

単核モリブデン光触媒を用いた二酸化炭素の選択的光還元反応の開発と機構解明

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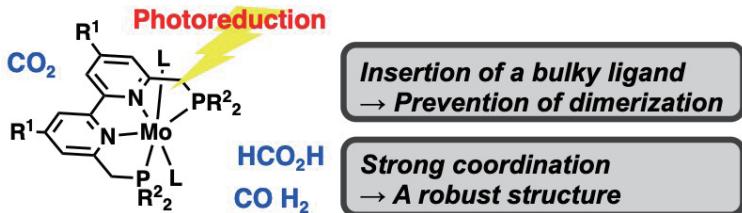
Development of a Mononuclear Mo Complex as a Photocatalyst for Selective Photocatalytic CO₂ Reduction and Their Mechanistic Study

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Carbon dioxide (CO₂) is cause of global warming, while it is an attractive carbon source because of its cheapness, low toxicity, and abundance in atmosphere. Recently, reduction of CO₂ to useful organic substances such as formic acid (HCO₂H) and carbon monoxide (CO) has attracted much attention to solve global warming and fossil fuel shortage. Herein, we reported that a new molybdenum (Mo) complex bearing a PNPP-type tetradentate ligand as a mononuclear self-photosensitized catalyst which is based a non-precious metal showed catalytic ability towards CO₂ reduction to produce HCO₂H as a main product under visible-light irradiation. Their mechanistic insights have been studied by nanosecond transient absorption spectrophotometer, EPR, and UV-vis measurements to detect the intermediates.

1. Introduction

Photocatalytic CO₂ reduction are attracting extensive interest since photocatalytic conversion of CO₂ to energy-rich compounds could occur under relatively mild conditions without any salt waste.¹ In particular, formic acid (HCO₂H), which could be produced from CO₂ reduction as a fine chemical such as a fuel in a direct formic acid fuel cell (DFAFC),² can be provided as a valuable energy storage source. However, for the reason that the homogeneous photochemical reduction of CO₂ is basically difficult to control multi-electron reduction, a two-component system using a transition metal catalyst, photosensitizer, and sacrificial reductant or supramolecular system has been a typical approach to achieve photocatalytic reduction of CO₂. There are some of examples of single-active-site photocatalysts which function as a both photosensitizer and catalyst for CO₂ reduction based on noble metals such as Ru and Ir.^{3,4} However, most of single-active-site photocatalysts for CO₂ reduction gave CO as a major product and the single-active-site photocatalysts consist of base metals are very rare. In a previous research, photocatalytic CO₂ reduction using a (PNPP)Ir complex in the presence of a sacrificial electron donor continuously gave us HCO₂H for over 1 week with a turnover number (TON) of 2560, indicating the Ir complex bearing a PNPP ligand is robust enough for the photocatalytic reaction.⁵ However, use of the more earth abundant metal complexes as photocatalysts for photocatalytic CO₂ reduction is still desired in terms of economy, sustainability, and green chemistry. Herein, we introduce a new tetradentate PNPP-type Mo complex (**1**) as a first example of a Mo photocatalyst without an additional photosensitizer for CO₂ reduction to give HCO₂H and H₂ in the presence of an electron donor, 1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo[d]imidazole (BIH), in a dimethylacetamide (DMA) solution under visible-light irradiation.



Scheme 1. Photocatalytic reduction of CO₂ with a Mo complex under photoirradiation ($\lambda \geq 400$ nm)

2. Photocatalytic CO₂ reduction

Photocatalytic reduction of CO₂ was examined using the Mo complex **1** in the presence of BIH as an electron donor under photoirradiation ($\lambda > 400$ nm) at one atmospheric pressure of CO₂. The amounts of products increased as the reaction solution was irradiated for a longer time, reaching turnover numbers (TONs) of > 173 and > 68 for HCO₂H and H₂, respectively, at 120 h. When a small amount of H₂O

was added to the reaction solution, the reactivity increased to furnish TONs of > 413 and > 235 for HCO_2H and H_2 at 120 h. Negligible amounts of products were produced in the absence of **1**, CO_2 , or light as the control experiments. A labeling experiment was performed with ^{13}C -labeled CO_2 ($^{13}\text{CO}_2$) in a $^{13}\text{CO}_2$ -saturated mixture of $\text{DMF}-d_7/\text{H}_2\text{O}$ (v/v = 199 : 1) to determine the carbon source of the products, revealing that the CO_2 gas was the source of the carbon atoms in the generated HCO_2H .

3. Mechanistic study

The mechanistic insight has been studied by nanosecond laser flash photolysis, EPR, and UV-vis measurements. The nanosecond transient absorption spectra of **1** excited at 450 nm exhibited appearance of characteristic absorption bands due to the triplet excited state (T_1) of **1** (Figure 1a). From the decay time profile of the absorbance at 500 nm, the lifetime of the T_1 excited state of **1** was determined to be $\tau = 8 \text{ ns}$ at 298 K. The decay rate of the T_1 excited state of **1** increased with increasing concentration of BIH (Figure 1b). The rate constant (k_{et}) of photoinduced electron transfer from BIH to **1** was determined to be $5.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. In order to detect the intermediates of photocatalytic CO_2 reduction, EPR measurements were performed before and after photoirradiation of an Ar-saturated DMA solution including **1** and BIH at 173 K. Upon photoirradiation of the reaction solution, a new EPR signal ($g = 2.003$) was observed corresponding to reduction of the ligand, $\text{Mo}^{\text{II}}(\text{PNNP})^{\cdot-}$. The formation of $\text{Mo}^{\text{II}}(\text{PNNP})^{\cdot-}$ was also confirmed by UV-vis spectral change of **1** in the presence of BIH under photoirradiation.

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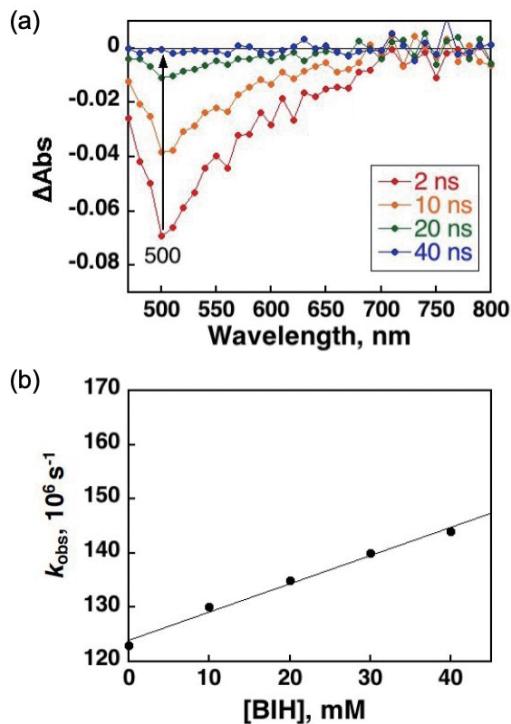


Figure 1. (a) Transient absorption spectral changes after nanosecond laser excitation at 450 nm in a deaerated DMA solution of **1** (0.1 mM) at 298 K. (b) Plot of the decay rate of the absorbance at 500 nm (k_{obs}) due to the decay of the excited state of **1** vs the concentration of BIH in a DMA solution at 298 K.