的催化性能的重要结构因素之一. 可见光照射1/[Ru(bpy)₃]²⁺/BIH (BIH = 1,3-二甲基-2-苯基-2,3-二氢-1H-苯并[d]-咪唑)体系4.5 h, **1**催化生成CO的循环数(TON)为710, 在初始1 h的转化率(TOF)为7.12 min⁻¹, CO的选择性达到97%, 内量子效率为2.8%. 有趣的是, 向体系中加入TEOA时可以调节**1**的催化选择性, 光化学反应能够在CO₂还原产生CO和质子还原产生H₂之间进行切换. 此外, 采用稳态荧光和瞬态吸收光谱研究了光催化体系中的电子转移, 提出可能的光催化反应机理. 该研究结果揭示了刚性硫-硫桥结构的氢化酶模拟物对光化学CO₂还原至CO的特殊催化活性, 拓展了铁铁氢化酶模拟物的催化多功能性.

关键词: 催化选择性; 二氧化碳还原; 一氧化碳; 双核铁配合物; 氢化酶模拟物; 光催化

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