

A Highly Selective and Robust Co(II)-Based Homogeneous Catalyst for Reduction of CO₂ to CO in CH₃CN/H₂O Solution Driven by Visible Light

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Supporting Information

ABSTRACT: Visible-light driven reduction of CO₂ into chemical fuels has attracted enormous interest in the production of sustainable energy and reversal of the global warming trend. The main challenge in this field is the development of efficient, selective, and economic photocatalysts. Herein, we report a Co(II)-based homogeneous catalyst, [Co(NTB)CH₃CN](ClO₄)₂ (**1**, NTB = tris(benzimidazolyl-2-methyl)amine), which shows high selectivity and stability for the catalytic reduction of CO₂ to CO in a water-containing system driven by visible light, with turnover number (TON) and turnover frequency (TOF) values of 1179 and 0.032 s⁻¹, respectively, and selectivity to CO of 97%. The high catalytic activity of **1** for photochemical CO₂-to-CO conversion is supported by the results of electrochemical investigations and DFT calculations.

The use of sunlight and catalysts to convert carbon dioxide (CO₂) into chemical fuels and feedstocks has attracted tremendous scientific interest for two main reasons: the shortage of energy and the problem of global warming.¹ To achieve both purposes, the development of artificial photosynthetic systems from which solar fuels can be produced from CO₂ and H₂O is essential.^{2,3} The past investigations have shown that the reduction products of CO₂ usually include CO,^{3a} formic acid,⁴ methane,⁵ methanol,^{3b} and oxalate,⁶ of which getting a single reduction production of CO has attracted particular attention.⁷ Over the past several decades, a number of metal complexes have been investigated as homogeneous electrochemical catalysts for reduction of CO₂ to CO,^{8,9} some of which have shown high electrocatalytic activities,⁹ even in a pure water catalytic system.^{9b–g} This has been supported by Saveant et al.^{9g,h} and Koper et al.,⁵ who proposed that electrocatalysts could remain highly selective toward CO₂-to-CO conversion in water after mechanistic studies. In the photochemical CO₂ reduction, a series of catalysts based on Ir,^{3a,b} Ru,^{4a} Mn,^{4b} Re,¹⁰ Os,¹¹ Co,¹² Fe,¹³ and Ni¹⁴ complexes have been created, some of which have also displayed good performance for CO₂-to-CO conversion, such as a Co(II)-

based complex reported by the Lau group exhibiting a TON value of 2660 in CH₃CN^{12a} (see Table S1). However, the good performances of most catalysts are achieved in nonaqueous solvent systems, as in water-containing systems, the easy occurrence of the photocatalytic proton reduction reaction is competitive with the CO₂ reduction reaction, which may inevitably lead to a decrease of the efficiency and selectivity for CO₂-to-CO conversion.^{8f,12g} Considering that a water-containing system is necessary for building an artificial photosynthesis cycle by combination of a CO₂ reduction with a water oxidation, it is meaningful to develop catalysts that can exhibit high activity and selectivity for the photocatalytic CO₂ reduction in a water-containing reaction system.

During the past two decades, tripodal ligands have been widely used for preparing metal-based homogeneous molecular catalysts,^{12a,15} as they are polydentate and can strongly bind with a metal center to form robust molecular complexes. The tetradentate tripodal ligands, usually impose C₃ symmetry and bond to a five-coordinated metal center, leaving one position available on the trigonal-bipyramidal metal center to combine with the solvent molecule. This solvent molecule is readily exchanged by the substrate molecule, facilitating the activation and catalytic transformation of the substrate molecule. Herein, we report a mononuclear cobalt(II) complex, [Co(NTB)CH₃CN](ClO₄)₂ (**1**, NTB = tris(benzimidazolyl-2-methyl)amine, Scheme S1a), which can perform as a highly selective and robust catalyst for photocatalytic reduction of CO₂ to CO in acetonitrile/water (*v/v* = 4:1). The TON and TOF values reach as high as 1179 and 0.032 s⁻¹, respectively, and the selectivity to CO reaches as high as 97%. Electrochemical investigations and DFT calculations have revealed that the high CO₂ reduction activity of **1** can be attributed to its lower onset CO₂ reduction potential, which originates from the existence of electron-rich benzimidazol groups of NTB in **1**.

The crystals of 1·3CH₃CN·1.25H₂O were obtained from the reaction of Co(ClO₄)₂·6H₂O and NTB in acetonitrile (see the Supporting Information). The result of single X-ray structural

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Table 1. Results of Control Experiments of Photocatalytic Reduction of CO₂ to CO^a

entry	catalyst	CO (μmol)	H ₂ (μmol)	selectivity to CO (%)	TON (CO)	TOF (s ⁻¹)	Φ _{CO} (%)
1	1	11.79	0.37	97%	1179	0.032	0.22
2	blank	0	0.049	0	0	0	0
3	1	0	1.93	0	0	0	0
4	1	0	0	0	0	0	0
5	1	0	0.21	0	0	0	0
6	1	0	0	0	0	0	0
7	CoCl ₂	4.1	0.12	97%	410	0.011	0.077
8	2	6.86	0.16	97%	686	0.019	0.13

^aEntries 1 with and 2 without catalyst 1 in CO₂; 3, with catalyst 1 in Ar; 4, without [Ru(phen)₃](PF₆)₂; 5, without TEOA; 6, without light; 7, with catalyst CoCl₂ in CO₂; 8: with catalyst 2 in CO₂. ^bReaction conditions: [Ru(phen)₃](PF₆)₂ (0.4 mM), TEOA (0.3 M), LED light (450 nm, 100 mW·cm⁻², irradiation area 0.8 cm²), 25 °C. TON and TOF values are averaged over three reactions, with deviations below 5%. Calculation details for TON, TOF and Φ_{CO} are illustrated in the Supporting Information.

analysis has revealed that 1·3CH₃CN·1.25H₂O crystallizes in the monoclinic space group *P*₂₁/*n* (Table S2). The central metal Co(II) is five-coordinated to four N atoms from an NTB ligand and one acetonitrile molecule, forming a slightly distorted trigonal bipyramid geometry (Figure S1). The lattice CH₃CN and H₂O molecules in 1·3CH₃CN·1.25H₂O can be removed by evacuation at 25 °C for 10 h to get 1. The UV-vis spectrum of 1 in CH₃CN/H₂O (*v/v* = 4:1) shows four absorption peaks at 213, 272, 279, and 528 nm (ϵ = 54 560, 37 108, 34 440, and 196 M⁻¹·cm⁻¹ respectively; Figure S2a), the former three peaks can be assigned to the $\pi \rightarrow \pi^*$ transitions of the NTB ligand, and the fourth peak can be assigned to the d-d transition of the Co(II) ion. After being irradiated by 450 nm LED light with an intensity of 100 mW·cm⁻² for 10 h, 3.7% of 1 degrades, illustrating that 1 is stable in CH₃CN/H₂O under irradiation (Figure S2b). The electrochemical behavior of 1 in CH₃CN/H₂O (*v/v* = 4:1) was investigated by cyclic voltammograms (CVs; see the Supporting Information). As shown in Figure S3, under an Ar atmosphere, the CV of 1 shows an irreversible reduction wave at -1.09 V vs NHE, corresponding to the reduction of [Co^{II}(NTB)-CH₃CN]²⁺ to [Co^I(NTB)CH₃CN]⁺. Under a CO₂ atmosphere, the CV of 1 exhibits enhanced current at $E_{\text{onset}} = -0.65$ V, and the current intensity increases over 3 times that under an Ar atmosphere. These results indicate that 1 can act as a catalyst for the reduction of CO₂.⁸

The photocatalytic experiments of CO₂ reduction were carried out using 1 as a catalyst, [Ru(phen)₃](PF₆)₂ as a photosensitizer, and triethylamine (TEOA) as a sacrificial reductant (see the Supporting Information). The UV/vis absorption spectrum depicted in Figure S4 shows that the [Ru(phen)₃](PF₆)₂ exhibits a broad absorption band in the visible region. Typically, under 1 atm of CO₂ and 25 °C, a glass reactor containing a mixture of 5 mL of CH₃CN/H₂O (*v/v* = 4:1), 1, [Ru(phen)₃](PF₆)₂, and TEOA was irradiated by a 450 nm LED light, with a light intensity of 100 mW·cm⁻². The generated gases were analyzed by gas chromatography (GC). The result showed that the visible-light photoredox cycle produced a significant amount of CO and a very small amount of H₂ (Table 1, entry 1; Figure 1), along with a trace amount of formate detected in the liquid phase by ion chromatograph (IC). Kinetic investigations have shown that the amount of CO production increases linearly with the concentration of 1 (Figure S5), suggesting a single site cobalt catalysis process. Using 2 μM cobalt catalyst, 11.79 μmol of CO and 0.37 μmol of H₂ were generated within 10 h, corresponding to the selectivity of 1 to CO of 97%, and the TON and TOF values

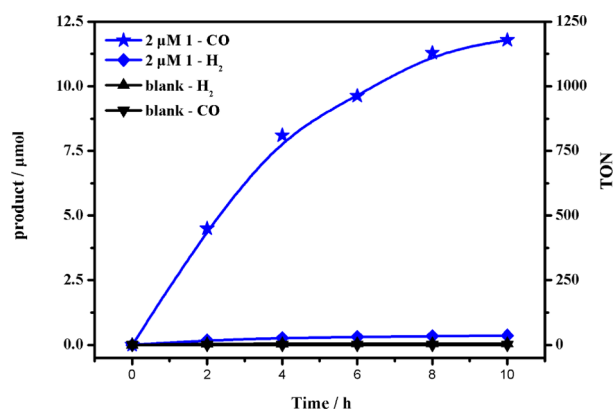


Figure 1. CO and H₂ evolution catalyzed by 1 (2 μM) under visible-light irradiation (450 nm LED light, light intensity of 100 mW·cm⁻²) in the presence of [Ru(phen)₃](PF₆)₂ (0.4 mM) and TEOA (0.3 M) in CH₃CN/H₂O (*v/v* = 4:1) solution at 25 °C under 1 atm of CO₂.

for CO of 1179 and 0.032 s⁻¹, respectively (Table 1, entry 1). The quantum yield of 1 to CO was determined to be 0.22% (see the Supporting Information), significantly lower than that of the most efficient reported catalyst, which can be attributed to the low light collection of this catalytic system, that is, the low efficiency of oxidative quenching of the sensitizer by 1 due to the low concentration of 1. However, the TON and TOF values based on 2 μM cobalt catalyst are comparable to those of the most efficient CO₂ reduction catalyst (Table S1), revealing that 1 behaves highly efficiently for the reduction of CO₂ to CO. The high catalytic activity of 1 for CO₂-to-CO conversion can be attributed to its low reduction potential of $E_{\text{onset}} = -0.65$ V under a CO₂ atmosphere, which leads to the easy reduction of the Co^{II} in 1 by [Ru^I(phen)₃]⁺, strongly accelerating the process of CO₂-to-CO conversion. It is worth noting that the high selectivity and activity of 1 for CO₂-to-CO conversion are achieved in CH₃CN/H₂O solution, a water-containing reaction system where almost all the reported molecular catalysts display inactivity for the photoreduction of CO₂ to CO.^{8f,12g} Obviously, these outstanding catalytic performances will greatly enhance the practical application of 1 for CO₂ reduction in combining with a water oxidation, to achieve a carbon neutral artificial photosynthesis cycle.

A series of control experiments were further performed to thoroughly investigate the photocatalytic CO₂-to-CO reduction reaction. First, the photocatalytic reaction was carried out in the absence of 1. The result showed that no CO was detected, and a tiny amount of H₂ was recorded (Table 1, entry 2), indicating

that the production of CO originates from the catalytic reduction of CO₂ by **1** rather than by [Ru(phen)₃](PF₆)₂. Second, the photocatalytic reaction was performed under an Ar atmosphere (Table 1, entry 3). The result showed that no CO was generated, suggesting that the CO formed in entry 1 comes from the reduction of CO₂ rather than the decomposition of **1** and/or photosensitizer/sacrificial reductant. This result was further confirmed by the isotope tracer experiment. Using ¹³CO₂ instead of CO₂, the generated gas is ¹³CO rather than CO (Figure S6), strongly evidencing that the generated CO originates from the reduction of CO₂ by **1**. Third, the photocatalytic reaction was performed without [Ru(phen)₃](PF₆)₂, TEOA, or visible light irradiation (Table 1, entries 4–6). The results showed that no CO was detected, suggesting that photosensitizer, sacrificial reductant, and visible-light irradiation are indispensable to the CO₂-to-CO conversion. Fourth, the photocatalytic reaction was operated using CoCl₂ instead of **1**. The results showed that the production of CO and H₂ dramatically decreased (Table 1, entry 7), indicating that formation of complex is significant for enhancing the catalytic activity of Co(II).

To intensively study the effect of the molecular structure of catalyst on the catalytic activity, a typical tetradentate tripodal ligand tris(2-pyridylmethyl)amine (TPA, Scheme S1b) and its Co(II) complex [Co(TPA)]Cl₂ (**2**) have been designed and synthesized.^{12a} Under the same conditions, **2** also exhibits activity for catalytic reduction of CO₂ to CO, with TON and TOF values of 686 and 0.019 s⁻¹, respectively (Table 1, entry 8). Obviously, **1** exhibits a better catalytic activity than **2**, which is consistent with the electrochemical results; that is, **1** has a more positive onset potential for electrochemical CO₂ reduction (−0.65 V vs NHE, Figure S3) than **2** (−0.92 V vs NHE, Figure S7). Complex **1** possessing higher catalytic activity than **2** can be attributed to the fact that the benzimidazol group of NTB in **1** is more electron donating than the pyridyl group of TPA in **2**. This result clearly reveals that the electron-rich groups of a ligand will enhance the catalytic activity of the corresponding metal complex for photochemical CO₂ reduction.

Besides activity and selectivity, durability of **1** has also been investigated. It has been found that over 10 h, the rate of CO generation apparently slows down (Figure S8). It is interesting to find that the production of CO can be resumed by an addition of equivalent [Ru(phen)₃](PF₆)₂ (0.4 mM, 2 μmol) to this nearly completed catalytic system (Figure S8a), while it cannot be recovered by an injection of equivalent TEOA (0.3 M, 0.015 mmol; Figure S8b), demonstrating that the deactivation of the system is the photodegradation of the photosensitizer rather than the deactivation of **1** or insufficiency of TEOA. This conclusion was further confirmed by the obvious hypochromism of the UV/vis absorption spectra of [Ru(phen)₃](PF₆)₂ after irradiation with an LED light (Figure S9). The result of dynamic light scattering (DLS) showed that no significant nanoparticle was generated in the solution after the reaction, further illustrating that **1** did not decompose during the photocatalytic process. The above observations demonstrate that **1** possesses good durability and can serve as a stable homogeneous catalyst for photochemical CO₂ reduction to CO.

To reveal the catalytic mechanism of **1** in the photochemical reduction of CO₂ to CO, the quenching mode of the [Ru(phen)₃]²⁺ in the excited state was initially investigated. As shown in Figure S10, the [Ru(phen)₃]²⁺ exhibits an

emission peak at 610 nm upon excitation at 450 nm.^{1e} As the fluorescence intensity of the deaerated [Ru(phen)₃]²⁺ solution (CH₃CN/H₂O; v/v = 4:1) dramatically decreased with the gradual addition of **1** (Figure S10a and b), rather than TEOA (Figure S10c and d), the quenched mode of the excited [Ru(phen)₃]²⁺ can be assigned to an oxidatively quenched pathway.^{1d} The catalytic mechanism of **1** was further studied at a molecular level. DFT calculations were carried out to evaluate the reaction processes and related active species (Figure S11). With detailed calculations, a reasonable reaction pathway is presented in Figure S12: (i) With the assistant of the photosensitizer [Ru(phen)₃](PF₆)₂ and visible light, [Co^{II}(NTB)(CH₃CN)]²⁺ is reduced to [Co^I(NTB)(CH₃CN)]⁺. (ii) [Co^I(NTB)(CH₃CN)]⁺ undergoes CO₂ reduction via transition state TS1 to generate [Co^{III}(NTB)(CO₂²⁻)]⁺ after a ligand exchange reaction. The activation free energy of TS1 is 14.3 kcal/mol relative to [Co^I(NTB)(CO₂)]⁺. A similar mechanism was also suggested by Fujita et al. in their [Co^{II}HMD]²⁺ systems.¹⁶ (iii) A proton-coupled electron transfer (PCET) reduction of Co^{III} in [Co^{III}(NTB)(CO₂²⁻)]⁺ to Co^{II} in [Co^{II}(NTB)(CO₂H⁻)]⁺ occurs before the C–O cleavage to generate CO. The calculated redox potential of the PCET from [Co^{III}(NTB)(CO₂²⁻)]⁺ to [Co^{II}(NTB)(CO₂H⁻)]⁺ is 0.93 V, indicating that [Ru^I(phen)₃]⁺ is able to promote this reduction. (iv) After the PCET reduction from [Co^{III}(NTB)(CO₂²⁻)]⁺ to [Co^{II}(NTB)(CO₂H⁻)]⁺, the C–O bond is cleaved at a Co^{II} center via the transition state TS2 (G[‡] = 21.8 kcal/mol) to yield CO and OH⁻. In contrast, without PCET, the cleavage via the Co^{III} center is verified to be very high in free energy (G[‡] = 46.9 kcal/mol, Figure S13). Thus, the C–O cleavage process should occur via the Co^{II} center after the PCET reduction. Similar one-electron reduction of the metal center before C–O cleavage has also been proposed by Fujita et al.¹⁶ and Song et al.¹⁷ After the release of CO and OH⁻, the catalyst [Co^{II}(NTB)(CH₃CN)]²⁺ is regenerated, and the catalytic cycle restarts. As depicted in the overall mechanism, the C–O cleavage is the rate-determining step with G[‡] = 21.8 kcal/mol, suggesting first-order kinetics with respect to the concentrations of **1**. This calculation result strongly supports the experimental observation that the catalytic mechanism is a single site cobalt catalysis process (Figure S5). Furthermore, the importance step (iii) of protonation revealed by the calculation also strongly supports that water, a protic solvent, is crucial for the high catalytic activity of **1** in the experiment (Table 1, entry 1).

In summary, we have demonstrated here that a mononuclear cobalt complex, [Co(NTB)CH₃CN](ClO₄)₂ (**1**), can act as a stable homogeneous photocatalyst for CO₂ reduction to CO, with selectivity to CO as high as 97% and TON and TOF values as high as 1179 and 0.032 s⁻¹, respectively (Table S1). The high CO₂ reduction activity of **1** can be attributed to its lower onset CO₂ reduction potential at E_{onset} = −0.65 V vs NHE, which originates from the existence of the electron-rich benzimidazol groups of NTB in **1**. The results of DFT calculations have revealed that during the process of CO₂ reduction to CO, the Co^I species promotes the reduction of CO₂, and a subsequent PCET reduction leads to the Co^{II}-mediated C–O cleavage to CO. The results presented here pave a new way toward the development of efficient, robust, and economic CO₂ reduction catalysts.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b00566.

Experimental and computational details and additional data (PDF)

■ Accession Codes

CCDC 1545986 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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■ Notes

The authors declare no competing financial interest.

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