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Substantial improvement in the efficiency and durability of a photocatalyst for carbon dioxide reduction using a benzoimidazole derivative as an electron donor

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ABSTRACT

We found a very suitable sacrificial electron donor, 1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo[d]imidazole (BIH), to demonstrate the proper ability of a Ru(II)–Re(I) supramolecular photocatalyst for CO_2 reduction. The efficiency, durability, and rate of the photocatalytic reaction were drastically improved ($\Phi_{CO} = 0.45$, $TON_{CO} = 3029$, $TOF_{CO} = 35.7\ min^{-1}$) using BIH as an electron donor compared to that using 1-benzyl-1,4-dihydronicotinamide as an electron donor ($\Phi_{CO} = 0.15$, $TON_{CO} = 207$, $TOF_{CO} = 4.7\ min^{-1}$). The reasons for the improvement were clarified based on the detailed mechanistic investigations.

1. Introduction

In recent years, the increase in the concentration of atmospheric CO_2 and the shortage of fossil fuels and carbon resources have become serious problems. The development of systems that convert solar energy into chemical energy would serve as an ideal solution to these problems.

The final target of such research should be the development of artificial photosynthesis systems that can reduce water to H_2 and/or reduce CO_2 to energy-rich compounds such as CO, formic acid, and methanol through the use of water as a reductant. A substantial amount of research has been focused on the development of photocatalysts for H_2 evolution [1–6] and CO_2 reduction [6–18] using the so-called sacrificial electron donors because such a reduction site is one of the key processes in artificial photosynthesis.

Recently, visible-light-driven photocatalytic systems with relatively high efficiency and high durability have been developed using transition-metal complexes [4,6–11,14]. In these systems, Ru(II) trisdiimine complexes have been the most common photosensitizers used to initiate photochemical electron transfer from the electron donor to the catalyst because these complexes absorb a wide range of visible light and because their excited and reduced forms are both relatively stable. Multinuclear photocatalysts, where the Ru(II) trisdiimine complex connects with a Re(I) diimine biscarbonyl complex as a catalyst, have also been reported to selectively reduce CO_2 to CO under visible-light irradiation [10].

For the evaluation of the photocatalysis in such systems, the limitation of the sacrificial electron donor is a serious problem. Although tertiary aliphatic amines such as triethylamine (TEA) [3–5] and triethanolamine (TEOA) [14,15,18], ascorbic acid [16,17], and coenzyme NAD(P)H models such as 1-benzyl-1,4-dihydronicotinamide (BNAH, Chart. 1) [7–11,14] have been commonly employed as sacrificial electron donors for various redox photocatalytic reactions, they cannot efficiently quench the excited state of the Ru(II) trisdiimine complexes because they lack sufficient reducing power. For example, in the case of the above described multinuclear photocatalysts, the excited state of the photosensitizer unit cannot be quenched by TEOA at all. However, BNAH, which has a lower oxidation potential ($E^{\circ ox} = 0.57$ V vs. SCE) [19], can function as a sacrificial electron donor in these photocatalytic CO_2 reduction reactions. Nonetheless, BNAH has two disadvantages [10,11]. First, the quenching fraction of the excited state (η_q) calculated according to Eq. (1) is still low (typically ~60%) even when the concentration of BNAH in the reaction solution is 0.1 M; this quenching fraction means that approximately 40% of the photons absorbed by the photocatalysts are wasted in the first stage of the photocatalytic reaction:

$$\eta_q = k_q \tau_{em}[\text{reductant}]/(1 + k_q \tau_{em}[\text{reductant}]) \quad (1)$$

where k_q is the quenching rate constant of emission from the photosensitizer unit and τ_{em} is the emission lifetime in the absence of a

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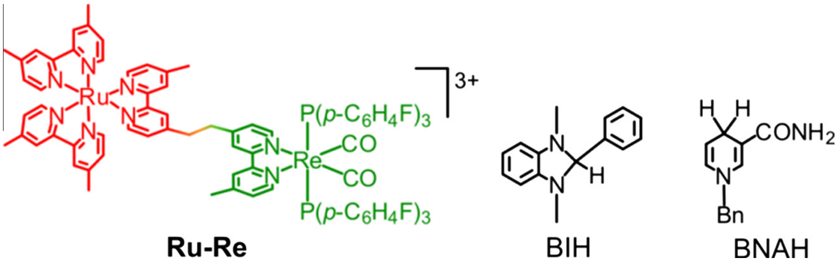
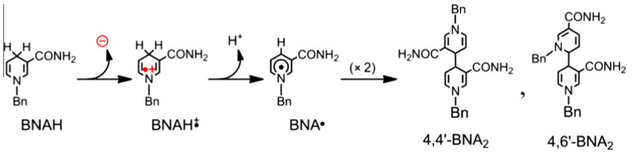


Chart. 1. Structures of **Ru–Re**, BIH, and BNAH. The counter anion of the complex was PF_6^-.

reductant. Second, the oxidized products of BNAH induce an inhibition effect. The BNA dimers (BNA_2s, Eq. (2)) formed via a dimerization reaction in combination with the deprotonation of the one-electron oxidized BNAH, i.e., $BNAH^{\cdot+}$, accumulate in the solution. The BNA_2s are stronger electron donors ($E^{\circ ox}$(4,4′-BNA_2) = 0.26 V) [20] than BNAH, and the one-electron oxidized forms of $BNA_2s^{\cdot+}$ ($BNA_2s^{\cdot+}$) are so stable that back electron transfer preferentially proceeds from the reduced photosensitizer to $BNA_2s^{\cdot+}$ (Eq. (3)). These reductive quenching and back electron transfer processes also waste the absorbed photon, and the competitive quenching of the excited photosensitizer by BNA_2s obstructs the reductive quenching by BNAH to diminish the photocatalytic ability.



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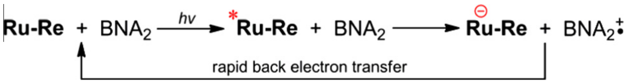

(3)

In some cases, aromatic amines such as *N*,*N*-dimethylaniline have been used as an electron donor [2]. Because one-electron oxidized forms of these amines are so stable, back electron transfer lowers the efficiencies of the photocatalytic reactions in these cases as well. Because of these limitations, we cannot say that the reported values of the photocatalytic abilities properly reflect their potentials. Because correct and standardized evaluations of the abilities of the photocatalysts are tremendously important, other sacrificial electron donors are required with the following properties: (1) strong reduction power, which is required for quantitative quenching of the excited state of the photosensitizer and (2) inertness of the oxidized products toward the photocatalytic reaction. In addition, the sacrificial electron donor should be simple to allow quantification of the amount of the donor consumed and the amount of its oxidized products.

In this study, we found that 1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo[*d*]imidazole (BIH, Chart. 1) is very suitable as an electron donor in the photocatalytic reactions. Although this compound has greater reducing power ($E^{ox}_{1/2}$ = 0.33 V) [21] than BNAH and has been used as a reductant in organic photochemistry [21–24], it has not been used in the field of solar energy conversion. The dinuclear complex **Ru–Re** composed of a Ru(II) trisdiimine unit and a Re(I) diimine biscarbonyl bisphosphine unit (Chart. 1) was employed as a photocatalyst because this complex exhibited the best selective photocatalytic ability for the reduction of CO_2 to CO when BNAH was used as an electron donor in the reported supramolecular photocatalysts [10]; the efficiency, durability, and rate of the photocatalytic reaction were reported to be the quantum yield Φ_{CO} = 0.15, the turnover number TON_{CO} = 207, and the turnover frequency TOF_{CO} = 4.7 min^{-1}, respectively [10]. The use of BIH instead of BNAH resulted in drastic improvements in all the measurements of photocatalysis (Φ_{CO} = 0.45, TON_{CO} = 3029, TOF_{CO} = 35.7 min^{-1}).

2. Results and discussion

To evaluate the photocatalysts, we determined the Φ, TON, and TOF of the product(s) with the following equations.

$$\Phi_{CO} = [\text{produced CO(mol)}]/[\text{absorbed photons (einstein)}] \tag{4}$$

$$TON_{CO} = [\text{produced CO (mol)}]/[\text{used } \mathbf{Ru{-}Re} \text{ (mol)}] \tag{5}$$

$$TOF_{CO} = [\text{produced CO (mol)}]/[\text{used } \mathbf{Ru{-}Re} \text{ (mol)} \times \text{irradiation time (min)}] \tag{6}$$

To obtain these values, the following reaction conditions were chosen (the details and the justifications of these conditions has been described elsewhere [11]).

Light irradiation condition (**LIC**)1 for determining Φ: 480-nm monochromic light was used for excitation; the light intensity was 4.3 × 10^{-9} einstein s^{-1}. The concentration of the photocatalyst was 0.3 mM, where the absorbance of the solution was greater than 3 when using a 1-cm light pass. The solution was vigorously mixed during the irradiation.

LIC2 for determining TON: >500-nm light was obtained using a 500-W high-pressure mercury lamp equipped with a uranyl glass and a K_2CrO_4 (30% w/w, *d* = 1 cm) aqueous solution filter. The concentration of the photocatalyst was 0.05 mM.

LIC3 for determining TOF: >420-nm light was obtained using a 500-W high-pressure mercury lamp with a short-wavelength cut-off filter. This visible-light source could irradiate the reaction solution with the most intense light flux in our laboratory. The concentration of the photocatalyst was 0.05 mM.

BIH and its oxidized products (BI^+) do not absorb >420-nm light (Fig. 1). The photosensitizer unit can be selectively excited using

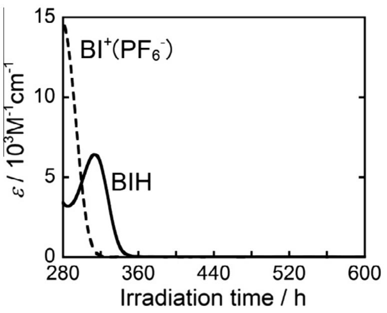

Fig. 1. UV–vis absorption spectra of BIH (solid line) and $BI^+(PF_6^-)$ (broken line) in DMF–TEOA (4:1 v/v).