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Highly Efficient and Robust Photocatalytic Systems for CO₂ Reduction Consisting of a Cu(I) Photosensitizer and Mn(I) Catalysts

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Supporting Information

ABSTRACT: The development of highly efficient, selective, and durable photocatalytic CO2 reduction systems that only use earthabundant elements is key for both solving global warming and tackling the shortage of energy and carbon resources. Here, we successfully developed CO₂ reduction photocatalysts using $[Cu_2(P_2bph)_2]^{2+}$ (CuPS) $(P_2bph = 4,7-diphenyl-2,9-di(diphenylphosphinotetramethylene)-1,10$ phenanthroline) as a redox photosensitizer and $fac-Mn(X_2bpy)(CO)_3Br$ (Mn(4X)) (X₂bpy = 4,4'-X₂-2,2'-bipyridine (X = -H and -OMe) or **Mn(6mes)** (6mes = 6,6'-(mesityl)₂-2,2'-bipyridne)) as the catalyst. The most efficient photocatalysis was achieved by Mn(4OMe): The total quantum yield of CO₂ reduction products was 57%, the turnover



number based on the Mn catalyst was over 1300, and the selectivity of CO₂ reduction was 95%. Electronic and steric effects of the substituents (X) in the Mn complexes largely affected both the photocatalytic efficiency and the product selectivity. For example, the highest selectivity of CO formation was achieved by using Mn(6mes) (selectivity $S_{CO} = 96.6\%$), whereas the photocatalytic system using Mn(4H) yielded HCOOH as the main product ($S_{\text{HCOOH}} = 74.6\%$) with CO and H₂ as minor products ($S_{CO} = 23.7\%$, $S_{H_2} = 1.7\%$). In these photocatalytic reactions, CuPS played its role as an efficient and very durable redox photosensitizer, while remaining stable in the reaction solution even after a turnover number of 200 had been reached (the catalyst used had a turnover number of over 1000).

INTRODUCTION

Recent concerns about global warming and the shortage of energy and carbon resources are the primary reasons behind the development of artificial photosynthetic systems that can reduce CO₂ to useful chemicals by using solar light as the energy source. From this viewpoint, photocatalytic CO₂ reduction systems that consist of metal complexes have attracted attention as a key component of artificial photosynthesis because of their high efficiency and the selectivity of the products. Since relatively low-energy multielectron reduction of CO_2 is necessary, as shown in eqs 1–3, such photocatalytic systems consist of two components: a redox photosensitizer, which initiates the photochemical one-electron transfer from a reductant to a catalyst, and the catalyst, which accepts electrons from the redox photosensitizer, activates CO2, and introduces the electrons into CO2. Recently, metal-complex photocatalytic systems for CO₂ reduction have been successfully applied to semiconductor hybrid systems, which can reduce \overline{CO}_2 using water as the reductant.^{1,2} A binuclear complex consisting of a Ru(II) redox photosensitizer and a Re(I) catalyst was adsorbed onto a p-type semiconductor electrode, which works as a molecular photocathode for CO₂ reduction, and was combined with an n-type semiconductor

photoanode (CoO_x-adsorbed TaON) for water oxidation. This photoelectrochemical cell photocatalytically reduces CO₂ by using water as the reductant and only visible light as the energy source:²

$$\mathrm{CO}_2 + \mathrm{e}^- \to \mathrm{CO}_2^{\bullet^-} \tag{1}$$

$$CO_2 + 2e^- + 2H^+ \rightarrow HCO_2H$$
 (2)

$$\mathrm{CO}_2 + 2\mathrm{e}^- + 2\mathrm{H}^+ \to \mathrm{CO} + \mathrm{H}_2\mathrm{O} \tag{3}$$

Although various combinations of metal-complex redox photosensitizers and catalysts have been reported, many of them used noble- and/or rare-metal complexes. Highly efficient and durable photocatalysts have been constructed by using Re(I) metal complexes,³ Ru(II) complexes, or both metals,⁴ and quantum yields Φ > 50% and turnover number (TON) > 1000 were reported. Fossil fuel-related CO₂ emissions reached 32 \pm 2.7 Gt/year in 2010 and have been increasing by a few percent every year.⁵ It is not feasible to treat this large volume of CO_2 by using rare-earth metals such

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as Re (only 0.7 ppb in the earth crust)⁶ or Ru (1 ppb in the earth crust)⁶ as photosensitizers and/or catalysts.

Reports on molecular photocatalytic systems for CO₂ reduction consisting of only earth-abundant elements have recently been increasing. Co(II) and Ni(II) macrocyclic complexes (Co: 25 ppm, Ni 84 ppm in the earth crust)⁶ have been investigated as catalysts for CO₂ reduction in both photocatalytic and electrocatalytic systems for a long time. Of these photocatalytic systems, Yanagida and Fujita et al.⁷ reported the most efficient photocatalytic systems using Co(II) complexes as the photosensitizer, however p-terphenyl only uses UV light ($\Phi_{CO+HCOOH}$ = 25% under irradiation at λ_{ex} = 313 nm). The durability of this system was also low; $TON(CAT)_{CO+HCOOH}$ < 20 (TON based on the catalyst used). Other photocatalytic systems that use Co and Ni complexes are combined with rare-metal photosensitizers, mostly $[Ru(N^N)_3]^{2+}$. In addition, in most of the reported cases, high efficiency, durability, and selectivity of the photocatalytic reduction of CO₂ were not achieved.³

We previously reported a photocatalytic system with a dinuclear Cu(I) complex as a redox photosensitizer (CuPS in Scheme 1) and $Fe^{II}(2,9-Me_2phen)_2(NCS)_2$ (phen = 1,10-

Scheme 1. Structure of the Cu^I Complex Redox Photosensitiser, CuPS, and the Mn^I Complex Catalysts, Mn(4X) and Mn(6mes)



phenantroline) as a catalyst ($\Phi_{CO} = 6.7\%$, TON(PS) = 55, $TON(CAT) = 273)^9$ (Cu: 60 ppm, Fe: 56300 ppm in the earth crust).⁸ Although homoleptic-type complexes, that is, $Cu^{I}(2,9-Me_{2}phen)_{2}^{+}$ and its derivatives, have an advantage of light absorption at longer wavelength up to 600 nm and were used as a photosensitizer in photocatalytic H₂ production systems,¹⁰ their weak oxidation power in the excited state caused lower efficiency of the photocatalytic reaction. Beller and his co-workers recently reported another mixed system consisting of a mononuclear Cu(I) photosensitizer complex and Fe(II) cyclopentadienone carbonyl complexes as catalysts, where $\Phi_{CO} = 13.3\%$ (TON(PS) = 97, TON(CAT) = 487).¹¹ Robert and co-workers reported a combination of an organic photosensitizer and a Fe quaterpyridine catalyst for CO₂ reduction to give CO (Φ_{CO} = 1.1%, TON(PS) = 341, TON(CAT) = 1365).¹² They also reported CH₄ formation using a Fe porphyrin in a combined system with an Ir(III) photosensitizer (Φ_{CH_4} = 0.18%, TON(PS) = 0.79, TON-(CAT) = 79.^{13,14}

The other notable earth-abundant metal complexes for the catalysis of CO₂ reduction are Mn(I) complexes, *fac*- $[Mn^{I}(N^{N})(CO)_{3}L]^{n+}$ (N^N = diimine ligand; L = Cl⁻, Br⁻, NCS⁻, MeCN) (Mn: 950 ppm in the earth crust).⁶ Since *fac*-Mn^I(bpy)(CO)₃Br (bpy = 2,2'-bipyridine) was first

reported as an electrochemical catalyst for CO₂ reduction by Deronzier and co-workers, 15,16 electrocatalysis by these Mn complexes has been widely investigated by several groups.¹ These studies clarified that the catalytic behavior of the Mn complexes and their mechanisms is very different from the Re(I) complexes, even though the structure and the ligands are the same. In most of the systems that use Mn complexes, the major product was CO. We first applied this Mn complex to a photocatalytic system for CO₂ reduction by combining it with $[Ru^{II}(N^N)_3]^{2+}$ as a redox photosensitizer. This system produced HCOOH as the major product with a quantum yield of 5.3%, and both TON(PS)_{HCOOH} and TON-(CAT)_{HCOOH} were 150.²⁵ Although some other groups also reported photocatalytic systems including Mn-complex catalysts, Ru and Zn porphyrin complexes were used as the redox photosensitizers, and the photocatalytic behavior was low $(\Phi_{\text{HCOOH}} < 4\%, \text{TON(PS)} < 13, \text{TON(CAT)} < 130).^{26-28}$ Although, as described above, CO₂ reduction photocatalytic systems without noble elements have recently become the center of attention, their photocatalytic properties are still much lower than the reported photocatalytic systems that consist of noble and/or rare metal complexes.

We herein report the most efficient and durable CO_2 reduction photocatalytic systems that only contain earthabundant metal complexes, that is, a combination of **CuPS** as the redox photosensitizer and *fac*-Mn^I(4,4'-X₂-bpy)(CO)₃Br or *fac*-Mn^I{6,6'-(mesityl)₂-bpy}(CO)₃Br, **Mn**(4X) or **Mn**(6mes), respectively (Scheme 1); $\Phi_{CO+HCOOH} = 57\%$, TON-(PS)_{CO+HCOOH} = 263, TON(CAT)_{CO+HCOOH} = 1314 in the case of **Mn**(4OMe). By changing the substituents, the distribution of the reduction products of CO₂ could also be controlled; CO:HCOOH = 93:6 for **Mn**(6mes) and 6:94 for **Mn**(4H).

RESULTS AND DISCUSSION

Photocatalytic Reduction of CO₂. A *N*,*N*-dimethylacetoamide (DMA)-triethanolamine (TEOA) (4:1, v/v) solution containing the Mn complex (Mn(4H), Mn(4OMe) or Mn(6mes)) as the catalyst (0.05 mM), CuPS as a redox photosensitizer (0.25 mM), and 1,3-dimethyl-2-phenyl-2,3dihydro-1*H*-benzo[d]imidazole (BIH; 10 mM) as a reductant was irradiated at $\lambda_{ex} = 436$ nm. In the case using Mn(4H) as the catalyst, the main product was HCOOH, and the TON based on the catalyst used (TON(CAT)) was 157 for 2 h irradiation (eq 4, Figure S2a).

$$CO_{2} \xrightarrow{Mn^{*} complex(0.05 \text{ mM}) + CuPS(0.25 \text{ mM})/h\nu(436 \text{ nm})}_{BIH(10 \text{ mM}) \text{ in DMA-TEOA}(4:1 \text{ v/v})} CO \text{ and/or HCOOH}$$
(4)

A certain amount of CO was also produced $(TON(CAT)_{CO} = 50)$, whereas H₂ evolution was minimal $(TON(CAT)_{H_2} = 4)$. It should also be noted that almost all of the BIH was consumed in the 2 h irradiation because BIH (40 μ mol) is a two-electron donor as shown in eq 5, and the production of all

the reduction products requires two electrons (the total amount of the reduction products was 41 μ mol). Therefore, the termination of the photocatalytic CO₂ reduction was attributed to the complete consumption of BIH.

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Figure 1. Quantum yield determination of photocatalytic CO2 reduction using Mn catalysts (0.05 mM) and CuPS (0.25 mM) in the presence of BIH (10 mM) in a CO₂-saturated DMA-TEOA (4:1, v/v) solution. (a) Mn(4H), (b) Mn(4OMe), and (c) Mn(6mes). The photocatalytic reactions were performed at 25 °C under 436 nm monochromatic light (intensity: 2.0×10^{-8} einstein s⁻¹).



Figure 2. Photocatalytic CO₂ reduction using a higher concentration of BIH (0.1 M); [Mn(4OMe)] = 0.05 mM, [CuPS] = 0.25 mM; CO₂saturated DMA-TEOA (4:1, v/v) solution, λ_{ex} = 436 nm, 25 °C. Time courses of (a) product formation and (b) decrease of BIH and CuPS in the solution during the photocatalytic reaction.

Table 1. Photocatalytic Properties of Systems Consisting of CuPS as the Redox Photosensitiser and Mn(I) Complexes As the Catalyst^a

	quant	um yield ^b	products ^c / μ mol (TON(CAT) ^d , distribution/%)			
Mn(I) complex	СО	НСООН	СО	НСООН	H_2	
Mn(4H)	0.02	0.30	9.9 (50, 23.7)	31.3 (157, 74.6)	0.7 (4, 1.7)	
Mn(4OMe)	0.33	0.24	32.7 (164, 66.3)	12.9 (65, 28.5)	0.2 (1, 5.2)	
Mn(6mes)	0.41	0.03	41.5 (208, 96.6)	0.9 (5, 0.2)	0.1 (0.5, 0.2)	

"The photocatalytic reaction performed using a 4 mL CH₃CN-TEOA solution containing CuPS (0.25 mM), a Mn complex (0.05 mM), and BIH (10 mM) under irradiation by 436 nm monochromatic light from a Hg lamp. ^bIntensity of the irradiated light was 2.0×10^{-8} einstein s⁻¹. ^cThe amount of products and their distribution (Figure S2). ^dTurnover number based on the catalyst used.

In the case of Mn(4OMe), the main product was CO with $TON(CAT)_{CO} = 150$ (Figure S2b), and less than half the amount of HCOOH $(TON(CAT)_{HCOOH} = 65)$ along with a small amount of H_2 (TON(CAT)_{H₂} = 11) were produced after 2 h irradiation. No further production of the reduction products after 1 h irradiation supports the full consumption of BIH. A very high selectivity of CO formation could be achieved by using Mn(6mes) as the catalyst (Figure S2c), where $TON(CAT)_{CO} = 208$, $TON(CAT)_{HCOOH} = 5$, and $TON(CAT)_{H_2} = 3.$

The formation quantum yields of the products were determined during the initial stage of the photocatalytic reactions, where the formation of the products increased in proportion to the irradiation time (Figure 1). In the photocatalytic system using Mn(4H), $\Phi_{HCOOH} = 30\%$ and

 Φ_{CO} = 2%. In the case of using Mn(4OMe), Φ_{CO} = 33% and Φ_{HCOOH} = 24%. Notably, the total quantum yield of the CO₂ reduction products $(\Phi_{ ext{total}})$ reached 57% in the photocatalytic system using Mn(4OMe). To the best of our knowledge, this is the highest quantum yield for CO₂ reduction using abundant elements. The photocatalytic system using Mn(6mes) showed the highest quantum yield of CO formation (Φ_{CO} = 41% with $\Phi_{\text{HCOOH}} = 3\%$).

To check the durability of the photocatalytic systems consisting of the Cu photosensitizer and the Mn catalyst, the amount of BIH was increased to 0.1 M in the Mn(4OMe) system (Figure 2a). After 24 h irradiation, $TON(CAT)_{CO}$ reached 1004 with TON(CAT)_{HCOOH} = 310 and TON- $(CAT)_{H_2} = 68 (TON(PS)s were 201, 62, and 14, respectively).$ Figure 2b shows the changes in the concentration of BIH and **CuPS** during the photocatalytic reaction. This clearly indicates that the consumption of BIH was also a reason for decreasing the rate of the photocatalytic reaction.²⁹ It also indicates that **CuPS** is a very stable and efficient redox photosensitizer, as decomposition was only 2% even after 12 h irradiation where the TON(PS) of all the reduction products was over 200 and most of the BIH was already consumed. As can be seen in the video (see Video S1), this system generated vigorous bubbles of CO from a few minutes after the photoirradiation, and the formation of bubbles was still observed even after 5.5 h. Interestingly, the selectivity of CO formation was 76% after 36 h irradiation, which is higher than that obtained in the quantum yield determination (58%). The concentration of BIH, which is a strong base, and/or the enhancement of the electron injection rate into the catalyst might be the reasons for these observations.

Table 1 summarizes the photocatalytic properties of the systems studied. In this section, we conclude that the combination of **CuPS** and the Mn catalysts is very efficient and durable visible-light-driven photocatalytic systems for CO_2 reduction. The distribution of CO and HCOOH can be controlled by changing the substituents on the bpy ligand of the Mn catalysts (CO:HCOOH was 93:6 and 6:94 for **Mn(6mes)** and (**Mn(4H)**, respectively).

Synthesis, Structure, and Properties of CuPS. In one of the previous papers,⁹ we briefly reported the synthesis of **CuPS** and its properties in MeCN. As **CuPS** works as a magnificent redox photosensitizer, we herein report more details about its structure and properties, especially in DMA and DMA–TEOA solutions. We successfully improved its synthesis method by optimizing the reaction condition (eq 6); the details are described in the Experimental Section. The isolated yield was 12%.



The crystal structure of CuPS was successfully obtained by X-ray analysis as shown in Figure 3. The crystallographic data and the selected bond lengths and angles are summarized in Tables S1 and S2. Two Cu-complex units in one molecule had the same structure, and the distance between the two Cu⁺ ions was 8.5 Å, which is too far for any interaction. The angle between the planes containing NCuN and PCuP was 88.5°, which is required for a long lifetime of the excited state of this type of Cu^I complexes.³⁰ The P-Cu-P bite angle was 113.4°, which was smaller than that of the corresponding mononuclear complex, $Cu^{I}(2,9-Me_{2}phen)(PPh_{2}Pr)_{2}(PF_{6})$ with one 2,9-Me₂phen and two monodentate phosphine ligands,⁹ indicating the angles were restricted by tethering the quarter dentate ligand with the phen structure in CuPS. It was shown that the phenyl planes at the 4,7-positions of the phen moiety in the ligands were twisted against the phen plane $(51.7 \text{ and } 68.9^{\circ})$ because of steric repulsion between hydrogen atoms. This result indicates that the π -conjugation between the phenyl groups and phen moiety in the ligands is not strong in the ground state of CuPS. The bond lengths around the Cu and P atoms and the phen-C lengths were similar to those in other Cu^I complexes, that is, Cu-P (2.3 Å), Cu-N (2.1 Å), P-C (1.8 Å), and C[phen]-C (1.5 Å).

The photocatalytic reactions using **CuPS** and Mn catalysts were conducted in DMA solutions. The photophysical and electrochemical properties of **CuPS** were remeasured in DMA, as these properties have only previously been measured in MeCN,⁹ and, in general, these properties of many Cu(I) complexes are highly dependent on the solvent.³¹ Figure 4a shows the UV–vis absorption spectrum of **CuPS** measured in DMA. The broad absorption band with $\lambda_{max} = 384$ nm is attributed to the singlet metal-to-ligand-charge-transfer (¹MLCT) transition from Cu^I to the phen moiety. The molar extinction coefficient at the absorption maximum was $\varepsilon_{384 \text{ nm}} = 9800 \text{ M}^{-1} \text{ cm}^{-1}$.

Figure 4a also shows the emission spectrum from CuPS excited at λ_{ex} = 444 nm, due to the delayed fluorescence via the ¹MLCT excited state which is thermally accessible from the



Figure 3. ORTEP drawing of the Cu complex: $CuPS(PF_6)_2$ ·SMeCN·MeOH. Displacement ellipsoids are shown at the 50% probability level. H atoms, PF_6 anions and solvent molecules were omitted for clarity.



Figure 4. (a) UV-vis absorption and emission spectra (excitation at 444 nm) and (b) emission decay (excited at 401 nm and monitored at 650 nm) of CuPS in DMA at 25 °C. (c) UV-vis absorption spectra of Mn(4H) (red), Mn(4OMe) (blue), and Mn(6mes) (green).

 3MLCT excited state. 32 The emission maximum and quantum yield were $\lambda_{\rm max}$ = 634 nm and $\Phi_{\rm em}$ = 2.7% in DMA, respectively.

Emission decay was measured at $\lambda = 650$ nm by using the single-photon counting method (Figure 4b, Supporting Information); just after excitation at $\lambda_{ex} = 401$ nm, a rapid decay was observed within the time resolution of the apparatus (1 ns), which is attributable to the dynamics relevant to the structural distortion, had been reached,³³ and then a slower decay was observed with $\tau_{em} = 810$ ns, which is attributed to the delayed fluorescence.³²

Figure 5a shows the cyclic voltammogram (CV) of **CuPS**; one reversible redox couple was observed at $E_{1/2} = -1.92$ V vs Ag/AgNO₃. This shows that the one-electron-reduced species (OERS) of **CuPS** is stable in the time scale of the CV measurement. Figure 6a shows the changes in the UV–vis absorption of an MeCN solution containing **CuPS** (0.25 mM) and Et_4NBF_4 (0.1 M) as a supporting electrolyte during flow electrolysis at various applied potentials under an Ar atmosphere. The dependence of the absorption at $\lambda = 720$ nm and the current on the applied voltage are shown in Figure 6b, which indicate that the OERS of **CuPS** is stable and its molar extinction coefficient is $\varepsilon = 5500$ M⁻¹ cm⁻¹ at $\lambda = 720$ nm.

Reaction Mechanism. In all the UV–vis absorption spectra of the Mn complexes, a broad ¹MLCT band was observed in the visible region (Figure 4c). The absorption maxima of the ¹MLCT bands and the absorbance at $\lambda = 436$ nm (the wavelength of the irradiation light in the photocatalytic reactions) are summarized in Table 2. Since the concentration of **CuPS** was five times higher than those of the Mn complexes, the absorbance of **CuPS** was found to be 8.6–10.6 times higher than those of the Mn complexes in the reaction solutions.

The excited-state lifetimes of the Mn complexes are too short to initiate the photocatalytic reactions.³⁴ Therefore, the photoinduced electron transfer from BIH to **CuPS** should be



Figure 5. CVs of CuPS (0.25 mM, a) and Mn(4X) (0.5 mM: b, X = H; c, X = OMe: d) or Mn(6mes) (0.5 mM) in DMA solutions containing 0.1 M Et₄NBF₄ as a supporting electrolyte under an Ar atmosphere: WE, glassy carbon (ϕ 3 mm); CE, Pt wire; RE, Ag/AgNO₃ (0.01 M); scan rate, 0.2 V s⁻¹.

the initial process in the photocatalytic CO₂ reduction, which was investigated by emission quenching and transient absorption spectroscopy as follows. Emission from **CuPS** was efficiently quenched by BIH, as shown in Figure 7a, from which a Stern–Volmer analysis showed linear plots with an intercept at 1 (Figure 7b). From the slope of this line ($K_{\rm SV} = k_{\rm q} \tau_{\rm em} = 1.04 \ {\rm mM}^{-1}$) and the emission lifetime $\tau_{\rm em} = 810 \ {\rm ns}$, the



Figure 6. UV–vis spectral changes obtained during the flow electrolysis of **CuPS** (0.25 mM) in MeCN containing Et_4NBF_4 (0.1 M) as a supporting electrolyte under an Ar atmosphere (flow rate: 0.2 mL min⁻¹, carbon felt as a working electrode, Pt wire as a counter-electrode, Ag/AgNO₃ (0.01 M) as a reference electrode). The electrolyzed solution was introduced into an optical cell (1.5 mm path length) for measuring the absorption spectrum. Gray circles show the current, and the blue squares show the absorbance at $\lambda = 720$ nm.

Table 2. Light-Absorbing Properties of the Cu and Mn Complexes

complex	λ_{\max}^{a}/nm ($\varepsilon^{b}/\mathrm{M}^{-1}~\mathrm{cm}^{-1}$)	A436
CuPS	384	(9800)	0.95
Mn(4H)	417	(2640)	0.11
Mn(4OMe)	403	(3000)	0.09
Mn(6mes)	388	(2390)	0.09

^{*a*1}MLCT absorption maxima. ^{*b*}Molar extinction coefficient. ^{*c*}Absorbance at 436 nm under photocatalytic condition (**CuPS**, 0.25 mM; Mn complexes, 0.05 mM; a 1 cm pass length).

quenching rate constant was determined as $k_q = 1.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

Laser-pulse irradiation (λ = 355 nm, 10 ns fwhm) of a DMA–TEOA (4:1, v/v) solution containing only **CuPS** (0.05 mM) induced a new transient absorption band with absorption maxima at 500 and 630 nm (Figure 8a). The absorption decayed with τ = 840 ns without undergoing any change in the shape. Since this lifetime was almost identical to the emission lifetime from **CuPS** (τ_{em} = 810 ns as described above), this transient absorption is therefore attributed to arise mostly from the ³MLCT excited state of **CuPS**, which might have a small contribution from its ¹MLCT excited state in thermal equilibrium. In the presence of BIH (10 mM), the absorption

of the excited state(s) was only observed in the early stage; however, it rapidly decayed and a new broad absorption band appeared at $\lambda_{max} \sim 750$ nm, which was attributed to the OERS of **CuPS** (**CuPS**^{•-}) (Figure 8b). These results clearly indicate that the reductive quenching of the excited state(s) of **CuPS** (***CuPS**) proceeded by BIH to give **CuPS**^{•-} (Figure 6).

Figure 8c shows the time course of the absorbance change at λ = 720 nm. There were two kinds of increase in the transient absorption: a fast increase within 100 ns from laser irradiation and then a following slow rise up until 5 μ s after the irradiation. Since, under these reaction conditions, 91% of the excited Cu complex was reductively quenched by BIH (10 mM) and the emission lifetime of CuPS was 71 ns, which coincides with the fast absorption rise in the transient absorption measurement, the first increase at $\lambda = 720$ nm can be mainly attributed to the photochemical electron transfer from BIH to *CuPS to produce CuPS^{•-}. It is noteworthy that this absorption change should include a decrease in *CuPS, which has a weaker absorption at this wavelength (Figure 8a). After 100 ns after laser irradiation, most of the *CuPS should disappear. Since it has been reported that BIH works as a twoelectron donor as shown in eq 4,³⁵ the slower increase in the transient absorption at $\lambda = 720$ nm should be caused by the reduction of the ground state of CuPS by the deprotonated product of BIH^{•+}, that is, BI[•] ($E_p^{ox} = -2.06 \text{ V vs Fc}^+/\text{Fc}^{36}$).



Figure 7. Emission spectra (excitation at 444 nm) of CuPS in DMA under an Ar atmosphere in the presence of various amounts of BIH (a) and the Stern–Volmer plot using the emission intensity (I) observed at 630 nm (b). I_0 is the emission intensity without any BIH.



Figure 8. Transient absorption spectra measured after irradiation with a 355 nm laser pulse of a DMA–TEOA (4:1, v/v) solution containing **CuPS** (0.05 mM) (a) in the absence or (b) in the presence of BIH (10 mM) under an Ar atmosphere. (c) Transient absorption change (red solid curve) monitored at λ = 720 nm and the excitation laser pulse intensity profile (green solid curve).

Scheme 2 summarizes the mechanism of the photochemical reduction of CuPS by BIH, including the back-electron-

Scheme 2. Initial Processes of the Photocatalytic Reaction.^a



^{*a*}I_{abs}: Absorbed photons. k_0 : Intrinsic decay rate constant of ***CuPS**. k_q : Quenching rate constant of ***CuPS** by BIH. k_{esc} : Escape rate constant from the solvated radical ion pair to the individually solvated free radical ions. k_{rec} : Back-electron-transfer rate constant from **CuPS**^{•-} to BIH^{•+} in the solvated ion cage. k_{rec} ': Back-electron-transfer rate constant between the solvated **CuPS**^{•-} and BIH^{•+}: k_{dp} : Deprotonation rate constant of BIH^{•+} by the base species, mostly TEOA: k_{et} : Electron-transfer rate constant from BI[•] to the ground-state **CuPS**.

transfer processes from $CuPS^{\bullet-}$ to the one-electron-oxidation species of BIH (BIH^{•+}) both in the state of the solvated radical ion pair $[CuPS^{\bullet-} \cdots BIH^{\bullet+}]_{sol}$ and the individually solvated free-radical ions.

For quantifying these **CuPS**^{•-}-generation processes, the rise in absorption at $\lambda = 720$ nm ($\Delta A(t)$) was analyzed by using the model shown in Scheme 2. Since, in the initial stage up to 250 ns after laser irradiation, both ***CuPS** and **CuPS**^{•-} should coexist in the reaction solution, the absorbance attributed to ***CuPS** was calculated by using the molar extinction coefficient of ***CuPS** (2700 M⁻¹ cm⁻¹ at 720 nm; see Supporting Information) and the time profile of ***CuPS**, which was obtained from the emission decay kinetics (Figure S4). By using this data and the molar extinction coefficient of **CuPS**^{•-} (5500 M⁻¹ cm⁻¹ at 720 nm: Figure 6), $\Delta A(t)$ can be converted into the concentrations of ***CuPS** and **CuPS**^{•-} as shown in Figure 9. From this figure, we could determine the formation yield of CuPS^{•–} as $16.2 \pm 0.6 \,\mu\text{M}$ in the initial stage,



Figure 9. Concentration changes of *CuPS (blue curve) and CuPS^{$\bullet-$} (red curve) as calculated from the transient absorption change of a DMA–TEOA (4:1, v/v) solution containing CuPS (0.05 mM) in the presence of BIH (10 mM) under an Ar atmosphere.

mostly attributed to the photochemical electron transfer from BIH to *CuPS, and 7.5 \pm 0.5 μ M in the slower process attributed to the electron transfer from BI[•] to the ground state of CuPS. Since the absorbed photon number was determined as 25.8 \times 10⁻⁶ einstein dm⁻³ (Supporting Information), the total quantum yield of formation of CuPS^{•-} was $\Phi_{\text{OER}} = 1.20$ \pm 0.06, which can be divided into $\Phi_1 = 0.82$ for the initial photochemical electron-transfer process and $\Phi_2 = 0.38$ for the slower process since the difference in the time scales between these two processes was very large. Our assumption of the absorbed photon number is the lowest possible value because we assumed that the formation quantum yield of the lowest ³MLCT excited state of the Cu photosensitizer, that is, *CuPS,

Table 3. Redox Potentials of the Mn Complexes and Their Reduc	ced Species As Observed by Flow Electrolysis
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	redox potential $(E_p)^a/V$ vs Ag/AgNO ₃		$\lambda_{ m max}/ m nm~(arepsilon/ m M^{-1}~ m cm^{-1})$			
complex	cathodic	anodic	Mn–Mn dimer		Mn^{-b}	
Mn(4H)	-1.59, -1.77	-1.37, -0.49	805	(11,500)	569	(13,600)
Mn(4OMe)	-1.73, -1.93	-1.55, -0.69	840	(7,500)	566	(8,800)
Mn(6mes)	-1.69	-1.43	nd ^c	nd ^c	572	(10,600)
^a Peak potential, ^b Two-electron reduced 5-coordinate 18-electron species ($[Mn(N^N)(CO)_2]^-$). ^c Not detected.						

which was used for determining the absorbed photon, is unity. It has been reported that the rate constant of intersystem crossing (k_{ISC}) is much larger than that of intrinsic direct deactivation from S_1 to S_0 (k_s) not only in Cu(I) bis-diimine complexes³³ but also in mononuclear Cu(I) dimine bisphosphine complexes $(k_{\rm ISC} \sim 10^{11} \text{ s}^{-1}, k_{\rm S} \sim 10^{7} \text{ s}^{-1})$,³⁷ which means that the quantum yields of the intersystem crossing were almost unity. It has been also reported that another Cu(I) dimer complex $Cu_2Cl_2(N^P)_2$ (N^P = 2-pyridyldiphenylphosphine), of which Cu(I)s interact each other through the Cl ligands, the intersystem crossing rate increases due to enhanced spin orbit coupling.³⁸ Although such intramolecular interaction might be small in CuPS because the two Cu(I) centers largely separated each other (8.5 Å), it should be reasonable to assume that the quantum yield of the intersystem crossing to produce *CuPS is almost unity. It is also noteworthy that Φ_2 should depend on the light intensity because the back-electron-transfer process, which lowers Φ_{2} , complies with second-order kinetics (Scheme 2; both the concentration of BIH⁺⁺ and CuPS⁺⁻ depend on light intensity), whereas Φ_1 is independent of light intensity. Since, here, Φ_2 was determined by using a very strong laser light for the excitation, the Φ_2 value in the photocatalytic reactions should be higher than that in the laser flash photolysis experiment.

From the results of this investigation, it should be interesting to compare the data obtained here with that of other redox photosensitizers, typically $[Ru^{II}(dmb)_3]^{2+}$ (dmb = 4,4'dimethyl-bpy), which has been frequently used in the photocatalytic reactions for CO₂ reduction; $\Phi_{OER} = 0.59$ (higher light intensity, i.e., 1.1×10^{-8} einstein s⁻¹) and 0.95 (lower light intensity, i.e., 1.1×10^{-9} einstein s⁻¹) with [BIH] = 0.1 M (100% quenching of the excited Ru complex),³⁵ which was determined by irradiation using a high-pressure mercury lamp with a much lower light intensity than the laser light used in this study. Therefore, the formation efficiency of OERS is higher in the case of **CuPS** when compared to $[Ru^{II}(dmb)_3]^{2+}$. This is another advantage of **CuPS**.

The next electron-transfer process should be from the produced CuPS^{•-} to the Mn complexes to produce the OERS of the Mn complexes because in all the cases it is an exergonic reaction; their CVs are illustrated in Figure 3b-d, and their reduction potentials are summarized in Table 3. In order to identify and quantify the intermediates formed during the photocatalytic reactions, the UV-vis absorption spectral changes during the flow electrolysis of the Mn complexes were first studied in MeCN containing Et_4NBF_4 (0.1 M) as a supporting electrolyte under an Ar atmosphere (Figure 9). In the case of Mn(4H) (Figure 9a), at applied potentials between -1.40 and -1.53 V vs Ag/AgNO₃, Mn-Mn dimer formation was observed, which is characterized by a rise in the absorption bands at ca. 650 and 800 nm.^{15,39} It was reported that the Mn-Mn dimer is produced via the coupling of the 17-electron species, that is, \bullet Mn(bpy)(CO)₃ (eq 7). Electrolysis at more



negative potentials changed the spectrum to one which had a strong absorption band at around $\lambda_{max} = 550$ nm corresponding to the 5-coordinated 18-electron species, that is, $[Mn(bpy)(CO)_3]^-$ (eq 8)^{15,39} with isosbestic points at 400, 500, and 700 nm.

Figure 10b shows the relationships of both the current and the absorbance at $\lambda = 569$ and 805 nm with the applied potential. These results clearly indicate that the Mn-Mn dimer accepted two electrons to quantitatively yield [Mn(bpy)- $(CO)_3$]⁻. The molar extinction coefficients of the Mn–Mn dimer is 11,500 M⁻¹ cm⁻¹ at λ = 805 nm and that of $[Mn(bpy)(CO)_3]^-$ is 13,600 M⁻¹ cm⁻¹ at $\lambda = 569$ nm. Similar spectral changes were observed in the case of Mn(4OMe), except that the applied potentials were more negative in the case of Mn(4OMe) (Figure 10c and d). The molar extinction coefficients are summarized in Table 3. In the case of Mn(6mes), the spectral changes and the potential-current relationship were very different from those of the other Mn complexes, as shown in Figure 10e; no formation of the Mn-Mn dimer was observed. This is reasonable because the sterically bulky mesityl groups should prevent the dimerization of the 17-electron species.¹⁸ Actually, the CV of Mn(6mes) shows a two-electron reduction wave at $E_p = -1.63$ V (Figure 5d). This was also supported by Figure 10f where only one two-electron reduction curve was observed at E = -1.60 V to -2.20 V.

Figures 11 and 12 show the UV–vis absorption spectral changes of a DMA–TEOA (4:1, v/v) solution containing the Mn complexes (0.05 mM), CuPS (0.25 mM) and BIH (10 mM) during irradiation under an Ar atmosphere and under a CO_2 atmosphere, respectively.

Under an Ar atmosphere, the Mn–Mn dimers rapidly formed in the initial stage ($\lambda_{max} = 810 \text{ nm}$) in the case of **Mn(4H)**. Further irradiation caused a decrease in the dimer accumulation, and the simultaneous formation of the 5coordinate 18-electron species ([Mn(bpy)(CO)₃]⁻, $\lambda_{max} = 565$ nm) was observed (Figure 10a). The formation of the Mn– Mn dimer was similarly observed in the case using **Mn(4OMe)** (Figure 11b). Further irradiation induced a decrease in the absorption of the dimer and the formation of the corresponding 5-coordinate 18-electron species. In the case of **Mn(6mes)**, on the other hand, the formation of the dimer was not observed while the corresponding 5-coordinate 18electron species accumulated after irradiation for 30 s ($\lambda_{max} =$



Figure 10. UV–vis spectral changes during the flow electrolysis of Mn(4H) (a), Mn(4OMe) (c), and Mn(6mes) (e) under an Ar atmosphere in MeCN containing Et_4NBF_4 (0.1 M) as a supporting electrolyte, carbon felt as a working electrode, Ag/AgNO₃ (0.01 M) as a reference electrode, and coiled Pt wire as a counter-electrode at a flow rate of 0.2–0.3 mL min⁻¹. The electrolyzed solution was introduced into an optical cell (1.5 mm path length) to measure the UV–vis absorption spectrum. On the right-hand side, the relationship of current and absorbance with applied voltage is illustrated (gray indicates current): (b) Mn(4H), absorption at 805 nm (green) and 565 nm (blue); (d) Mn(4OMe), absorption at 840 nm (green) and 566 nm (blue); (f) Mn(6mes), absorption at 572 nm (blue). The absorption maxima of the reduced species are summarized in Table 3.

573 nm), followed by the accumulation of $CuPS^{\bullet-}$. Reduction of Mn(6mes) by $CuPS^{\bullet-}$ should proceed because it is a thermodynamically favorable process (Table 2) and it produces the OERS of Mn(6mes). Release of the Br⁻ ligand from the OERS of Mn(6mes) gave the 17-electron species, and then its further reduction yielded the 5-coordinate 18electron species. This reduction process might proceed by either another $CuPS^{\bullet-}$ or BI[•] (eq 9).

$$\begin{array}{c} \overbrace{N}^{N} \underset{CO}{\text{Min}} \underset{CO}{\overset{e}{\text{co}}} \xrightarrow{e} \\ \overbrace{N}^{N} \underset{CO}{\overset{Min}} \underset{CO}{\overset{Hin}} \xrightarrow{} \underset{EO}{\overset{Hin}} \xrightarrow{} \underset{EO$$

Under a CO₂ atmosphere, the Mn–Mn dimer steadily accumulated as the photocatalytic CO₂ reduction proceeded in the cases using Mn(4H) and Mn(4OMe) (Figure 12a and b). In contrast to these Mn complexes, almost no accumulation of the reduced Mn complex was observed in the case of Mn(6mes) (Figure 12c). These results provide important information on the intermediates of the photocatalytic reduction of CO₂ (Scheme 3). In the case of Mn(6mes), the reactive intermediate should be the 5-coordinate 18-electron species,¹⁸ which reacts with CO₂ to give CO selectively. In the case of Mn(4OMe), on the other hand, the Mn–Mn dimer probably reduces CO₂ giving CO.¹⁶ Although a similar



Figure 11. UV–vis absorption spectral changes of a DMA–TEOA (4:1, v/v) solution containing the Mn complexes (0.05 mM): **Mn(4H)** (a); **Mn(4OMe)** (b); **Mn(6mes)** (c) and **CuPS** (0.25 mM), and BIH (10 mM) during irradiation under an Ar atmosphere; $\lambda_{ext} = 436$ nm, 25 °C. (d) Without a Mn complex.

reaction of the Mn dimer made from Mn(4H) might also proceed, its reaction rate with CO₂ was probably slower²⁵ than that of the dimer made from Mn(4OMe) because the oxidation potential of the dimer with X = H was more negative than that when X = OMe (the anodic scan in Table 3). In both cases, using either Mn(4H) or Mn(4OMe), the 5coordinate 18-electron species probably contributed to the CO₂ reduction because its absorption was not observed in the CO₂ atmosphere even though that of the Mn–Mn dimer was observed as the photocatalytic reaction proceeded. We cannot identify the product distribution of this reaction at the present stage.

CONCLUSION

We successfully constructed a new, efficient, selective, and durable photocatalytic system for CO₂ reduction, which only consists of earth-abundant metal complexes, that is, CuPS and Mn(4OMe) (the maximum values: $\Phi_{\rm CO+HCOOH}$ = 57%, $TON(CAT)_{CO+HCOOH} = 1314$, $TON(PS)_{CO+HCOOH} = 263$, selectivity (CO + HCOOH): H_2 = 95:5). The Cu(I) dinuclear complex CuPS can work as an outstanding redox photosensitizer, which has a long excited-state lifetime and a much stronger reduction power of its OERS ($E_{1/2} = -1.92$ V vs Ag/ AgNO₃) compared to most other photosensitizers (e.g., $E_{1/2}$ = -1.65 V in the case of $[Ru^{II}(bpy)_3]^{2+}$). The product selectivity between CO and HCOOH could be controlled from CO:HCOOH = 93:6 (Mn(4H)) to 6:94 (Mn(6mes)) by changing the substituents of the bpy ligand. The mechanistic studies suggested that the intermediate(s) for CO_2 reduction is (are) the 5-coordinate 18-electron species in the case using Mn(6mes) and the Mn-Mn dimer and/or the 5-coordinate 18-electron species in the cases using Mn(4H) or Mn(4OMe).

EXPERIMENTAL SECTION

Materials. DMA was dried over 4 Å molecular sieves and distilled at reduced pressure. TEOA was distilled at reduced pressure. Tetraethylammonium tetrafluoroborate (Et_4NBF_4) was recrystallized twice from MeCN-ethyl acetate and dried *in vacuo* at 100 °C overnight just before use. A sacrificial reductant, BIH,³² was prepared by the method previously defined. **Mn(4H)**²⁵ and **Mn(6mes)**¹⁸ were synthesized according to the literature method. Synthetic procedures of **Mn(4OMe)** are described in the Supporting Information. All other reagents were of reagent-grade quality and were used without further purification.

Synthesis. PPh₂PrBr. Under a N₂ atmosphere, n-BuLi (4.1 mL, 6.6 mmol, 1.60 M in hexane) was added dropwise to a mixture of tetrahydrofuran (THF; 8.3 mL) containing HPPh₂ (1.3 mL, 6.5 mmol) at 0 °C. This mixture was stirred for 50 min at room temperature. The obtained red solution was transferred to a closed flask containing 1,3-dibromopropane (2.7 mL, 26.9 mmol) at room temperature through a cannula under a N₂ atmosphere. The solution was stirred for 20 min at room temperature. The organic solvents were then removed with a rotary evaporator, and the residue was extracted with CH_2Cl_2 (6 mL) after the addition of H_2O (6 mL). The organic layer was dried by using Na₂SO₄, and then the solvent was removed using a rotary evaporator. The obtained oil was purified by column chromatography on silica gel (40–50 μ m, N60 (Kanto)) with CH_2Cl_2-n -hexane (1:4, v/v) to give 396.6 mg of a colorless oil containing PPh2PrBr as a mixture with 25 mol % of Ph2P-(CH₂)₃PPh₂, as judged by the ¹H NMR spectrum. This compound was used without further purification for the following procedures as described below because of the instability of PPh2PrBr. ¹H NMR (chloroform-*d*): δ (ppm) 7.44–7.32 (m, 10H, PPh₂–), 3.48 (t, J = 7.2



Figure 12. UV-vis absorption spectral changes during the photocatalytic reactions using the Mn complexes (0.05 mM): Mn(4H) (a); Mn(4OMe) (b); Mn(6mes) (c), CuPS (0.25 mM), and BIH (10 mM) in a CO₂-saturated DMA-TEOA (4:1, v/v) solution; λ_{ext} = 436 nm, 25 °C. (d) Without a Mn complex.

Scheme 3. Mechanism of the CO₂ Reduction Catalyzed by the Mn(I) Complexes



Hz, 2H, BrCH₂-), 2.21-2.17 (m, 2H, PPh₂CH₂-), 2.02-1.93 (m, 2H, PPh₂CH₂CH₂-).

CuPS. A cyclohexane solution (1.0 mL) containing lithium diisopropylamide (1.5 M) was added dropwise to a THF solution (15 mL) containing bathocuproine (bcp) (143.9 mg, 0.40 mmol) at -45 °C under a dry Ar atmosphere and was then stirred for 15 min. The solution was added via cannula into an Ar-deoxygenised THF solution (15 mL) containing the product and **PPh₂PrBr** (396.6 mg, *ca*. 1 mmol), as described above, and CuI (76.0 mg, 0.40 mmol) at 0 °C, and then the solution was stirred for 16 h at room temperature. The reaction solution was quenched with water containing an excess amount of KPF₆. The products were extracted with CH₂Cl₂ (70 mL) four times. Column chromatography on alumina (aluminum oxide 90 standard (Merck)) with CH₂Cl₂/Et₂O (1:1, v/v) provided a solution was achieved by recrystallization from an MeCN, Et₂O and *n*-hexane solution. The yellow precipitates were filtered off, washed with Et₂O

and dried in vacuo. Yield: 49.2 mg (12.0%). The $^1\mathrm{H}$ NMR spectrum data was consistent with the reported one. 9

General Procedures. ¹H NMR spectra were measured in chloroform-*d* using a JEOL ECA400II (400 MHz) system. UV–vis absorption spectra were recorded on a JASCO V-565 or V-670 spectrometer. FT–IR spectra were measured by a JASCO FT/IR-610 or FT/IR-6600 spectrometer at 1 cm⁻¹ resolution in an MeCN solution. Emission spectra were recorded on a JASCO FP-6500 spectrometer. Emission quantum yields were collected using a Hamamatsu Photonics C9920-02G absolute photoluminescence quantum-yield measurement system consisting of a calibrated integrating sphere and a multichannel spectrometer. Sample solutions were degassed by freeze–pump–thaw cycles before the emission measurements. CVs were measured using Et₄NBF₄ (0.1 M) as a supporting electrolyte under an Ar atmosphere using a BAS CHI620EX or CHI760Es electrochemical analyzer with a glassy-carbon working electrode (diameter, 3 mm), an Ag/AgNO₃ (0.01 M)

as a reference electrode, and a Pt counter-electrode at a scan rate of 200 mV s⁻¹. Procedures of single crystal X-ray analysis of **CuPS** and emission decay lifetime measurement are described in the Supporting Information.

Photocatalytic Reaction. A 4 mL DMA-TEOA (4:1, v/v) solution containing CuPS (0.25 mM), the Mn complexes (0.05 mM), and BIH (10 mM or 0.1 M) in a necked quartz cubic cell (1 cm pass length; 11 mL volume) was bubbled with CO₂ for over 30 min, and the cell was sealed using a septum. The sample solution was irradiated by an Ushio Optical Module high-pressure Hg lamp (BA-H500) with a 436 nm band-pass filter (fwhm: 10 nm), purchased from Asahi Spectra Co., and a $CuSO_4 \cdot 5H_2O$ aqueous solution (20 g L⁻¹, 5 cm pass length) filter. A neutral density (ND) glass filter was used to adjust the light intensity. The solution was constantly mixed by a magnetic stirrer bar during the photoirradiation. The temperature of the reaction solution was maintained at 25 ± 0.1 °C using an IWAKI CTS-134A cooling thermo pump during irradiation. The UV-vis absorption spectral changes of the reaction solutions during photoirradiation were recorded on a Photal MCPD-6800 photodiode-array spectrometer.

For the determination of the quantum yields of the photocatalytic reactions, the sample solution was irradiated using a SHIMADZU QYM-01 photoreaction quantum yield evaluation system. A 4 mL solution in an 11 mL quartz cubic cell (light path length: 1 cm) was irradiated with 436 nm monochromatic light using a 300 W xenon lamp (MAX-303 ASAHI SPECTRA) with a band-pass filter. The solution was constantly mixed by a magnetic stirrer bar during the photoirradiation. The temperature of the solutions was controlled at 25 °C using an IWAKI CTS-134A constant temperature system during irradiation. The light intensity was controlled at 2.0×10^{-8} einstein s⁻¹. The amount of formic acid in the reaction solution was analyzed by a capillary electrophoresis system (Otsuka Electronics Co. CAPI-3300I or 7100L) with a buffer solution (pH 6.0) consisting of quinolinic acid, hexadecyltrimethylammonium hydroxide, and 2amino-2-hydroxymethyl-1,3-propanediol as the electrolyte. The amounts of CO and H₂ were analyzed using GC-TCD (GL science GC323) with an active carbon column. The TONs for the products, TON(CAT), were calculated as the amount of product divided by the amount of the Mn catalyst used, whereas TON(PS) was calculated as the amount of the product divided by the amount of the CuPS used.

The amounts of **CuPS** in the reaction solution before and after the photocatalytic reaction were determined by the high-performance liquid chromatography (HPLC) analysis⁴⁰ with a system consisting of a JASCO 880-PU pump, a pair of Shodex PROTEIN KW402.5 columns with a KW-LG guard column, a Rheodyne 7125 injector, and a JASCO MD-2010 plus UV–vis photodiode-array detector. The column temperature was kept at 40 °C in a JASCO 860-CO column oven. An MeCN–MeOH (1:1, v/v) mixed solution containing CH₃COONH₄ (0.5 M) was used as the mobile phase. For quantitative analysis of BIH, an HPLC system consisting of a JASCO 880-PU pump, a Develosil ODS-UG-5 column, a JASCO 880-S1 degasser and a JASCO MD-2010 plus UV–vis photodiode-array detector was used.³² The column temperature was maintained at 30 °C using a JASCO-860-CO column oven. A mixed solution consisting of MeCN–buffer (pH 7, NaOH–KH₂PO₄ (0.05 M), 3:2, v/v) was used as the mobile phase.

For taking the movie of the photocatalytic CO_2 reduction, the system consisting of **CuPS**, **Mn(40Me)** and BIH was used. The CO_2 -saturated DMA–TEOA (4:1, v/v) solution (4 mL) containing **CuPS** (0.25 mM), **Mn(40Me)** (0.05 mM), and BIH (0.1 M) was loaded in the quartz cell closed at the top of the neck and was irradiated with constant stirring for 5.5 h. The photoirradiation was carried out at $\lambda = 450$ nm using a Cell System IRS-450F LED lamp with an output current controlled constantly at 2000 mA by a Cell System Iris-S software. The temperature of the cell was maintained at 25 °C by a water bath connected to an EYELA NCB-1210 temperature controlling circulator during the photoirradiation.

Flow Electrolysis. Flow electrolysis^{40,41,42} was used to obtain the UV–vis absorption spectra of the OER species of the complexes. The working electrode was contained in a porous glass tube (1 mm *i.d.*, 2

mm o.d., 20 mm length) and consisted of carbon felt. The counterelectrode was a Pt wire coiled around the porous glass tube. The Ag/ AgNO₃ (0.01 M) reference electrode was positioned near the counter-electrode. An MeCN solution containing a complex (0.5 mM for Mn complexes: 0.25 mM for **CuPS**), and Et₄NBF₄ (0.1 M) as an electrolyte, was purged with Ar for 20 min and was then passed into the flow-through cell at a rate of 0.2 mL/min using a Fisher Scientific Variable-Flow Peristaltic Pump with a Cole-Parmer Masterflex C-Flex tubing. Immediately after electrolysis using a BAS CHI760Es electrochemical analyzer, the solution was transferred to a quartz cell (pass length 1.5 mm) for spectral measurements. The spectral changes were recorded on a BAS SEC2000-UV–vis spectrometer with a SEC2000-DH light source. The number of electrons reduced per Mn complexes or Cu unit in **CuPS** (*n*) was determined using

$$n = (i - i_0) / C_0 F \nu \tag{10}$$

where *i* is the current (A) applied in the constant potential electrolysis of the complexes, i_0 (A) is the background current, C_0 (M) is the initial concentration of the Mn complexes or the Cu unit in **CuPS** (0.5 mM), *F* is the Faraday constant (96,500 A/mol), and *v* is the flow rate of the solution (0.26 mL/min for **CuPS**, 0.23 mL/min for **Mn(4H)**, and **Mn(4OMe)**, 0.27 mL/min for **Mn(6mes)**). For example, the quantitative one-electron reduction (n = 1) of each complex unit requires 0.16 mA ($= i - i_0$) according to this equation when v = 0.2 mL/min is employed.

Time-Resolved UV-vis Transient Absorption Spectroscopy. Third-harmonic-generation light at 355 nm produced by a Spectra-Physics Quanta-Ray LAB-150-10 pulsed Nd:YAG laser was used for excitation (10 ns fwhm). An Ushio 300-W Xe arc lamp was operated in a pulse-enhanced mode (500 μ s duration) using an XC-300 power supply and a YXP-300 light pulsar (Eagle Shoji) as the monitoring light source. The monitoring light beam was passed through the quartz cuvette $(10 \times 10 \times 40 \text{ mm})$ that contained a sample and was directed into an R926 photomultiplier tube (Hamamatsu Photonics) on a Jobin-Yvon HR-320 monochromator. Time profiles of the monitoring light intensity were stored using a LeCroy WaveRunner 640zi oscilloscope (4 GHz bandwidth). Transient spectra were obtained with an Andor Technology iStar H320T-18F-03 (690 channels; minimum gate width: 5 ns) ICCD detector head mounted on the HR-320 monochromator. A DMA-TEOA (4:1, v/v) solution that contained CuPS was bubbled with Ar prior to the laser flash photolysis.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b10619.

Crystallographic Data for **CuPS** (CCDC reference: 1863041) embedding RES and structure factors (CIF) Experimental details, synthesis and ¹H NMR spectrum of **Mn(40Me)**, the single-crystal X-ray crystallography of **CuPS**, time courses of the photocatalytic CO₂ reduction, details of the photochemical formation of **CuPS**^{•-}, evaluation of $\varepsilon_{\rm T}(\lambda)$, and the absorbed photon numbers in the transient absorption measurement (PDF)

Video S1: Movie of the beginning and ending of the photocatalytic CO_2 reduction using the system consisting of **CuPS**, **Mn(40Me)** and BIH under 450 nm light irradiation for 5.5 h is available (AVI)

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Notes

The authors declare no competing financial interest.

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