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(Citation)
Nature Chemistry,15(6):794-802

(Issue Date)
2023-03-23

(Resource Type)
journal article

(Version)
Accepted Manuscript

Metal-free reduction of CO_2 to formate using a photochemical organohydride-catalyst recycling strategy

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Abstract

Increasing levels of CO_2 in the atmosphere is a problem that must be urgently resolved if the rise in current global temperatures is to be slowed. Removing CO_2 by chemically reducing it into compounds that are useful as energy sources and carbon-based materials would be helpful in this regard but for the CO_2 reduction reaction (CO_2RR) to be operational on a global scale, the catalyst system must: use only renewable energy, be built from abundantly available elements and not require high-energy reactants. Although light is an attractive renewable energy source, most existing CO_2RR methods use electricity and many of the catalysts used are based on rare heavy metals. Herein, we present a transition-metal-free catalyst system that uses an organohydride catalyst based on benzimidazoline for the CO_2RR that can be regenerated using a carbazole photosensitizer and visible light. The system is capable of producing formate with a turnover number exceeding 8000 and generates no other reduced products (such as H_2 and CO).

The increase in the atmospheric concentration of greenhouse gas carbon dioxide (CO_2) has become a societal issue; thus, the CO_2 reduction reaction (CO_2RR) is a significant subject as one of the CO_2 fixation processes.[1-4] Although CO_2 is a nonpolar molecule, it is chemically reactive because of its polarized C=O double bonds. Carbon dioxide can be reduced electrochemically[5,6] or by using strong reductants or organometallic nucleophiles.[7] However, it is essential to achieve endergonic CO_2RR using renewable energy sources as the input instead of energy sources derived from fossil fuels to render the overall CO_2RR process sustainable and reduce the atmospheric concentration of CO_2.

In this context, photochemical CO_2RR using light, particularly solar energy, as a sole external energy source has gained increasing attention. Because the potential of the $CO_2/CO_2^{\bullet -}$ redox couple is considerably negative (E^0 (in dimethylformamide) = –2.21 V vs. standard calomel electrode (SCE)), reduction via the single-electron transfer (ET) mechanism is difficult (Fig. 1a).[8-10] In contrast, the energetic barrier of CO_2RR via the proton-assisted multi ET mechanism is small (for example, E^0 ($CO_2 + 2H^+ + 2e^- \rightarrow CO$

+ H_2O) = –0.77 V vs. SCE).[11] Therefore, transition metals such as Co,[12,13] Re, Ru,[14] and Ni,[15] with accessible multiple oxidation states, were used as catalysts in most previous studies, in addition to photosensitizers (PSs). In these studies, the CO_2 coordination with the transition metal catalysts enabled the multi-electron CO_2 reduction via the inner-sphere ET mechanism (Fig. 1b).[16] Although a high turnover number (TON) and/or turnover frequency (TOF) were obtained in some cases, the requirement of transition metals, particularly the noble and rare metals, could be an issue for large-scale practical applications.[17,18] In addition, the production of H_2 by reducing water, which is thermodynamically favored over CO_2RR, is a potential competitive pathway in transition metal catalysis,[19,20] and its suppression is a key challenge to achieve for high selectivity.[21-24]

Formic acid, a reduced compound of CO_2, is widely used as a reductant, acid, and C1 carbon source in the industry.[25,26] Formic acid and formates are also potent silage ingredients, preservatives, and agrichemicals.[27] Moreover, formic acid and formates can potentially serve as safe liquid organic carriers of hydrogen and energy, thereby attracting attention in mobile vehicle research areas.[28-30] To date, selective generation of formate via photochemical CO_2RR using soluble molecular catalysts has been reported. For example, MacDonnell et al reported the photochemical reduction reaction of CO_2 to formate using a ruthenium complex and pyridine as a PS and catalyst, respectively.[31] Ishitani et al achieved a selective photochemical reduction of CO_2 to formate using a well-designed trinuclear ruthenium complex as a photocatalyst, wherein a benzimidazoline derivative was used as a stoichiometric terminal reductant.[14,32] Although these examples are of great scientific significance, they rely on the intrinsic capability of transition metals.

In contrast to transition metal complexes, non-metal organomolecules do not have multiple oxidation states or coordination sites for CO_2. Therefore, organomolecules that undergo multi-electron CO_2RR are limited.[33-40] Successful examples are reactions using a combination of frustrated Lewis pairs and metalloid hydride species (B–H or Si–H) (Fig. 1c).[41] However, the issue of low TON and the requirement of stoichiometric high-energy metalloid hydride species remains unaddressed. Recently, Lim and Musgrave et al reported that 1,2,3-trimethylbenzimidazoline (**BIH**) reacts with CO_2 to afford formate without the assistance of transition metals or frustrated Lewis pairs (Fig. 1d).[42] This reaction is a groundbreaking example of two-electron CO_2RR achieved exclusively by non-metal organohydrides.[43] Noteworthy in this organomolecular process is the exclusive selectivity in formate formation over H_2 or CO formation. However, a stoichiometric amount of **BIH** was required, and an excess amount (40 equiv to **BIH**) of the metal salt ($NaBF_4$) was used to shift the equilibrium to the product side, which remained obvious tasks to be solved.

Lim and Musgrave et al achieved the regeneration of **BIH** from its oxidized form, 1,2,3-trimethylbenzimidazolium cation (**BI$^+$**), via electrochemical reduction, albeit in a vessel separated from the CO_2RR system.[42] We hypothesized that the photochemical reduction of **BI$^+$** to **BIH** in the same reaction vessel as CO_2RR could render the CO_2RR system truly catalytic for **BIH** (Fig. 1e). Catalytic reduction of chemicals other than CO_2 with the concept of the *in situ* photochemical regeneration of organohydrides has been developed.[44-52] However, compared to the previous studies that used nicotinamide adenine dinucleotide (NAD^+)-mimicking organohydrides, **BI^+** had a significantly negative reduction potential ($E = -1.88$ V vs. NHE in dimethylsulfoxide (DMSO)),[42] which renders its photochemical reduction challenging. Therefore, benzimidazoline organohydrides have been used as a stoichiometric reductant to date.[53-57] Another concern is the dimerization of the organohydride species via its intermediate radical during the regeneration process.[58] Herein, we report that the visible-light-driven CO_2RR to generate formate based on the *in situ* photochemical organohydride regeneration is viable. The employed PS and catalyst were non-metallic small molecules with a high TON of up to 8820 at ambient temperature with 1 atm of CO_2.

Results and Discussion

Photocatalytic CO_2RR

We first investigated the photochemical reduction of **BI^+** to determine whether **BIH** can be photochemically recycled. Because **BI^+** demonstrates a profoundly negative reduction potential, a PS with a strong reducing capability is required. Conversely, benzimidazoline such as **BIH** is a good electron donor (generally $E_{ox} < +0.5$ V vs. SCE).[59] The excited state of common PSs readily oxidizes **BIH**, leading to the unproductive consumption of **BIH** and photon; therefore, a judicious choice of PS is required. Our group focused on developing non-metallic (organic) PSs with high reducing capability. We recently discovered that 3,6-bis(dimethylamino)carbazole molecules could serve as a capable PS with a significantly high reducing capability in its excited state (up to $E^* = -2.75$ V vs. SCE). This class of carbazoles is characterized by a red-shifted absorption of approximately 80 nm compared to that of the parent carbazole, and absorbs visible light.[60,61] The photocatalytic reduction of **$BI^+(I^-)$** to its reduced-state **BIH** employing **1** as a PS remarkably proceeded in 66% yield at 15 min under visible light irradiation (400 nm) in a water-containing solvent system in the presence of ascorbic acid (**H_2A**) as a sacrificial reductant (Fig. 2 and Supplementary Table 1). The mass balance of this reaction was almost quantitative even after 20 h, suggesting that **BI^+** and **BIH** have sufficient stability to be competent for long-term catalytic performance.

With the promising data obtained for the photochemical regeneration of **BIH**, we next investigated the photochemical CO_2RR using a catalytic amount of **BIH**. A mixed solution of CH_3CN and H_2O (4:1 v/v) containing **H_2A** (50 mM), K_2CO_3 (55 mM), PS **1** (1.5 mM), and **$BI^+(I^-)$** (2.5 mM) was irradiated (400 nm) under 1 atm of CO_2 atmosphere. In proton nuclear magnetic resonance (^1H NMR) analysis of the reaction mixture, a gradual increase in the peak of formate, a CO_2-reduced product, was observed over time (Supplementary Fig. 3 and Supplementary Table 2), and the yield of formate reached 72 mM after 4 h (Fig. 3). The peak assignment of formate in ^1H NMR analysis was corroborated by heteronuclear multiple quantum coherence (HMQC) NMR analysis and a mixing test with the authentic sample (Supplementary Section 5). Thus, a visible-light-driven photocatalytic CO_2RR for generating C1 product using a non-metallic small molecular catalyst was achieved. The amount of generated formate (72 mM) was more than that of starting **H_2A** (50 mM), indicating that **H_2A** donated more than two electrons (Supplementary Section 6). Methanol, formaldehyde, and oxalate were not detected as a product by ^1H NMR or carbon-13 NMR (^{13}C NMR) analysis of the solution phase (Supplementary Fig. 4 and 7). The gas chromatography (GC) analysis of the reactor headspace revealed that the evolution of gaseous products, CO or H_2, was below the detection limit (the detection limits for H_2 and CO are 50 and 400 μM, respectively) (Supplementary Section 8). Thus, our protocol for CO_2RR exhibits exclusive selectivity to afford formate as the sole product. The quantum yield of CO_2RR was 6.5% (Supplementary Sections 9 and 10).

The results of further investigation on the reaction conditions are summarized in Fig. 3 (further details in Supplementary Table 4). A base, light irradiation, **H_2A**, and PS **1** are indispensable in this reaction, as revealed by control experiments. The yield dropped to 4 mM without **$BI^+(I^-)$**, suggesting its importance as a catalyst. Consistent with the working hypothesis, the use of **BIH** instead of **$BI^+(I^-)$** gave comparable results (71 mM). This result indicates that iodide anions are not involved in the catalytic cycle. In addition, K_2CO_3 was replaced with other inorganic salts, implying that the type of counter cations and basic anions moderately affects the reaction. Inorganic sacrificial reductants, Na_2SO_3 and $NaHSO_3$, were used instead of **H_2A**, resulting in yields of 32 and 30 mM, respectively. Although the yields were lower than that of **H_2A**, Na_2SO_3 and $NaHSO_3$ were capable reductants because they donated two electrons per molecule (the maximum product yield is 50 mM). Formate was generated even without CO_2 gas in the presence of K_2CO_3; however, minimal formate was generated without CO_2 gas or K_2CO_3, suggesting that CO_3^{2-} could serve as a source of CO_2 in the present system. The reaction temperature increased up to 43 °C under the standard condition even with fan cooling. The CO_2RR still proceeded at 30 °C with a slightly lower yield, revealing that heat is dispensable for the present catalysis (Supplementary Section 11). Next, the PSs were screened. Carbazole-based organic PSs with electron-withdrawing groups (PS **2**–**4**) did not generate formate due to the insufficient reducing capability of the excited states of these PSs. PS **5**, with an electronic feature similar to that of **1**, gave a comparable formate yield of 64 mM. Tris(2-phenylpyridinato)iridium (III) or $Ir(ppy)_3$ (**7**) could also serve as a competent PS, affording formate of 66 mM. Without **$BI^+(I^-)$**, $Ir(ppy)_3$ did not afford formate, suggesting that the $Ir(ppy)_3$-catalyzed CO_2RR proceeded via a **$BI^+(I^-)$**-involving mechanism, similar to the reaction using **1**. Tris(2,2'-bipyridyl)ruthenium (II) chloride hexahydrate or $Ru(bpy)_3Cl_2{\bullet}6H_2O$ (**8**) did not promote the reaction. The reaction under natural sunlight also afforded formate (Supplementary Section 12). Molecules **9**–**11**, in which the carbazole and benzimidazolium moieties were covalently connected, showed moderate catalytic activity, which is ascribed to the unproductive back ET (Supplementary Section 17). The highest TON for carbazole PS and **$BI^+(I^-)$** observed in this work reached 8820 and 6080, respectively (Extended Data Table 1).

We utilized $^{13}CO_2$ instead of $^{12}CO_2$ (Extended Data Fig. 1a) to confirm that the singlet peak at 8.8 ppm in ^1H NMR spectrum was assigned to formate, thereby confirming that the carbon source of formate was derived from CO_2.[62-64] Sodium hydroxide was used as the base to avoid the contamination of $^{12}CO_2$ derived from K_2CO_3. ^1H NMR analysis revealed that ^{13}C-formate, characterized by a set of doublet peaks ($^1J_{CH}$ = 192.8 Hz), was obtained in 45 mM, along with a yield of 2 mM of ^{12}C-formate (Extended Data Fig. 1b and Supplementary Fig. 14). The formation of ^{12}C-formate is ascribed to $^{12}CO_2$ released from **H_2A** (Supplementary Fig. 6). In the ^{13}C NMR spectrum of the same reaction, an intense ^{13}C-formate was observed at 169.4 ppm (Extended Data Fig. 1c). These results demonstrate that the main carbon source of the product formate is gaseous CO_2 introduced exogenously.

Mechanistic Study

Mechanism for photosensitization

Because **$BI^+(I^-)$** did not demonstrate absorption at 400 nm (Supplementary Fig. 16), the excitation of PS carbazole initiated photosensitization. The steady-state ultraviolet-visible absorption analysis revealed that the formation of an electron donor–acceptor (EDA) complex between PS **1** and **$BI^+(I^-)$** was unlikely (Supplementary Fig. 21). The existence of the exciplex was improbable because the normalized emission spectra of PS **1** in the presence and absence of **$BI^+(I^-)$** were identical (Supplementary Fig. 22). We further examined the involvement and influence of the excited states (singlet or triplet) of PS in reducing **$BI^+(I^-)$**. Thus, the rate constants of fluorescence quenching (k_q) of PS **1** by **$BI^+(I^-)$** and ascorbate anion (**HA^-**) were determined according to the Stern–Volmer equation,

$I_0/I = 1 + k_q \cdot \tau_0 \cdot [Q]$

where I_0 and I represent the fluorescence intensity in the absence and presence of the different concentrations of the quencher, respectively; τ_0 represents the lifetime of the excited state of PS; [Q] is the quencher concentration. The time-resolved fluorescence measurement of PS **1** provided a value of τ_0 of 19.2 ns (Supplementary Fig. 23). The ET fluorescence quenching of PS **1** in the presence of varying concentrations of **$BI^+(I^-)$** as a quencher (Supplementary Fig. 27) revealed the k_q by **$BI^+(I^-)$** to have a value of 2.71×10^9 mol^{-1} L s^{-1}, indicating that a single ET from the excited **1** to **$BI^+(I^-)$** occurred efficiently. These results do not contradict the experimentally characterized optoelectronic properties of **1** and **$BI^+(I^-)$** (Supplementary Section 23). In contrast, fluorescence quenching of **1** by **HA^-** was not observed. Thus, an oxidative quenching cycle of carbazole PS was suggested.

The detection of the radical cation of PS carbazole was attempted by transient absorption spectroscopy to directly confirm that ET occurred via the excited states of carbazole. As a preliminary step, **$5^{\bullet+}$** was chemically generated by treating **5** with an equimolar amount of magic blue, a single electron oxidant (E_{red} = +1.1 V vs. SCE),[65] and the steady-state absorption spectrum of **$5^{\bullet+}$** was measured (Fig. 4a, red line). The absorption bands at 470, 550, 700, and >1100 nm (marked with black arrows) were assigned to **$5^{\bullet+}$** (Supplementary Fig. 31), which was corroborated by the time-dependent density functional theory (TD-DFT) calculations (Supplementary Table 13); the calculated wavelength of the absorption peaks (Fig. 4a, orange bars) matched the experimental spectrum. After obtaining the authentic absorption spectrum of **$5^{\bullet+}$**, the transient absorption of the solution of **5** in the presence of **$BI^+(I^-)$** was measured (Fig. 4b). Long-lived absorption bands with millisecond decay were observed at 470, 550, and 700 nm. These bands were assigned to **$5^{\bullet+}$** generated via ET from the excited state of **5** to **BI**$^+$**(I**$^-$**)** determined from the almost perfect overlay compared to those of the chemically generated species (Fig. 4c). The time profile analysis of the absorption bands revealed that the observed millisecond decays were not exponential and obeyed total second-order kinetics (Fig. 4d and Supplementary Fig. 33); thus, they were attributed to the bimolecular charge-recombination reactions between **5**$^{\bullet+}$ and **BI**$^\bullet$. The ET or energy transfer from the triplet excited state of **5** to **BI**$^+$**(I**$^-$**)** was not the major pathway for reducing benzimidazolium cations (Supplementary Section 26). In conclusion, the reduction of **BI**$^+$**(I**$^-$**)** to **BIH** is initiated by ET from the singlet state of **5** (^{1}**5***) to **BI**$^+$**(I**$^-$**)**.

Mechanism for converting BI$^\bullet$ to BIH

The electrochemical conversion from **BI**$^+$ to **BIH** via **BI**$^\bullet$ was thoroughly investigated by Lim and Musgrave et al.[42] Two pathways were initially proposed for the conversion of **BI**$^\bullet$ to **BIH**: ET followed by proton transfer (PT) (ET–PT) and PT followed by ET (PT–ET). Based on the results that (1) an irreversible reduction of **BI**$^+$ was observed in the absence of acid, which was ascribed to the dimerization of **BI**$^\bullet$ and (2) the current intensity of the first reduction wave increased in the presence of acid, they concluded that **BI**$^\bullet$ underwent PT to generate **BIH**$^{\bullet+}$, followed by ET to give **BIH** in their system. In our reaction (Fig. 5), the PT to **BI**$^\bullet$ is unlikely based on the employed basic condition and low basicity of **BI**$^\bullet$ (**BIH**$^{\bullet+}$, pK_a = 15.4 in DMSO).[58] Conversely, the ET from ^{1}**5*** (E (**5**$^{\bullet+}$/^{1}**5***) = –2.65 V vs. SCE) to **BI**$^\bullet$ (E (**BI**$^\bullet$/**BI**$^-$) = –2.6 V vs. SCE) is exothermic. However, ^{1}**5*** and **BI**$^\bullet$ are transient species with short lifetimes in low-concentration catalytic amounts, making the ET difficult before the dimerization of **BI**$^\bullet$. Alternatively, we examined the possibility of hydrogen atom transfer (HAT), a process wherein protons and electrons are transferred simultaneously. The Gibbs energy change of HAT from **HA**$^-$ to **BI**$^\bullet$ is largely negative ($\Delta G^\circ = -17.2$ kcal mol^{-1}) with a small activation energy of $\Delta G^\ddagger = 10.2$ kcal mol^{-1}, thus a more plausible channel for converting **BI**$^\bullet$ to **BIH** has been identified.[66] The HAT from **HA**$^\bullet$ to **BI**$^\bullet$ may also be operative (ΔG° = –20.9 kcal mol^{-1}) (Supplementary Section 25) .

Mechanism for the reduction of CO_2

During the study, we found that the initial premise was incorrect; the reaction of CO_2 (1 atm) and **BIH** did not afford formate in the dark. The results are shown in Supplementary Section 27. The reaction of CO_2 and **BIH** did not proceed below 75 °C, even in the presence of a significant amount of inorganic salts. Formate was detected at 110 °C, although in low yield (entry 8 in Supplementary Table 14). Considering that the backward reaction that generated CO_2 and **BIH** from formate and **BI**$^+$ did not proceed (Supplementary Fig. 37), the reaction of CO_2 with **BIH** in the dark is formidable kinetically rather than thermodynamically.[67] Therefore, the initially hypothesized mechanism (Fig.1e) needed to be revised.

We found that the reaction of CO_2 with **BIH** proceeded with light in the presence of PS **1** (entry 9 in Supplementary Table 14). Because **BIH** did not absorb visible light (Supplementary Fig. 38) and this reaction required PS **1** (entries 11 and 12 in Supplementary Table 14), the excited state of PS was involved in the reaction of CO_2

with **BIH**. The triplet energy transfer from the triplet excited state of **1** to **BIH** was unlikely (Supplementary Fig. 39). Fluorescence quenching of **1** by **BIH** was marginal in the concentration range used in the CO_2RR (Supplementary Fig. 40), indicating that ET from **BIH** to the singlet excited state of **1** (^{1}**1***) is a minor pathway. In contrast, fluorescence quenching of **1** occurred under 1 atom of the CO_2 atmosphere (Supplementary Fig. 41). Similarly, the luminescence quenching of **7**, a competent PS in the photochemical CO_2RR, was also observed under a CO_2 atmosphere, while no fluorescence quenching was observed for PS **2** that demonstrated no catalytic activity. These results suggest that ET from the excited PS to CO_2 occurs to give $CO_2^{\bullet-}$, which leads to formate prodution. The ET from ^{1}**1*** to CO_2 was at least 20 times faster than that from **BIH** to ^{1}**1*** under the standard reaction conditions (Supplementary Fig. 41).

Subsequently, the production of formate from $CO_2^{\bullet-}$ was investigated. In the present system, the protonation of $CO_2^{\bullet-}$ and further ET to $CO_2^{\bullet-}$ to yield CO_2^{2-} are not plausible. Therefore, we examined the HAT pathway from **BIH** to $CO_2^{\bullet-}$, which was revealed to be plausible at ambient temperature ($\Delta G^{\ddagger} = 20.1$ kcal mol^{-1}) by the DFT calculation (Supplementary Section 25).

Compared to when **H_2A** was used as a sacrificial electron donor in the presence of catalytic **BI$^+$**, the yield of formate was much lower when **BIH** was used as a sacrificial electron donor (8 mM (entry 9 in Supplementary Table 14) vs. 72 mM (Fig. 3)). This phenomenon was observed because when **BIH** was used as a sacrificial electron donor, the concentration of **BI$^+$** increased as the reaction progressed, which could function as a quencher of the excited PS or as an electron-acceptor for $CO_2^{\bullet-}$ to hamper the reaction. Thus, the catalytic use of **BI$^+$** is advantageous in avoiding these detrimental inhibition effects, which is a characteristic of the present catalytic system.

Mechanism for the entire photocatalytic CO_2RR

Based on the obtained results, the mechanism for the entire photocatalytic CO_2RR is proposed in Fig. 6 with **5** as a representative PS. PS **5** has extended absorption into the visible-light region and is excited by a light of 400 nm, generating the singlet excited state (^{1}**5***). This excited state is characterized by a deeply negative oxidation potential (E (**5**$^{\bullet+}$/^{1}**5***) = –2.65 V vs SCE)) and undergoes ET to **BI$^+$** (E_{red} = –1.96 V vs SCE), forming **5**$^{\bullet+}$ and **BI$^\bullet$**. Subsequently, **5**$^{\bullet+}$ (E_{red} = 0.34 V vs SCE) accepts an electron from **HA$^-$** (E_{ox} = 0.47 V vs SCE)[68] to regenerate **5** and form **HA$^\bullet$**. The use of a base is indispensable for generating **HA$^-$**, a stronger electron donor than **H_2A** (Supplementary Section 28). The HAT process from **HA$^-$** or **HA$^\bullet$** to **BI$^\bullet$** effectively reduces **BI$^\bullet$** to **BIH**. The resultant **BIH** does not react with CO_2 under the employed conditions in the dark. In contrast, under photoirradiation, $CO_2^{\bullet-}$ generated by the ET from ^{1}**5*** to CO_2 reacts with **BIH** via the HAT mechanism, generating **BI$^\bullet$** and formate. According to this mechanism, one photon is required for transferring two electrons and reducing CO_2 to formate. **BI$^\bullet$** can undergo the ET to **5**$^{\bullet+}$ and return to **BI$^+$**. This unproductive loss of **BI$^\bullet$** can be readily compensated using a photon and the **BI$^\bullet$/BIH** catalyst cycle is recovered. In addition to CO_2 from the external source, CO_2 generated along with the conversion of **A** to **INT1** serves as a carbon source for formate (Supplementary Section 6). Intermediates **INT1** and **INT2** resulting from **A** could function similarly to **HA$^-$** and

HA$^•$, respectively; thus, **H$_2$A** can serve as a four-electron reductant in this CO$_2$RR. A small amount of formate was obtained without **BI$^+$(I)$^−$** (Fig. 3), deducing that the direct HAT from **HA$^−$** to CO$_2$$^{•−}$ could also proceed slightly, which is supported by the DFT calculation (Supplementary Section 25). The feasibility of the other possible reaction routes is discussed in Supplementary Section 29.

Summary

The reduction of CO$_2$ was achieved using a transition metal-free PS and catalyst. In this reaction organohydride **BIH** with a high reduction capability was photocatalytically regenerated. Contrary to the initial working hypothesis, the formate generation from **BIH** and CO$_2$ required photoenergy; the carbazole-based PS underwent ET to CO$_2$ to generate CO$_2$$^{•−}$ under visible-light irradiation, then HAT process operated to bypass the following demanding ET process (CO$_2$$^{•−}$ → formate). High selectivity for formate over H$_2$ enabled by the use of organohydride catalysts was observed in this developed system, which is in contrast to the transition metal-catalyzed reduction of CO$_2$ that competes with the thermodynamically favored H$_2$ production.[19,20]

Despite these progress, the following issues remain to be addressed to realize truly sustainable artificial photosynthesis. The first issue is the requirement of a sacrificial reductant, which is an evident drawback. Thus, coupling the developed CO$_2$RR with the reaction system of the water oxidation, possibly without using a transition metal, is the next attractive target. The second issue is the visible-light-triggered single ET from the PS to CO$_2$. This is a distinguishing feature enabled by carbazole-based PSs; however, relying on this mechanism in the future can limit the operative PSs, considering the deeply negative redox potential of the CO$_2$/CO$_2$$^{•−}$ couple. Therefore, the hydride-transfer mechanism from an organohydride to CO$_2$ can be an attractive alternative pathway to avoid the single-electron CO$_2$ reduction. The third issue to be addressed is the conversion of **BI$^•$** to **BIH** capitalizing on the HAT process with ascorbate. This HAT process will not be available when the water oxidation is coupled with the CO$_2$RR in the future, where protons and electrons are supplied independently. The possible solution to this is the PT–ET mechanism for organohydride generation (**BI$^•$** → **BIH$^{•+}$** → **BIH**), which was reported promising.[58] The basic condition is currently required to activate the electron donor, ascorbic acid, making the protonation of **BI$^•$** difficult. Therefore, coupling with water oxidation that performs under neutral or acidic conditions can enable the **BIH** generation via the PT–ET mechanism. In addition, CO$_2$RR should yield formic acid rather than formate salt under these neutral or acidic conditions, which is beneficial from the atom-economical viewpoint. The last issue is the requirement of high-energy visible light (400 nm). Considering that the formidable one-electron reduction of CO$_2$ can be evaded by utilizing the hydride transfer from the modified organohydride as mentioned earlier, the scope of operative PSs can be broadened, thus elongating the required light wavelength. Further study to address these issues is ongoing in our laboratory.

Acknowledgments

R.M. is thankful for the financial support from ENEOS TonenGeneral

Research/Development Encouragement & Scholarship Foundation, Takahashi Industrial and Economic Research Foundation, the Takano Science Foundation, Kanamori Foundation, and Fukuoka Naohiko Memorial Foundation. This work was partially supported by JSPS KAKENHI Grant-in-Aid for Transformative Research Areas, "Dynamic Exciton" (JP20H05832 to Y.K.) and Grant Nos. JP20K21174, JP20KK0120, and JP22K19008 to Y.K. We thank Ms. Tomoko Amimoto from the Natural Science Center for Basic Research and Development (N-BARD), Hiroshima University for mass analysis measurements. We also thank Prof. Takashi Tachikawa and Dr. Zhujun Zhang at Kobe University for their assistance on GC analysis and Mr. Tatsuhiro Harada at Kobe University for determining the mechanism elucidation hint.

Author contributions

R.M. conceived and directed the project. R.M., W.X., and Y.K. wrote the paper. W.X., J.X., and U.M.I. performed most experiments under the supervision of R.M. and M.H. J.K., M.F., and Y.K. conducted transient absorption spectroscopy and fluorescence lifetime measurements. M.Y. conducted the computational calculation for the transition states. All the authors discussed the results and commented on the manuscript.

Competing interests

The authors declare no competing interests.

Fig. 1 Reduction of CO_2 using different strategies. a, Reported photocatalytic one-electron reduction of CO_2. This process is challenging owing to the considerably negative potential of the $CO_2/CO_2^{\bullet-}$ redox couple. **b**, Most previous studies utilized transition metal catalysts to enable photocatalytic multi-electron reduction of CO_2. **c**, Reported multi-electron reduction of CO_2 with organomolecules and metalloid hydrides. **d**, A groundbreaking example of two-electron reduction of CO_2 with metal-free organohydride was reported by Lim and Musgrave et al, which became the basis of our research. **e**, We hypothesized that the photochemical regeneration of **BIH** from **BI**$^+$ in the same vessel as CO_2RR could realize the catalytic metal-free CO_2RR.

Fig. 2 Reduction of BI$^+$ to BIH via visible light-driven photoreaction. In the presence of catalytic amount of PS **1**, **BI$^+$(I$^-$)** was photochemically reduced to **BIH** using **H_2A** as a reductant; visible light irradiation for 15 min provided **BIH** in 66% yield. The mass balance (sum of the yield of **BIH** and the recovered **BI$^+$(I$^-$)**) was almost quantitative even after 20 h, suggesting the sufficient stability of **BIH** and **BI$^+$(I$^-$)** in this photoreaction.

Fig. 3 Photocatalytic CO_2 reduction reaction. A solution of **1** (1.5 mM), **BI$^+$(I$^-$)** (2.5 mM), **H_2A** (50 mM), and K_2CO_3 (55 mM) was irradiated (λ_{max} = 400 nm) for 4 h under 1 atm of CO_2 atmosphere (this condition is denoted as "standard condition"), affording formate in 72 mM. The generation of 72 mM of formate from 50 mM of electron-donor **H_2A** indicates that **H_2A** donated more than two electrons. Control experiments revealed that a base, light irradiation, **H_2A**, and PS are indispensable. Formate was produced without CO_2 as long as K_2CO_3 was used as a base, because carbonate served as a CO_2 donor. Depending on the conditions, the reaction temperature was increased up to 43 °C even with fan cooling, although heat was dispensable based on the fact that the CO_2RR still proceeded at 30 °C. Other than PS **1**, PS **5**, **6**, and **7** also promoted the CO_2RR. Only moderate yield of formate was generated using molecules **9**–**11** as a catalyst in which the carbazole and benzimidazolium moieties were covalently connected. This moderate activity of PS **5**, **6**, and **7** was ascribed to the unproductive back electron transfer.

Fig. 4 Mechanistic studies of the generation of carbazole radical cation. a, The absorption of $\mathbf{5}^{\bullet+}$ (red line) and the calculated oscillator strength of $\mathbf{5}^{\bullet+}$ (orange bar) and $\mathbf{BI}^{\bullet}$ (blue bar), a one-electron reduced form of $\mathbf{BI}^{+}$. Carbazole radical cation $\mathbf{5}^{\bullet+}$ was generated by treating **5** (100 μM) with magic blue (100 μM) in CH_2Cl_2. The absorption bands at 470, 550, 700, and >1100 nm (marked with black arrows) newly appeared, which were assigned to $\mathbf{5}^{\bullet+}$. The oscillator strengths were calculated by the time-dependent density functional theory (TD-DFT) method. The calculated wavelength of the absorption peaks matched the experimental spectrum. **b**, Two-dimensional data of the absorbance change (transient absorption) obtained by the laser irradiation of 355 nm of the DMSO solution of **5** (0.2 mM) in the presence of $\mathbf{BI}^{+}(\mathbf{I}^{-})$ (30 mM) at 293 K. The long-lived absorption bands were observed at 470, 550, and 700 nm and assigned to the transient absorption composed of $\mathbf{5}^{\bullet+}$ and $\mathbf{BI}^{\bullet}$. **c**, Overlay of the steady-state absorption spectrum of the chemically generated $\mathbf{5}^{\bullet+}$ (red) over the transient absorption spectrum of **5** in the presence of $\mathbf{BI}^{+}(\mathbf{I}^{-})$ in the laser flash photolysis (blue). The transient absorption spectrum (blue) is made by averaging the ΔA values at the delay time from 5 μs to 6 μs in **b**. Observation of the almost perfect overlay suggested that $\mathbf{5}^{\bullet+}$ was generated upon photoirradiation of **5** in the presence of $\mathbf{BI}^{+}(\mathbf{I}^{-})$. **d**, The Time profiles of the absorbance changes obtained in **b** from the delay time of 0 ms to 35 ms. These non-exponential decays obeyed second-order kinetics (Supplementary Fig. 33), which was ascribed to the bimolecular charge-recombination reactions between $\mathbf{5}^{\bullet+}$ and $\mathbf{BI}^{\bullet}$.

Fig. 5 Pathway for the conversion of $\mathbf{BI}^{\bullet}$ to BIH. There are three possible routes from $\mathbf{BI}^{\bullet}$ to **BIH**; PT followed by ET (PT–ET), ET followed by PT (ET–PT), and HAT pathways. In the present CO_2RR system, the PT–ET pathway is unlikely owing to the basic condition. The ET–PT pathway is difficult to occur because $^{1}\mathbf{5}^{*}$ and $\mathbf{BI}^{\bullet}$ are both transient species with short lifetimes in low-concentration catalytic amounts. Alternatively, the HAT process in which protons and electrons are transferred simultaneously is plausible based on the calculated Gibbs energy change (ΔG^{o}) and activation energy ($\Delta G^{\ddagger}$). The pK_a and potential values are those determined in DMSO and from the literature.[58] All potentials are referred to SCE.

Fig. 6 The proposed reaction mechanism for the overall photocatalytic CO_2RR. a, PS **5** is excited by visible light and generates $^{1}\mathbf{5}^{*}$, which undergoes ET to $\mathbf{BI}^{+}$, forming $\mathbf{5}^{\bullet+}$ and $\mathbf{BI}^{\bullet}$. **BIH** is generated from $\mathbf{BI}^{\bullet}$ via the HAT from $\mathbf{HA}^{-}$ or $\mathbf{HA}^{\bullet}$. CO_2 accepts an electron from $^{1}\mathbf{5}^{*}$ to form $CO_2^{\bullet-}$, which reacts with **BIH** via the HAT mechanism, generating product formate. **b**, **H_2A** functions as a four-electron donor in the present system. **HA^-**, an activated electron donor, is generated by deprotonation of **H_2A** with a base. **HA^-** can undergo either ET or HAT, and is eventually transformed to **A**. **A** is converted to **INT1** via decarboxylation (Supplementary Section 6). **INT1** can function as a two-electron donor. Gibbs free energy changes are represented in kcal mol^{-1}. Standard redox potentials are referred to saturated calomel electrode (SCE).

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Methods

A general method for photocatalytic CO_2RR (entry 1 in Supplementary Table 4 as a representative example) was followed: A flame-dried 50-mL Schlenk tube with a Teflon cap and a magnetic stir bar was charged with **$BI^+(I^-)$** (7.2 mg, 0.025 mmol, 2.5 mM), PS **1** (3.8 mg, 0.015 mmol, 1.5 mM), ascorbic acid (88.1 mg, 0.500 mmol, 50 mM), and K_2CO_3 (76.0 mg, 0.550 mmol, 55 mM). CH_3CN (8 mL) and distilled water (2 mL) were then introduced into the mixture, and the reaction mixture was degassed by three freeze–pump–thaw cycles. Subsequently, the reaction mixture was backfilled with CO_2 (>99.995% purity), and the CO_2 atmosphere was maintained using a balloon. The reaction mixture was stirred under visible-light irradiation (λ_{max} = 400 nm) for 4 h. After the reaction, 1,3,5-trimethyoxybenzene (40.6 mg) as an internal standard and distilled water (4 mL) were added to the resulting reaction mixture. Finally, 0.6 mL of the solution was transferred to an NMR tube and subjected to ^1H NMR spectroscopic analysis using the solvent suppression technique. The yield of formate was 72 mM.

Data Availability

The additional discussions and the data supporting the plots within this paper and other findings of this study, such as ^1H NMR and ^{13}C NMR spectra, cyclic voltammograms, optical spectra, experimental procedures, and quantum chemical calculations, are available in the Supplementary Information.

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