

Communication

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Photocatalytic CO₂ Reduction Using Cu(I) Photosensitizers with a Fe(II) Catalyst.

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Supporting Information Placeholder

ABSTRACT: Photocatalytic systems developed from complexes with only abundant metals. i.e. $Cu^{I}(dmp)(P)_{2}^{+}$ = 2,9-dimethyl-1,10-(dmp phenanthroline; P = phosphine ligand) as a redox photosensitizer and Fe^{II}(dmp)₂(NCS)₂ as a catalyst, produced CO as the main product by visible light irradiation. The best photocatalysis was obtained using a Cu¹ complex with a tetradentate dmp ligand tethering two phosphine groups, where the turnover number and quantum yield of CO formation were 273 and 6.7%, respectively.

Photocatalytic CO₂ reduction is one of the most important reactions in artificial photosynthesis research, and is expected to become a key technology for addressing global warming and shortage of energy and carbon resources.¹ Metal polypyridine complexes are often used as a main component, i.e., a redox photosensitizer (PS) and/or a catalyst (CAT), in various photocatalytic systems for CO₂ reduction.² In most studies, complexes with expensive and rare metal ions, e.g., Ru^{II} and Re^I, have been used as the PS and/or CAT because of their fascinating photochemical and/or electrochemical properties.³ Recently, Ir^{III} complexes as a PS or as a photocatalyst have been applied in the photocatalytic reduction of CO₂.⁴ However, photocatalytic systems using only abundant elements need to be developed because considerable CO_2 is expected to be utilized in the future. Although a limited number of complexes with more abundant metals, i.e., Co^I and Ni^I macrocycles, Fe^{II} porphyrins, and Co^{II} and Mn^I diimine complexes, were reported as CATs in the photocatalytic reduction of CO₂, rare metal complexes, i.e., Ru and Ir complexes, were used as PSs.^{4b-d, 5} A Fe^{III} porphyrin was successfully used as a photocatalyst for the reduction of CO_2 to CO_2^{6} however, the durability of the CAT was low $(TON_{CO} = ca.$ 30).^{6b} Although mixed systems of Fe^{III} porphyrin as a CAT with 9-cyanoanthracene as an organic PS showed better durability (TON_{CO} = ca. 60), the quantum yield of CO formation was very low $(8 \times 10^{-4} \%)$.^{4c}

Herein, we report a novel, efficient, and durable CO_2 reduction photocatalytic system using only nonprecious-metal complexes, i.e., Cu^{I} diimine complexes as the PS and a Fe^{II} diimine complex as the CAT (Fig. 1).



Fig. 1. Structures of the Cu^I PSs (a) and the Fe^{II} CAT (b), and an ORTEP drawing of **Cu3** (c). Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms, PF₆ anions, and solvent molecules were omitted in (c) for clarity.

As the PS, we chose heteroleptic Cu^I complexes with both diimine and phosphine ligands, as shown in Fig. 1a because of their longer lifetimes $(>10 \text{ }\mu\text{s})^7$ and stronger oxidation power in the excited state compared with homoleptic $Cu^{I}(N^{A}N)_{2}^{+}$ -type complexes (N^A = diimine ligand); Cu1 and Cu3 were newly synthesized using tetradentate ligands, where the two phosphine ligands are tethered to the 2,9-positions of phenanthroline (phen) and bathophenanthroline (baphen) with propyl chains (abbreviated as P₂phen and P₂baphen, respectively). Xray single-crystal analysis of Cu3 (Fig. 1c) showed that two Cu¹ complexes dimerized with two P₂phen molecules as bridging ligands, each supplying the bidentate phen moiety and one monodentate phosphine moiety to one Cu¹ center and another phosphine moiety to another Cu¹ center. Each Cu¹ complex unit had a tetrahedral structure, which is similar to that of the corresponding mononuclear complex, i.e., **Cu5** (Fig. S1b). Variabletemperature (VT) ¹H NMR analyses of the phenylphosphine groups in **Cu3** (Figs. S2-S7) indicated that two types of phosphine moieties exchanged with each other in CD₃CN solution, even at 22 °C ($k_{ex} = 40 \text{ s}^{-1}$, $\Delta G^{\ddagger} = 15 \text{ kJ mol}^{-1}$). Because this phenomenon can be simulated by assuming only a simple exchange between the corresponding proton peaks, the dimeric structure of **Cu3** should be maintained in solution, even at temperatures between -44 °C and 75 °C. Similar phenomena were observed in the VT-NMR spectrum of **Cu1** (50 s⁻¹ at 22 °C, $\Delta G^{\ddagger} = 15 \text{ kJ mol}^{-1}$). This clearly indicates that **Cu1** has dimeric structure to similar to that of **Cu3** in solution.

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In the photocatalytic reactions, the concentrations of the binuclear Cu complexes (Cu1 and Cu3) were half those of the mononuclear complexes (Cu2, Cu4, and Cu5), i.e., 0.25 mM and 0.5 mM, respectively. As a sacrificial reductant, 1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo[d]imidazole (BIH)⁸ was used; this compound efficiently quenched the excited states of the Cu complexes, as shown below. Fe^{II}(dmp)₂(NCS)₂ (Fe, Fig. 1b)⁹ was used as the CAT in the photocatalytic reactions for two reasons: this complex had electrocatalytic ability toward CO₂ reduction at >E = -1.5 V vs. Ag/AgNO₃, which was indicated by its cyclic voltammogram (CV) measured in CH₃CN-triethanolamine (TEOA) (5:1 v/v) under a CO₂ atmosphere (Fig. S8), and the complex had relatively weak absorption in the visible region (Fig. S9).

In a typical photocatalytic reaction, a CH₃CN-TEOA (5:1 v/v) mixed solution (4 ml) containing Cu1 (0.25 mM), Fe (0.05 mM), and BIH (10 mM) was irradiated using 436 nm monochromic light, giving CO as the main product with H₂ but almost no HCOOH (Fig. S10); the turnover number (TON^{CAT}) based on the used Fe reached 95 (19.0 µmol) for CO and 56 (11.1 µmol) for H_2 after 5 h irradiation, and the selectivity of the CO formation was 70.5%. Note that more than 75% of the added BIH should already be consumed during the irradiation because CO and H₂ are two-electron-reduced products of CO₂ and protons, respectively, and BIH is a two-electron donor.⁸ Accordingly, BIH concentration in the reaction solution was increased to 50 mM. After 12 h irradiation, 54.5 μ mol of CO (TON^{CAT}_{CO} = 273) and 15.0 μ mol of H₂ (TON^{CAT}_{H2} = 75) were produced; the selectivity of CO formation was 78%. Note that almost all of the added Cu1 remained in the reaction solution even after the irradiation (Fig. S11). Thus, Cu1 is a tremendously stable redox PS.

A control experiment without Cu1 gave neither CO nor H₂. In the absence of Fe, on the other hand, Cu1 photocatalyzed only H₂ evolution, giving 9.5 μ mol H₂ with a very small amount of CO (0.3 μ mol). Decomposition of Cu1 in the photocatalytic reaction might give other catalysts for only H₂ evolution but not CO₂ reduc-

tion. Since, however, Cu1 was very stable in the presence of the Fe catalyst in the photocatalytic reaction condition, the effects of the decomposition products of Cu1 should not be so important for determining the product distribution. The carbon source of the produced CO was confirmed by a tracer experiment using 13 CO₂ (99% of the 13 C content). The produced ratio of 13 CO to 12 CO was 99:1 (Fig. S12), indicating that CO was produced by the reduction of CO₂. These results clearly show that the photocatalytic CO₂ reduction requires both Cu1 as the PS and Fe as the CAT, and the Cu1-Fe system can photocatalyze CO₂ reduction with high efficiency. The formation quantum yields (Φ) of CO and H₂ were 6.7% and 2.8%, respectively. This efficiency is the highest among the reported photocatalytic systems using Fe complexes as the CAT. Note that the ratio of PS to CAT was 10:1 in this system; however, in many of the photocatalytic systems using abundant metal complexes as the CAT, the ratio of PS to CAT was much higher, i.e., 10000:100; meanwhile, the TON based on the PS used was very low, even though TON^{CAT} was high.

Table 1. Photocatalytic abilities of mixed systems with Cu^I PSs and Fe^{II} CAT

~~~	<b>Fe</b> (0.05 r	<b>* +</b> mM)	(Dimeric Co (Monomeric (	PS mplex: 0.25 mM) Complex: 0.5 mM	)/hv(43	6 nm)
	$J_2 \longrightarrow$ BIH (10 mM) <i>in</i> CH ₃ CN / TEOA (5:1 v/v)					
•	PS	t ^a	Products ^b / µmol		$\Phi^{c}$ 0000	
		h	СО	$H_2$	СО	$H_2$
	Cu1	1	14.6	9.0	6.7	28
		5	19.0	11.1		2.8
	Cu1 ^d	12	54.5	15.0		
	Cu1 ^e	5	0.3	9.5		
	none	5	$n.d.^{f}$	$n.d.^{f}$		
	Cu2	1	11.1	7.6	2.6	2.0
		5	23.4	15.5		
	Cu3	1	6.1	5.6	2.3	1.1
		5	13.4	9.0		
	Cu4	1	5.9	4.8	1.1 0	0.6
		5	13.9	11.7		0.0
-	Cu5	5	n.d. ^f	n.d. ^f		

*a*, Irradiation time. *b*. a high-pressure Hg lamp ( $\lambda_{ex} = 435.8$  nm, see Experimental Details in SI) was used. *c*, Quantum yield as a ratio of the number of the product molecules and absorbed photons (Fig. S13 in SI). A Xe lamp was used with a band-pass filter ( $\lambda_{ex} = 436 \text{ nm} \pm 5 \text{ nm}$ , light intensity:  $5 \times 10^{-8}$  einstein s⁻¹, see Experimental Details in SI). *d*, The concentration of BIH was 50 mM. *e*, In the absence of **Fe**. *f*, Not detected.

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Table 1 summarizes the results of the photocatalytic reactions, including systems using other Cu¹ complexes as the CAT instead of Cu1 ([BIH] = 10 mM). Although another dimeric Cu complex, Cu3, with P₂phen ligands instead of P₂baphen, could also be used as the CAT, the efficiency was lower than that obtained using Cu1. In the three photocatalytic systems using the monomeric Cu complexes, Cu2 showed the highest TON_{CO}, which was similar to the system using the dimer Cu1. However,  $\Phi_{CO}$  (2.6%) was much lower compared to the system using Cu1. The photocatalytic ability for CO₂ reduction using Cu4, which contains a 2,9-dimethyl-phen ligand, was much lower than that using Cu2, which contains the 2,9-dimethyl-baphen ligand (Fig. S13). Interestingly, the system using Cu5 as the PS showed photocatalytic ability for neither CO₂ reduction nor H₂ evolution; the reason for this is discussed later. The comparison between the photocatalytic activities of these systems clearly shows that the introduction of either phenyl groups or two phosphine units into the phen ligand enhanced the ability of the Cu complex as a PS.

To clarify the reason(s) behind this result, we investigated the photophysical, electrochemical, and photochemical properties of the Cu complexes in detail (Tables S3 and S4). UV-Vis absorption spectra of all Cu¹ complexes (Fig. S14) showed a broad band at 350–450 nm, attributable to singlet metal-to-ligand charge transfer (¹MLCT) excitation. The spectra of **Cu2** and **Cu5** only contained a small shoulder, which was not observed in that of CH₂Cl₂, at around 450–500 nm due to a partial ligand exchange proceeding even in the dark to produce the corresponding homoleptic Cu¹(N^N)₂⁺ complexes (N^N = diimine ligand).¹⁰ On the other hand, spectral characteristics due to the ligand exchange were not observed in the cases of Cu¹ complexes having the tetradentate ligand, i.e., **Cu1** and **Cu3**.

In CH₂Cl₂, all Cu^I complexes showed broad emissions at 450–800 nm with high quantum yields ( $\Phi_{em} = 0.17$ – 0.52) and long lifetimes ( $\tau_{em} = 11.0-19.4 \ \mu s$ ), even at room temperature. It has been reported that emission from Cu¹ diimine complexes can be attributed to delayed fluorescence from their ¹MLCT excited states and is significantly quenched in solvent; this is because solvent molecules can coordinate to metal ions following flattening of the tetrahedral structures of the Cu complexes.¹¹ In CH₃CN, emission from the Cu^I complexes (Fig. S14) was partially quenched in the cases of Cu1-Cu4 and completely quenched in the case of Cu5; however, the emissive properties of Cu1 and Cu3 were relatively well preserved, with  $\tau_{em}$  of ~4 µs and  $\Phi_{em}$  of ~0.04, compared with those of Cu2 and Cu4 ( $\tau_{em} \sim 1 \mu s$  and  $\Phi_{em} \sim 0.03$ ) (Fig. S16 and Table S3). The lack of photocatalysis of the system using Cu5 is likely due to the short lifetime of the excited Cu5 in CH₃CN. Reductive quenching of the excited states of Cu1-Cu4 by BIH was investigated by Stern-Volmer experiments (Figs. S1620); linear relationships were observed between BIH concentration and both  $I_0/I$  and  $\tau_0/\tau$ , and these two plots overlapped each other in all cases. This clearly indicates that the quenching of emission from the Cu complexes by BIH was a dynamic process. The excited-state quenching rates ( $k_q^{\text{BIH}}$ ) of the Cu^I complexes by BIH were 2.2–5.6 × 10⁹ M⁻¹s⁻¹ (Table. S4), and most of the excited **Cu1–Cu4** complexes were quenched by 10 mM of BIH (the quenching fractions,  $\eta_q^{\text{BIH}}$ , were 95–97%). On the other hand, quenching by **Fe**, CO₂, or TEOA, which is required as a base for removing a proton from the one-electron-oxidized species of BIH, was not observed under the photocatalytic reaction conditions.

UV-vis absorption spectral changes in CH₃CN-TEOA (5:1 v/v) solutions containing Cu1 or Cu2 were observed during irradiation in the presence of BIH (10 mM) under an Ar atmosphere (Fig. S21a and d). Just after the irradiation began, a new broadband arose around 700 nm, which is attributable to the one-electronreduced species (OERS) of the Cu complex because a similar absorption was observed in controlled electrolysis of the Cu¹ complexes at -2.0 V vs. Ag/AgNO₃ (Figs. S21b and e; CVs of Cu1 and Cu2 are shown in Fig. S25). The OERSs accumulated immediately after starting the irradiation and then reached the maximum amounts (Figs. S21c and f). Although further irradiation caused a decrease in the OERSs, this decrease was much slower in the case of Cu1 than Cu2. In the cases of Cu3 and Cu4, on the other hand, the OERSs were not observed even in the first stage of irradiation (Fig. S22). These results suggest that the higher stability of the OERS of **Cu1** induced more efficient capability as a PS.

The stability of the OERS of **Cu1** was also confirmed by its CV (Fig. S25); a reversible one-electron reduction wave was observed at  $E_{1/2} = -1.95$  V vs. Ag/AgNO₃. Although the first reduction wave in the CV of **Cu2** was also reversible ( $E_{1/2} = -1.96$  V), the reversibility of the first reduction waves of **Cu3**, **Cu4**, and **Cu5** ( $E_{1/2} = -$ 2.01, -2.03, and - 1.98 V, respectively) was clearly lower, and the reverse scan to the positive potential after the cathodic scan gave an additional sharp peak or peaks at -0.20 V and -0.55 V in the case of **Cu4** and at -0.60 V in the case of **Cu5**.

The first reduction wave of **Fe**, which was measured in CH₃CN-TEOA (5:1 v/v) under a CO₂ atmosphere, was observed at  $E_p = -1.61$  V, followed by a catalytic wave, with an onset potential of -1.8 V (Fig. S8). This clearly indicates that both first and second reductions of **Fe** by the OERS of all Cu complexes are thermodynamically favorable processes. Actually, under the photocatalytic reaction conditions in the presence of both CO₂ and **Fe**, accumulation of the OERSs of the Cu complexes could not be observed, even in the experiments using **Cu1** and **Cu2** (Figs. S21c and f, S23, and S24).

In conclusion, we successfully constructed an efficient and durable photocatalytic system for  $CO_2$  reduction using abundant-metal complexes, i.e., **Cu1** as the PS and **Fe** as the CAT. The abilities of the Cu¹ complexes can be improved by the introduction of both a tetradentate ligand and phenyl groups into the 4,7-position of the phen moiety of the tetradentate ligand. The photocatalytic reduction of CO₂ proceeded via (1) reductive quenching of the excited Cu PS with BIH and (2) first and second electron transfer processes from the OERS of the Cu PS to the Fe CAT. A more detailed mechanistic study of CO₂ reduction, especially CO₂ reduction processes on the Fe CAT, is underway in our laboratory.

## ASSOCIATED CONTENT

#### Supporting Information.

Experimental details, crystallographic data, dynamic NMR analysis, cyclic voltammograms, photophysical data, quenching experiments, time courses of the product formation, HPLC analysis of the photosensitizer, spectral changes during photoirradiation, tracer experiment using ¹³CO₂, and ESI-MS and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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