Non-metal photochemical reduction of CO$_2$ to formate with organohydride-recycle strategy

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Abstract
The increasing CO$_2$ concentration in the atmosphere is an urgent social problem that has to be resolved. Reducing CO$_2$ into compounds useful as energy sources and carbon materials is desirable. For the CO$_2$ reduction reaction (CO$_2$RR) to be operational on a global scale, the catalyst system must: (1) use only renewable energy, (2) be built from abundantly available elements, and (3) not require high-energy reactants. Although light is an alluring energy source, most existing methods utilize electricity. Furthermore, catalyst systems are based on rare heavy metals. Herein, we present a transition-metal-free catalyst system for CO$_2$RR using visible light and containing a carbazole photocatalyst and an organohydride co-catalyst based on benzimidazoline. It produced formate with a turnover number exceeding 8000. No other reduced products such as H$_2$ and CO were generated, confirming the high selectivity of the system. This finding is essential for operating artificial photosynthesis on a useful scale.
studies, in addition to the photocatalysts (PCs). In those cases, the CO₂ coordination with the transition metal co-catalysts enabled the multi-electron CO₂ reduction via the inner-sphere ET mechanism (Fig. 1B). Although a high turnover number (TON) and/or turnover frequency (TOF) were obtained in some cases, the requirement of transition metals became an issue for large-scale practical applications. In addition, kinetically favored production of H₂ by reducing water is a potential competitive pathway in transition metal catalysis, the suppression of which is often formidable.

Formic acid, one of the reduced compounds of CO₂, is a widely used as a reductant, acid, and C1 carbon source in the industry. Formic acid and formates are also potent silage ingredients, preservatives, and agrichemicals. 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. To date, selective generation of formate via photochemical CO₂RR using soluble molecular catalysts has been reported. For example, MacDonnell reported the photochemical reduction reaction of CO₂ to formate using a ruthenium complex and pyridine as a PC and co-catalyst, respectively. Ishitani achieved selective photochemical reduction of CO₂ to formate using a well-designed trinuclear ruthenium complex as a catalyst, wherein a benzimidazoline derivative was used as a stoichiometric terminal reductant. 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 CO₂. Therefore, organomolecules that undergo multi-electron CO₂RR are limited. Successful examples are reactions using a combination of frustrated Lewis pairs and metalloid hydride species (B–H or Si–H) (Fig. 1C). However, the issue of low TON and requirement of stoichiometric high-energy metalloid hydride species remains unaddressed. Recently, Musgrave reported that 1,2,3-trimethylbenzimidazoline (BIH) reacts with CO₂ to afford formate without the assistance of transition metals or frustrated Lewis pairs (Fig. 1D). This reaction is a groundbreaking example of two-electron CO₂RR achieved exclusively by non-metal organohydrides. Noteworthy in this organomolecular process is the exclusive selectivity in formate formation over H₂ or CO formation. However, a stoichiometric amount of BIH was required, and an excess amount (40 equiv to BIH) of the metal salt (NaBF₄) was used to shift the equilibrium to the product side, which remained obvious tasks to be solved.

Musgrave 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 CO₂RR system. We hypothesized that photochemical reduction of BI⁺ to BIH in the same reaction vessel as CO₂RR could render the CO₂RR system truly catalytic with respect to BIH (Fig. 1E). Catalytic reduction of chemicals other than CO₂ with the concept of the in situ photochemical regeneration of organohydrides has been developed. However, compared to the previous reports that used nicotinamide adenine dinucleotide-mimicking organohydrides, BI⁺ had a significantly negative reduction potential (E = −2.12 V vs. SCE), which renders its photochemical reduction challenging. Therefore, benzimidazoline organohydrides have been used as a
stoichiometric reductant to date.\textsuperscript{45-49} Furthermore, the dimerization of the organohydride species via its intermediate radical during the regeneration process is another concern.\textsuperscript{50} Herein, we report that the visible-light-driven CO$_2$RR to generate formate based on the concept of \textit{in situ} photochemical organohydride regeneration is viable. The employed PCs were non-metallic small molecules with a high TON of up to 8820 at ambient temperature with 1 atm of CO$_2$.\textbf{}}
(A) Photocatalytic one-electron reduction of \( \text{CO}_2 \)

\[
\text{PC} \quad \text{hv} \quad \text{CO}_2 \quad \text{PC}^+ \quad \text{CO}_2^{2-}
\]

Formidable \((E(\text{CO}_2/\text{CO}_2^{2-}) = -2.21\text{V vs SCE})\)

(B) Photocatalytic multi-electron reduction of \( \text{CO}_2 \)

\[
\text{h}^+ \quad \text{PC} \quad \text{red}_M \quad \text{CO}_2 \quad \text{CO}_2, \text{HCO}_2\text{H, CH}_3\text{OH}
\]

General and precedent
Transition metal catalyst is required.

\(M = \text{Ni, Re, Ru, Ir etc}\)

(C) Multi-electron reduction of \( \text{CO}_2 \) with organomolecules and metalloid hydrides

\[
\text{CO}_2 + M-H \rightarrow \text{H}_2\text{C-M} \quad (M = \text{metalloid})
\]

Frustrated Lewis pair (catalytic or stoichiometric)

\[
\begin{align*}
\text{B(C_6F_5)_3} & \quad \text{or} \quad \begin{array}{c}
\text{Ph}_2\text{P} \\
\text{B(cat)}
\end{array} \\
\text{cat = catecholate}
\end{align*}
\]

Reductant

\[
\begin{align*}
\text{Et}_3\text{Si-H} \\
\text{B(cat)-H} \\
\text{BH}_3\text{-NH}_3
\end{align*}
\]

Turnover number is low.
Stoichiometric metalloid hydrides are required.

(D) Two-electron reduction of \( \text{CO}_2 \) with organohydride

\[
\begin{align*}
\text{BIH} \quad \text{Me} & \quad \text{Me} \quad \text{Me} \\
& \quad \text{Me} \quad \text{Me}
\end{align*}
\]

\[
\begin{align*}
\text{CO}_2 & \quad \text{KBF}_4 (40 \text{ equiv}) \\
& \quad \text{DMSO-d}_6, 50 \text{ °C, 18 h} \\
& \quad 66\% \text{ yield}
\end{align*}
\]

\[
\text{BI}^+\text{(HCOO)}^-
\]

No transition metal is required.
Stoichiometric reaction

(E) Working hypothesis of present work

\[
\begin{align*}
\text{BIH} \quad \text{Me} & \quad \text{Me} \\
& \quad \text{Me} \quad \text{Me}
\end{align*}
\]

\[
\begin{align*}
\text{CO}_2 & \quad \text{HCOO}^- \\
& \quad \text{BI}^+
\end{align*}
\]

Non-metal PC
Sacrificial reductant

No transition metal is required.
Catalytic for organohydride
Results and Discussion
Photocatalytic CO$_2$RR

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 PC 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). The excited state of common PCs readily oxidizes BIH, leading to the unproductive consumption of BIH and photon. Therefore, a judicious choice of PC is required. Our group focused on developing non-metallic (organic) PCs with high reducing capability. We recently discovered that 3,6-bis(dimethylamino)carbazole molecules could serve as a capable PC 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 as compared to the parent carbazole, and absorbs visible light. The photocatalytic reduction of BI$^+$(I) to its reduced-state BIH employing 1 as a PC remarkably proceeded in 44% yield 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). The mass balance of this reaction was almost quantitative, suggesting that both 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$_2$RR using a catalytic amount of BIH. Entry 1 of Table 1 illustrates the developed procedure. Formate was obtained as a CO$_2$-reduced product, with a yield of 143% ($100 \times \text{the amount of formate formed (mol)/the amount of employed sacrificial reductant (mol)}$), which was revealed by proton nuclear magnetic resonance ($^1$H NMR) analysis. To the best of our knowledge, this is the first
example of a visible-light-driven photocatalytic CO₂RR to generate any reduced C1 product using a non-metallic small molecular catalyst. The observed yield of more than 100% indicates that H₂A donates more than two electrons, which will be discussed later. Methanol, formaldehyde, and oxalate were not detected as a product by ¹H NMR or carbon-13 NMR (¹³C NMR) analysis of the solution phase (Fig. S2). The gas chromatography (GC) analysis of the reactor headspace revealed that the evolution of gaseous products, CO or H₂, was below the detection limit (0.1% and <0.8% yield for H₂ and CO, respectively) (Fig. S3 and S4). Thus, our protocol for CO₂RR exhibits exclusive selectivity to afford formate as the sole product, which contrasts the previous transition metal-catalyzed CO₂RR, where concomitant H₂ generation is often an issue. The quantum yield of CO₂RR was 6.5% (Fig. S7).

Base, light irradiation, H₂A, and PC 1 are indispensable in this reaction, as revealed by control experiments (Table 1, entries 2–6). The yield dropped to 8% (entry 7) 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 (entry 8 vs. entry 1). This result indicates that iodide anions are not involved in the catalytic cycle. In addition, K₂CO₃ was replaced with other inorganic salts (entries 9–14), implying that the type of counter cations and basic anions moderately affects the reaction. In entries 15 and 16, inorganic sacrificial reductants, Na₂SO₃ and NaHSO₃, were used instead of H₂A, resulting in 64% and 61% yields, respectively. Although the yields were lower than that of entry 1, Na₂SO₃ and NaHSO₃ were capable reductants because they donated two electrons per molecule (the maximum product yield is 100%). Formate was generated even without CO₂ gas in the presence of K₂CO₃ (entry 17); however, minimal formate was generated without CO₂ gas or K₂CO₃ (entry 18), suggesting that CO₂⁻ could serve as a source of CO₂ in the present system. Next, the PCs were screened (entries 19–25, Fig. 3). Carbazole-based organic PCs with electron-withdrawing groups did not generate formate (entries 19–21) due to the insufficient reducing capability of the excited states of these PCs to transfer an electron to BI⁺. PC 5, with electronic feature similar to that of 1, gave a comparable formate yield of 127% (entry 22). Tris(2-phenylpyridinato)iridium (III) or Ir(ppy)₃ (7) could also serve as a competent PC, affording formate in 132% yield (entry 24). Without BI⁺(I), Ir(ppy)₃ did not afford formate, suggesting that the Ir(ppy)₃-catalyzed CO₂RR proceeded via a BI⁺(I)-involving mechanism, similar to the reaction using 1. Thus, the catalyst combination of Ir(ppy)₃ and BI⁺(I) was unprecedented and a new discovery in the present study. Tris(2,2’-bipyridyl) ruthenium (II) chloride hexahydrate or Ru(bpy)₃Cl₂•6H₂O (8) did not promote the reaction (entry 25).
Table 1. Photocatalytic CO$_2$ reduction reaction.

\[
\begin{array}{cccc}
\text{CO}_2 (1 \text{ atm}) & \overset{\text{hv} (\lambda_{\text{max}} = 400 \text{ nm})}{\rightarrow} & \text{HCOO}^- \\
\text{CH}_3\text{CN/H}_2\text{O (4/1, 0.05 M), 25 °C, 4 h} & \text{"standard condition"}
\end{array}
\]

| Entry | Variation from above “standard condition” | Yield/%$^a$ |
|-------|------------------------------------------|------------|
| 1     | None                                      | 143        |
| 2     | Without K$_2$CO$_3$                       | 0          |
| 3     | KCl (2.0 eq) instead of K$_2$CO$_3$       | <1         |
| 4$^b$ | No light                                  | 0          |
| 5$^b$ | Without H$_2$A                            | <1         |
| 6     | Without 1                                 | 0          |
| 7     | Without BI$^+$I                           | 8          |
| 8     | BIH instead of BI$^+$I                    | 142        |
| 9     | Li$_2$CO$_3$ (1.1 eq) instead of K$_2$CO$_3$ | 68        |
| 10    | Na$_2$CO$_3$ (1.1 eq) instead of K$_2$CO$_3$ | 114       |
| 11    | Cs$_2$CO$_3$ (1.1 eq) instead of K$_2$CO$_3$ | 122       |
| 12    | KOH (2.2 eq) instead of K$_2$CO$_3$       | 78         |
| 13    | NaOH (2.2 eq) instead of K$_2$CO$_3$      | 103 (117)$^b$ |
| 14    | K$_3$PO$_4$ (2.2 eq) instead of K$_2$CO$_3$ | 143       |
| 15    | Na$_2$SO$_3$ instead of H$_2$A             | 64 (52)$^c$ |
| 16    | NaHSO$_3$ instead of H$_2$A               | 61 (3)$^c$ |
| 17    | Argon instead of CO$_2$                   | 104        |
| 18    | Argon instead of CO$_2$, NaOH (2.2 eq) instead of K$_2$CO$_3$ | 5          |
| 19    | 2 instead of 1                            | 0          |
| 20    | 3 instead of 1                            | 0          |
| 21    | 4 instead of 1                            | 0          |
| 22    | 5 instead of 1                            | 127        |
| 23    | 6 instead of 1                            | 111        |
| 24    | 7 instead of 1                            | 132 (0)$^d$ |
| 25    | 8 instead of 1                            | 0          |

$^a$ 100 $\times$ the amount of formate formed (mol)/the amount of employed sacrificial reductant (mol)

$^b$ Reaction time: 20 h

$^c$ Without K$_2$CO$_3$

$^d$ Without BI$^+$I
Figure 3. Employed photocatalysts.

We utilized $^{13}$CO$_2$ instead of $^{12}$CO$_2$ (Fig. 4A) to confirm that the singlet peak at 8.8 ppm in $^1$H NMR spectrum was assigned to formate, thereby confirming that the carbon source of formate was derived from CO$_2$. Sodium hydroxide was used as the base to avoid contaminating $^{12}$CO$_2$ derived from K$_2$CO$_3$ (Table 1, entry 17). $^1$H NMR analysis revealed that $^{13}$C-formate, characterized by a set of doublet peaks ($^1J_{CH} = 192.8$ Hz), was obtained in 90% yield, along with a 3% yield of $^{12}$C-formate (Fig. 4B). The formation of $^{12}$C-formate is ascribed to $^{12}$CO$_2$ released from H$_2$A (vide infra, Fig. 6). In the $^{13}$C NMR spectrum of the same reaction, an intense $^{13}$C-formate at 169.4 ppm was observed (Fig. 4C). These results demonstrate that the main carbon source of the product formate is gaseous CO$_2$ introduced exogenously.
Figure 4. Carbon-13 ($^{13}$C)-labeling experiment. (A) Reaction conditions. (B) Proton nuclear magnetic resonance ($^1$H NMR) spectrum of the reaction mixture. The singlet peak at 6.57 ppm is trimethoxybenzene (internal standard). (C) $^{13}$C NMR spectrum of the reaction mixture.

Next, we focused on developing catalysts with carbazole and $\text{BI}^+$ moieties in one
molecule. We designed 9, 10, and 11 to probe the conceptual feasibility of the presumed all-in-one catalyst. The carbazole and BI\textsuperscript{+} moieties were covalently connected by the alkyl-chain linkers in 9 and 10, while 11 was the reduced form of 10 (Fig. 5). The synthesis of these molecules is illustrated in Fig. S8. The absorption spectra of 9 and 10 are similar to the average of those of 1 and BI\textsuperscript{+} added together, suggesting no significant electronic interaction between the carbazole and benzimidazolium parts in the ground state (Fig. S9). Visible light-driven CO\textsubscript{2}RR using 1 mol% of all-in-one catalysts 9, 10, and 11 provided formate in 72, 68, and 56% yields, respectively (Table S1). These data proved that photochemical CO\textsubscript{2}RR using a single molecular catalyst is conceptually viable. The observed moderate catalytic activity of 9–11 is ascribed to the unproductive back ET; further optimization of the catalyst structure is required.

Figure 5. Structures of all-in-one photocatalysts.

TON and TOF are parameters used to evaluate the durability and kinetic activity of the catalyst. Higher TON and TOF for the potential PCs (1, 5, 6, and 7) were sought for the developed CO\textsubscript{2}RR using 0.01 mol% of PC and 5 mol% of BI\textsuperscript{+}(I) at 4 h reaction time (Table 2, entries 1–4). Using organic PC 6, TON and TOF reached 8820 and 2205 h\textsuperscript{-1}, respectively (entry 3). TON and TOF for BI\textsuperscript{+}(I) were 6070 and 1520 h\textsuperscript{-1}, respectively using 1 mol% of PC 5 and 0.01 mol% of BI\textsuperscript{+}(I) (entry 6). These large values indicate that the employed PCs and BI\textsuperscript{+}(I) have high durability and activity for CO\textsubscript{2}RR. The catalyst loadings of both PC 5 and BI\textsuperscript{+}(I) could be simultaneously reduced to 0.1 mol% (entry 8), while further decreasing the catalyst loading led to low yields (entries 9 and 10).

Table 2. Investigation on the decrease of the catalyst loading.

| Entry | Photocatalyst (PC) | x | Yield /% | TON (PC/BI\textsuperscript{+}(I)) | TOF /h (PC/BI\textsuperscript{+}(I)) |
|-------|---------------------|---|----------|-------------------------------|-------------------------------------|
| 1     | 1 (0.01 mol%)       | 5 | 27       | 2750/5                        | 687/1                               |

hv (\(\lambda_{\text{max}} = 400\) nm)
PC, BI\textsuperscript{+}(I) (x mol%)
H\textsubscript{2}A (1.0 eq.), K\textsubscript{2}CO\textsubscript{3} (1.1 eq.)
CH\textsubscript{3}CN/H\textsubscript{2}O (4/1, 0.05 M), 25 °C, 4 h

HCOO\textsuperscript{-}
Mechanistic Study

Investigating the role of H2A

In some photocatalytic CO2RRs using H2A as a sacrificial reductant (for example entry 1 in Table 1), the yields based on the loading of H2A exceeded 100%, assuming that H2A is a two-electron donor. This result implies that H2A releases more than two electrons per molecule. The proposed pathway for the conversion of H2A is shown in Fig. 6. After releasing two electrons, H2A was converted to dehydroascorbic acid (A). Delactonization of A yielded 12, which was converted to aldehyde 13 with the release of CO2. Further, 13 underwent deprotonation to form 14, which was a potential electron donor because it has an enediol structural motif analogous to H2A. A commercially available A was used instead of H2A in the photocatalytic CO2RR to verify the above hypothesis (Table 3, entry 2). Formate was obtained in 74% yield, corroborating the hypothesis that A also served as a reductant. Next, 13CO2 was used instead of 12CO2 under identical conditions (entry 3). As a result, 17% and 45% of 12C- and 13C-formate was yielded, respectively. Formate was obtained in 30% yield even without CO2 gas (entry 4). Two possible pathways were suggested to explain these results: path (1): A degraded to CO2, which was converted to formate in the photocatalytic cycle of CO2RR, and path (2): A directly degraded to formate. Several control experiments were conducted to clarify the plausible mechanism (entries 5–7). No formation of formate without BI'(I) (entry 5) strongly supported path (1). The omission of base or 1, both indispensable in photocatalytic CO2RR, did not form formate, which was also consistent with path (1). Thus, the following conclusions are drawn: (a) According to the proposed mechanism shown in Fig. 6, H2A can operate as a four-electron donor; (b) H2A releases CO2 during its oxidation, which can be a carbon source of formate; (c) direct generation of formate derived from the degradation of H2A is implausible.
**Figure 6.** Proposed mechanism for the conversion of H₂A.

**Table 3.** Utilization of A as a sacrificial reductant.

| Entry | Sacrificial reductant | CO₂ | Yield/%<sup>a</sup> |
|-------|-----------------------|-----|---------------------|
| 1<sup>b</sup> | H₂A | ^12CO₂ | 143 |
| 2 | A | ^12CO₂ | 74 |
| 3 | A | ^13CO₂ | 45 (^13C-formate) |
|  |  |  | 17 (^12C-formate) |
| 4 | A | Not used | 30 |
| 5<sup>c</sup> | A | Not used | 0 |
| 6<sup>d</sup> | A | Not used | 0 |
| 7<sup>e</sup> | A | Not used | 0 |

<sup>a</sup> 100 × the amount of formate formed (mol)/the amount of employed sacrificial reductant (mol)

<sup>b</sup>K<sub>3</sub>PO<sub>4</sub> (2.2 eq) was used

<sup>c</sup>Without BI<sup>+</sup>(I)

<sup>d</sup>Without K<sub>3</sub>PO<sub>4</sub>

<sup>e</sup>Without I

**Mechanism for photosensitization**

Next, we focused on the organohydride regeneration mechanism. Light irradiation was required for CO₂RR (Table 1, entry 4). Because BI<sup>+</sup>(I) did not demonstrate absorption at 400 nm (Fig. S9), the excitation of PC carbazole initiated photosensitization. We performed experiments to gain insight into the mechanism of the initial photosensitization. For the following experiments, 1 or 5 was used as a representative PC. First, the formation of an electron donor-acceptor (EDA) complex between PC 1 and BI<sup>+</sup>(I) was explored by measuring the steady-state ultraviolet-visible absorption of the mixed solution (Fig. S11). No new peak was observed compared to
the original spectrum of each compound, suggesting that no EDA complex was generated. The existence of the exciplex was improbable because the normalized emission spectra of PC 1 in the presence and absence of BI⁺(I⁻) were identical (Fig. S12). We further examined the involvement and influence of the excited states (singlet or triplet) of PC in reducing BI⁺(I⁻). Thus, the rate constants of fluorescence quenching ($k_q$) of PC 1 by BI⁺(I⁻) and ascorbate anion (HA⁻) were determined according to the Stern-Volmer equation, $I_0/I = 1 + k_q\tau_0[Q]$, where $I_0$ and $I$ represent the fluorescence intensity in the absence and presence of the different concentrations of the quencher, respectively; $\tau_0$ represents the lifetime of the excited state of PC; [Q] is the quencher concentration. The time-resolved fluorescence measurement of PC 1 yielded a value of $\tau_0$ of 19.2 ns (Fig. S13). The results of the ET fluorescence quenching of PC 1 in the presence of varying concentrations of BI⁺(I⁻) as a quencher are illustrated in Fig. 7. Therefore, the $k_q$ by BI⁺(I⁻) had a value of $2.71 \times 10^9$ mol L⁻¹ s⁻¹, indicating that a single ET from the excited 1 to BI⁺(I⁻) occurred efficiently. In contrast, fluorescence quenching of 1 by HA⁻ was not observed (Fig. 7). Thus, an oxidative quenching cycle was suggested. The fluorescence quantum yield $\Phi_l$ and lifetime $\tau_0$ of 1, 9, 10, and 11 are listed in Table S3. The values of $\Phi_l$ and $\tau_0$ of 9 and 10 were two orders of magnitude lower than those of 1, while 11 had values of $\Phi_l$ and $\tau_0$ similar to those of 1. In addition, these results suggested that the singlet excited state of the carbazole moiety underwent a single ET to the benzimidazolium cation.

![Figure 7](image_url)

**Figure 7.** Fluorescence quenching of photocatalyst 1 in the presence of varying concentrations of BI⁺(I⁻) or HA⁻ as quenchers. Solvent: DMSO for BI⁺(I⁻), CH₃CN/H₂O (1/1 v/v) for HA⁻. The concentration of 1: $1.0 \times 10^{-5}$ mol L⁻¹. The ratios of fluorescence intensities at 450 nm in the presence (I) and absence ($I_0$) of the quenchers are represented by the function of the quencher concentrations.
Although the involvement of the singlet excited state of PC in reducing $\text{BI}^+ (\text{I})$ was evident, the involvement of the triplet excited state of PC could not be excluded. Therefore, we experimentally characterized the optoelectronic properties of PC 5 and $\text{BI}^+ (\text{I})$ (Fig. S17–S19). The results are summarized in Table 4. The oxidation potential of the singlet excited state of 5 (hereafter denoted as $^1S^*$) was $E (S^*/S^* \text{BI}) = -2.65 \text{ V vs. SCE.}$ The obtained oxidation potential was more negative than the reduction potential of $\text{BI}^+ (\text{I})$ ($E_{\text{red}} = -1.96 \text{ V vs. SCE}$), suggesting that the ET from $^5S^*$ to $\text{BI}^+ (\text{I})$ was possible. These results are consistent with those of the Stern-Volmer experiments. The oxidation potential of the triplet excited state of 5 (hereafter denoted as $^3S^*$) was $E (S^*/S^* \text{BI}) = -2.30 \text{ V vs. SCE.}$ Additionally, the ET from $^3S^*$ to $\text{BI}^+ (\text{I})$ was exothermic with $\Delta G_{\text{CS}} = -0.34 \text{ eV}$, where $\Delta G_{\text{CS}}$ is the Gibbs free energy change for charge separation. The triplet state energies ($E_T$) of 5 and $\text{BI}^+ (\text{I})$ were 2.64 and 3.02 eV, respectively, deducing that the triplet energy transfer was endothermic from $^3S^*$ to $\text{BI}^+ (\text{I})$.

**Table 4. Optoelectronic data of 5 and $\text{BI}^+ (\text{I})$.**

|       | $E_S$ /eV | $E_T$ /eV | $E_{\text{ox}}$ (vs SCE) | $E_{\text{red}}$ (vs SCE) | $^1E_{\text{ox}}$* (vs SCE) | $^3E_{\text{ox}}$* (vs SCE) |
|-------|-----------|-----------|-------------------------|--------------------------|---------------------------|---------------------------|
| 5     | 2.99      | 2.64      | 0.34                    | -2.75                    | -2.65                     | -2.30                     |
| $\text{BI}^+ (\text{I})$ | 4.22 \text{a} | 3.02 | (0.31)\text{b} | -1.96 | – | – |

$E_S$, $E_T$: singlet and triplet state energies approximated as the high-energy onset of fluorescence and phosphorescence spectra, respectively, where the emission intensity is 10% of the obtained at the maximum emission wavelength.\textsuperscript{55,56} $E_{\text{ox}}$, $E_{\text{red}}$: oxidation and reduction potentials of the ground state of molecules obtained from cyclic voltammetry analysis, respectively. When reversible cyclic voltammograms were obtained, standard reduction potentials ($E^0$) were calculated by averaging the forward and reverse peak potentials. When irreversible cyclic voltammograms were obtained, half-peak potentials ($E_{p/2}$), corresponding to the potential at half the maximum current of the cyclic voltammogram, were used as an estimate of $E^0$\textsuperscript{57} $^1E_{\text{ox}}$, $^3E_{\text{ox}}$: oxidation potential of the singlet and triplet excited states of molecules, respectively, calculated using the Rehm-Weller equation.\textsuperscript{58} \textsuperscript{a}The value of $\text{BI}^+ (\text{BF}_4)$ is presented because $\text{BI}^+ (\text{I})$ demonstrated phosphorescence instead of fluorescence even at 293 K due to the heavy atom effect. \textsuperscript{b}This value was ascribed to iodide oxidation.

The detection of the radical cation of PC 5 was attempted by transient absorption spectroscopy to directly confirm that the ET event occurs via the excited states of 5. As a preliminary step, $5^{**}$ was chemically generated by treating 5 with an equimolar amount of magic blue, a single electron oxidant ($E_{\text{red}} = +1.1 \text{ V vs. SCE}$),\textsuperscript{59} and the steady-state absorption spectrum of $5^{**}$ was measured (Fig. 8, red line). The absorption bands at 470, 550, 700, and $>1100 \text{ nm}$ (marked with black arrows) were assigned to $5^{**}$ (Fig. S20), which was corroborated by the time-dependent density functional theory (TD-DFT) calculations (Table S4); the calculated wavelength of the absorption peaks
(Fig. 8, orange bars) matched the experimental spectra. After obtaining the authentic absorption spectrum of 5+, the transient absorption of the solution of 5 in the presence of BI+(F) was measured (Fig. 9). Long-lived absorption bands with millisecond decay were observed at 470, 550, and 700 nm. These bands were assigned to 5+ generated via ET from the excited state of 5 to BI+(F), although they could partially contain the absorption of BI+, which was predicted to appear at 560 nm by the TD-DFT calculation (Fig. 8, blue bars). The time profile analysis of the absorption bands revealed that the observed millisecond decays were not exponential and obeyed total second-order kinetics (Fig. 10 and 11); thus, they were attributed to the bimolecular charge-recombination reactions between 5+ and BI+. The time profiles of the absorbance changes in the region of microseconds manifested a quick decay component at 700 nm (Fig. 12). This decay was attributed to the T1-Tn absorption of 5 (Fig. S21–S23), with a lifetime of 1.1 µs in the presence of BI+(F). The lifetime of 35+ in the absence of BI+(F) was 0.89 µs (Fig. S23). Because the lifetime of 35+ was not significantly affected by the addition of BI+(F), the ET or energy transfer from 35+ to BI+(F) was not the major pathway for reducing benzimidazolium cations. The lack of triplet quenching by the ET pathway suggests that the bimolecular rate constant between 35+ and BI+ for the small exothermicity of -ΔGCS = 0.34 eV. This smaller rate constant than kq = 2.71 × 109 mol L−1 s−1 for the 15+-precursor case (−ΔGCS = 0.69 eV) is explained by large reorganization energy exceeding 1 eV, which is consistent with the solvent reorganization energy in highly polar solvents such as acetonitrile and DMSO. In conclusion, the reduction of BI+(F) to BIH is initiated by the ET from 15+ to BI+(F).

**Figure 8.** The absorption of 5+ (red line) and the calculated oscillator strength of 5+ (orange bar) and BI+(F) (blue bar). 5+ was generated by treating 5 (100 µM) with magic blue (100 µM) in CH2Cl2. The oscillator strengths were calculated by the time-dependent density functional theory (TD-DFT) method at the B3LYP/6-
31++G(d,p)/CPCM (DMSO) level based on the geometries optimized by the DFT method at the ULC-BLYP/6-31++G(d)/CPCM(DMSO) level.

Figure 9. 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 BI\(^+\)(I) (30 mM) at 293 K. The long-lived absorption bands were observed at 470, 550, and 700 nm and are assigned to the transient absorption composed of 5** and BI\(^+\), a one-electron reduced form of BI\(^+\).

Figure 10. Time profiles of the absorbance changes obtained in Fig. 9 from the delay
time of 0 ms to 35 ms. These non-exponential decays obey a second-order kinetics as shown in Fig. 11.

**Figure 11.** Time profiles of the inverse values ($1/\Delta A$) of the absorbance changes obtained from Fig. 10. This dependence of the decay on the second-order kinetics is attributed to the bimolecular charge-recombination reaction between $5^{**}$ and $BI^*$. 

**Figure 12.** Time profiles of the absorbance changes obtained in Fig. 9 from 0 µs to 9
µs delay time. At 700 nm, the quick decay component corresponds to $T_1-T_n$ absorption of 5, which decay lifetime was obtained to be 1.1 µs. The lifetime of $^3S_0$ (0.89 µs obtained in Fig. S23) was not affected by the addition of BI+ (I) but by the triplet-triplet annihilation, denoting that the ET or energy transfer from $^3S_0$ to BI+ (I) is not the major pathway for the reduction of benzimidazolium cation.

**Mechanism for converting BI* to BIH**

After confirming the possible influence of ET in the initial photochemical step, we examined the mechanism for converting the photochemically generated BI* to BIH. The electrochemical conversion from BI* to BIH via BI* was thoroughly investigated by Lim et al. Two pathways were initially proposed with respect to the conversion of BI* to BIH: ET followed by proton transfer (PT) and PT followed by ET. Based on the results that (1) the irreversible reduction of BI* was observed in the absence of acid, which was ascribed to the dimerization of BI* and (2) the current intensity of the first reduction wave increased in the presence of acid, Lim et al. concluded that BI* underwent PT to generate BIH++, followed by ET to give BIH. In our reaction (Fig. 13), the PT to BI* is unlikely based on the employed basic condition and low acidity of BIH++ ($pK_a = 15.4$ in DMSO). Conversely, the ET from $^1S_0$ ($E([5^*]/[5^*]) = -2.65$ V vs. SCE) to BI* ($E([BI^*/BI]) = -2.42$ V vs. SCE) is exothermic. However, both $^1S_0$ and BI* are transient species with short lifetimes in low-concentration catalytic amounts, making the ET difficult before dimerization of BI*. Alternatively, we examined the possibility of hydrogen atom transfer (HAT), a process wherein protons and electrons are transferred simultaneously. The enthalpy change of HAT from HA− or HA* to BI* is largely negative ($\Delta H^o = -31.1$ or $-25.4$ kcal/mol, respectively), thus more plausible channel for converting BI* to BIH has been identified.

![Figure 13. Pathway for the conversion of BI* to BIH.](image)

**Mechanism for the entire photocatalytic CO$_2$RR**

The mechanism for the entire photocatalytic CO$_2$RR is proposed in Fig. 14. PC 5, which had extended absorption into the visible light region, was excited by the light of 400 nm, generating the singlet excited state ($^1S_0$). This excited state was characterized by a
deeply negative oxidation potential \((E(5^{**}/5^*) = -2.65 \text{ V vs SCE})\) and underwent ET to \(\text{BI}^+ (E_{\text{red}} = -1.96 \text{ V vs SCE})\), resulting in the formation of \(5^{**}\) and \(\text{BI}^*\). Subsequently, \(5^{**} (E_{\text{red}} = 0.34 \text{ V vs SCE})\) accepted an electron from \(\text{HA}^- (E_{\text{ox}} = 0.47 \text{ V vs SCE})\) to regenerate \(5\) along with the formation of \(\text{HA}^*\). This process was slightly endothermic. The HAT process from \(\text{HA}^-\) or \(\text{HA}^*\) to \(\text{BI}^*\) was effective \((\Delta H = -31.1 \text{ or } -25.4 \text{ kcal/mol, respectively})\) in reducing \(\text{BI}^*\) to \(\text{BIH}\). The resultant \(\text{BIH}\) readily captured \(\text{CO}_2\) under ambient conditions \((1 \text{ atm } \text{CO}_2, \text{ at } 293 \text{ K})\) to produce \(\text{BI}^'(\text{HCOO}^-)\), according to a previous report.\(^{34}\) In addition to \(\text{CO}_2\) from the external source, \(\text{CO}_2\) generated along with the conversion of \(\text{A}\) to \(14\) served as a carbon source for formate. Products \(14\) and \(15\) resulting from \(\text{A}\) could function similarly as \(\text{HA}^-\) and \(\text{HA}^*\), respectively; thus, \(\text{H}_2\text{A}\) served as a four-electron reductant in this \(\text{CO}_2\)RR. A small amount of formate was obtained without \(\text{BI}^'(\text{I})^+\) \((\text{Table 1, entry 7})\), deducing that the direct ET from \(15^*\) to \(\text{CO}_2\) could also proceed slightly; however, it was a minor pathway because oxalate, a dimer of \(\text{CO}_2^*\), was not detected as a product.\(^{62}\) Formate often acts as an electron or hydrogen atom donor;\(^{53,64}\) Therefore, the reverse reaction, that is, conversion from formate to \(\text{CO}_2\), could occur during \(\text{CO}_2\)RR, which could deteriorate the reaction efficiency and quantum yield. Therefore, we irradiated a mixture of formate and \(\text{BI}^'(\text{I})\) in the presence of \(5\) under argon purging conditions to check the reversibility of \(\text{CO}_2\)RR \((\text{Fig. S24})\). No \(\text{BIH}\) was detected in this reaction, indicating that the reverse reaction was negligible.
Figure 14. The proposed reaction mechanism for the photocatalytic CO\textsubscript{2}RR. \textsuperscript{a}Standard enthalpy change for the reaction (B\textsuperscript{i*} + HA\textsuperscript{-} \rightarrow BIH + A\textsuperscript{*}) calculated using the density functional theory (DFT) method with (U)LC-BLYP/6-31++G(d)/PCM(DMSO) basis sets. \textsuperscript{b}Estimated value by the DFT calculation. Standard redox potentials are referred to saturated calomel electrode (SCE). ISC = intersystem crossing; HAT = hydrogen atom transfer; SET = single electron transfer.

In summary, the approach delineated in this study enables the transition metal-free photocatalytic CO\textsubscript{2}RR with a high TON and TOF. The critical reaction is the photocatalytic regeneration of organohydrides with a high reduction capability. In the present system, high selectivity for the product formate is appealing and characteristic of using organohydride catalysts; the obvious drawback is the requirement of a sacrificial reductant. Thus, the coupling of the developed CO\textsubscript{2}RR with the reaction system of the water oxidation without using transition metal catalysts is an attractive target for realizing artificial photosynthesis with water as a terminal reductant, an ongoing project in our laboratory.

Methods
General method for the photocatalytic CO$_2$RR (entry 1 in Table 1 as a representative example): 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, 5 mol%), PC 1 (3.8 mg, 0.015 mmol, 3 mol%), ascorbic acid (88.1 mg, 0.500 mmol, 1.0 eq.), and K$_2$CO$_3$ (76.0 mg, 0.550 mmol, 1.1 eq.) Then, CH$_3$CN (8 mL) and distilled water (2 mL) were introduced into the mixture. 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 was stirred under visible light irradiation ($\lambda_{\text{max}} = 400$ nm) for 4 h. After the reaction, 1,3,5-trimethoxybenzene (40.6 mg) was added as an internal standard and distilled water (3 mL) was added to the resulting reaction mixture. Then, 0.6 mL of the solution was transferred to an NMR tube and subjected to $^1$H NMR spectroscopic analysis using the solvent suppression technique. The yield of formate was 143% based on the ascorbic acid employed.

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

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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 of the 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. All the authors discussed the results and commented on the manuscript.

Competing interests
The authors declare no competing interests.

References
1 White, J. L. et al. Light-driven heterogeneous reduction of carbon dioxide: Photocatalysts and photoelectrodes. Chem. Rev. 115, 12888-12935 (2015).
2 MacDowell, N. et al. An overview of CO$_2$ capture technologies. Energy Environ. Sci. 3, 1645-1669 (2010).
3 Aresta, M., Dibenedetto, A. & Angelini, A. Catalysis for the valorization of
exhaust carbon: From CO₂ to chemicals, materials, and fuels. Technological use of CO₂. *Chem. Rev.* **114**, 1709-1742 (2014).

4 Ra, E. C. *et al.* Recycling carbon dioxide through catalytic hydrogenation: Recent key developments and perspectives. *ACS Catal.* **10**, 11318-11345 (2020).

5 Qiao, J., Liu, Y., Hong, F. & Zhang, J. A review of catalysts for the electroreduction of carbon dioxide to produce low-carbon fuels. *Chem. Soc. Rev.* **43**, 631-675 (2014).

6 Takeda, H., Cometto, C., Ishitan, O. & Robert, M. Electrons, photons, protons and earth-abundant metal complexes for molecular catalysis of CO₂ reduction. *ACS Catal.* **7**, 70-88 (2017).

7 Seyferth, D. The grignard reagents. *Organometallics* **28**, 1598-1605 (2009).

8 Seo, H., Liu, A. & Jamison, T. F. Direct β-selective hydrocarboxylation of styrenes with CO₂ enabled by continuous flow photoredox catalysis. *J. Am. Chem. Soc.* **139**, 13969-13972 (2017).

9 Seo, H., Katcher, M. H. & Jamison, T. F. Photoredox activation of carbon dioxide for amino acid synthesis in continuous flow. *Nat. Chem.* **9**, 453-456 (2017).

10 Matsuoka, S., Kohzuki, T., Pac, C. & Yanagida, S. Photochemical reduction of carbon dioxide to formate catalyzed by p-terphenyl in aprotic polar solvent. *Chem. Lett.* **19**, 2047-2048 (1990).

11 Matsuoka, S., Yamamoto, K., Pac, C. & Yanagida, S. Enhanced p-terphenyl-catalyzed photoreduction of CO₂ to co through the mediation of Co(III)-cyclam complex. *Chem. Lett.* **20**, 2099-2100 (1991).

12 Zhang, X., Cibian, M., Call, A., Yamauch, K. & Sakai, K. Photochemical CO₂ reduction driven by water-soluble copper(I) photosensitizer with the catalysis accelerated by multi-electron chargeable cobalt porphyrin. *ACS Catal.* **9**, 11263-11273 (2019).

13 Tamaki, Y., Morimoto, T., Koike, K. & Ishitan, O. Photocatalytic CO₂ reduction with high turnover frequency and selectivity of formic acid formation using Ru(II) multinuclear complexes. *Proc. Natl Acad. Sci. USA* **109**, 15673-15678 (2012).

14 Lee, S. E. *et al.* Visible-light photocatalytic conversion of carbon dioxide by Ni(II) complexes with N₄S₂ coordination: Highly efficient and selective production of formate. *J. Am. Chem. Soc.* **142**, 19142-19149 (2020).

15 Liu, X., Inagaki, S. & Gong, J. Heterogeneous molecular systems for photocatalytic CO₂ reduction with water oxidation. *Angew. Chem. Int. Ed.* **55**, 14924-14950 (2016).

16 Tsujiguchi, T. *et al.* Acceleration of electrochemical CO₂ reduction to formate at the Sn/reduced graphene oxide interface. *ACS Catal.* **11**, 3310-3318 (2021).

17 Hietala, J. *et al.* in *Ullmann's encyclopedia of industrial chemistry* 7th edn (eds Bellussi, G. et al.) (2016); https://doi.org/10.1002/14356007.a12_013.pub3.

18 Yang, J. Y., Kerr, T. A., Wang, X. S. & Barlow, J. M. Reducing CO₂ to HCO₃⁻ at mild potentials: Lessons from formate dehydrogenase. *J. Am. Chem. Soc.* **142**, 19438-19445 (2020).
Lorenzo, B. F. & O’Kiely, P. Alternatives to formic acid as a grass silage additive under two contrasting ensilability conditions. *Irish J. Agr. Food Res.* **47**, 135-149 (2008).

Bahuguna, A. & Sasson, Y. Formate-bicarbonate cycle as a vehicle for hydrogen and energy storage. *ChemSusChem* **14**, 1258-1283 (2021).

Enthaler, S. Carbon dioxide—the hydrogen-storage material of the future? *ChemSusChem* **1**, 801-804 (2008).

Joó, F. Breakthroughs in hydrogen storage—formic acid as a sustainable storage material for hydrogen. *ChemSusChem* **14**, 1258-1283 (2021).

Enthaler, S. Carbon dioxide—the hydrogen-storage material of the future? *ChemSusChem* **1**, 801-804 (2008).

Joó, F. Breakthroughs in hydrogen storage—formic acid as a sustainable storage material for hydrogen. *ChemSusChem* **1**, 801-804 (2008).

Boston, D. J., Xu, C., Armstrong, D. W. & MacDonnell, F. M. Photochemical reduction of carbon dioxide to methanol and formate in a homogeneous system with pyridinium catalysts. *J. Am. Chem. Soc.* **135**, 16252-16255 (2013).

Tamaki, Y., Koike, K. & Ishitani, O. Highly efficient, selective, and durable photocatalytic system for CO₂ reduction to formic acid. *Chem. Sci.* **6**, 7213-7221 (2015).

P, S. & Mandal, S. K. From CO₂ activation to catalytic reduction: A metal-free approach. *Chem. Sci.* **11**, 10571-10593 (2020).

Oh, Y. & Hu, X. Organic molecules as mediators and catalysts for photocatalytic and electrocatalytic CO₂ reduction. *Chem. Soc. Rev.* **42**, 2253-2261 (2013).

Lim, C.-H., Holder, A. M., Hynes, J. T. & Musgrave, C. B. Catalytic reduction of CO₂ by renewable organohydrides. *J. Phys. Chem. Lett.* **6**, 5078-5092 (2015).

Keith, J. A. & Carter, E. A. Theoretical insights into electrochemical CO₂ reduction mechanisms catalyzed by surface-bound nitrogen heterocycles. *J. Phys. Chem. Lett.* **4**, 4058-4063 (2013).

Alherz, A. et al. Renewable hydride donors for the catalytic reduction of CO₂: A thermodynamic and kinetic study. *J. Phys. Chem. B* **122**, 10179-10189 (2018).

Wen, F. et al. Amide-bridged conjugated organic polymers: Efficient metal-free catalysts for visible-light-driven CO₂ reduction with H₂O to CO. *Chem. Sci.* **12**, 11548-11553 (2021).

Wang, Y., Godin, R., Durrant, J. R. & Tang, J. Efficient hole trapping in carbon dot/oxygen-modified carbon nitride heterojunction photocatalysts for enhanced methanol production from CO₂ under neutral conditions. *Angew. Chem. Int. Ed.* **60**, 20811-20816 (2021).

Mazzanti, S. et al. All-organic Z-scheme photoreduction of CO₂ with water as the donor of electrons and protons. *Appl. Catal. B: Environ.* **285**, 119773 (2021).

Courtemanche, M.-A., Légaré, M.-A., Maron, L. & Fontaine, F.-G. A highly active phosphine–borane organocatalyst for the reduction of CO₂ to methanol using hydroboranes. *J. Am. Chem. Soc.* **135**, 9326-9329 (2013).

Lim, C.-H. et al. Benzimidazoles as metal-free and recyclable hydrides for CO₂ reduction to formate. *J. Am. Chem. Soc.* **141**, 272-280 (2019).

Rueping, M., Dufour, J. & Schöpke, F. R. Advances in catalytic metal-free reductions: From bio-inspired concepts to applications in the organocatalytic synthesis of pharmaceuticals and natural products. *Green Chem.* **13**, 1084-1105 (2011).
Lu, L.-Q., Li, Y., Junge, K. & Beller, M. Iron-catalyzed hydrogenation for the in situ regeneration of an NAD(P)H model: Biomimetic reduction of α-keto-/α-iminoesters. *Angew. Chem. Int. Ed.* **52**, 8382-8386 (2013).

Chen, Q.-A. *et al.* Dihydrophenanthridine: A new and easily regenerable NAD(P)H model for biomimetic asymmetric hydrogenation. *J. Am. Chem. Soc.* **134**, 2442-2448 (2012).

Chen, Q.-A. *et al.* Biomimetic asymmetric hydrogenation: In situ regenerable Hantzsch esters for asymmetric hydrogenation of benzoxazinones. *J. Am. Chem. Soc.* **133**, 16432-16435 (2011).

Paul, C. E., Arends, I. W. C. E. & Hollmann, F. Is simpler better? Synthetic nicotinamide cofactor analogues for redox chemistry. *ACS Catal.* **4**, 788-797 (2014).

Wu, H. *et al.* Methods for the regeneration of nicotinamide coenzymes. *Green Chem.* **15**, 1773-1789 (2013).

Ohtsu, H. & Tanaka, K. An organic hydride transfer reaction of a ruthenium NAD model complex leading to carbon dioxide reduction. *Angew. Chem. Int. Ed.* **51**, 9792-9795 (2012).

Emmanuel, M. A., Greenberg, N. R., Oblinsky, D. G. & Hyster, T. K. Accessing non-natural reactivity by irradiating nicotinamide-dependent enzymes with light. *Nature* **540**, 414-417 (2016).

Wang, J., Zhu, Z.-H., Chen, M.-W., Chen, Q.-A. & Zhou, Y.-G. Catalytic biomimetic asymmetric reduction of alkenes and imines enabled by chiral and regenerable NAD(P)H models. *Angew. Chem. Int. Ed.* **58**, 1813-1817 (2019).

Ohtsu, H. & Tanaka, K. Drastic difference in the photo-driven hydrogenation reactions of ruthenium complexes containing nad model ligands. *Chem. Commun.* **48**, 1796-1798 (2012).

Ma, B. *et al.* Efficient visible-light-driven CO₂ reduction by a cobalt molecular catalyst covalently linked to mesoporous carbon nitride. *J. Am. Chem. Soc.* **142**, 6188-6195 (2020).

Shon, J.-H. *et al.* Photoredox catalysis on unactivated substrates with strongly reducing iridium photosensitizers. *Chem. Sci.* **12**, 4069-4078 (2021).

Hong, D., Tsukakoshi, Y., Kotani, H., Ishizuka, T. & Kojima, T. Visible-light-driven photocatalytic CO₂ reduction by a Ni(II) complex bearing a bioinspired tetradoentate ligand for selective CO production. *J. Am. Chem. Soc.* **139**, 6538-6541 (2017).

Kamada, K. *et al.* Photocatalytic CO₂ reduction using a robust multifunctional iridium complex toward the selective formation of formic acid. *J. Am. Chem. Soc.* **142**, 10261-10266 (2020).

Hasegawa, E. *et al.* Photoinduced electron transfer reactions of α,β-epoxy ketones with 2-phenyl-N,N-dimethylbenzimidazoline (PDBMI): Significant water effect on the reaction pathway. *Tetrahedron Lett.* **37**, 7079-7082 (1996).

Ilic, S., Alherz, A., Musgrave, C. B. & Glusac, K. D. Importance of proton-coupled electron transfer in cathodic regeneration of organic hydrides. *Chem. Commun.* **55**, 5583-5586 (2019).
Hasegawa, E. *et al.* Photoinduced electron-transfer systems consisting of electron-donating pyrenes or anthracenes and benzimidazolines for reductive transformation of carbonyl compounds. *Tetrahedron* **62**, 6581-6588 (2006).

Matsubara, R. *et al.* UVA- and visible-light-mediated generation of carbon radicals from organochlorides using nonmetal photocatalyst. *J. Org. Chem.* **83**, 9381-9390 (2018).

Yabuta, T., Hayashi, M. & Matsubara, R. Photocatalytic reductive C–O bond cleavage of alkyl aryl ethers by using carbazole catalysts with cesium carbonate. *J. Org. Chem.* **86**, 2545-2555 (2021).

Kimoto, E., Tanaka, H., Ohmoto, T. & Choami, M. Analysis of the transformation products of dehydro-L-ascorbic acid by ion-pairing high-performance liquid chromatography. *Anal. Biochem.* **214**, 38-44 (1993).

McClure, L. J. & Ford, P. C. Ligand macrocycle effects on the photophysical properties of rhodium(III) complexes: A detailed investigation of cis- and trans-dicyano(1,4,8,11-tetraazacyclotetradecane)rhodium(III) and related species. *J. Phys. Chem.* **96**, 6640-6650 (1992).

Ota, E., Wang, H., Frye, N. L. & Knowles, R. R. A redox strategy for light-driven, out-of-equilibrium isomerizations and application to catalytic C–C bond cleavage reactions. *J. Am. Chem. Soc.* **141**, 1457-1462 (2019).

Roth, H. G., Romero, N. A. & Nicewicz, D. A. Experimental and calculated electrochemical potentials of common organic molecules for applications to single-electron redox chemistry. *Synlett* **27**, 714-723 (2016).

Rehm, D. & Weller, A. Kinetics of fluorescence quenching by electron and H-atom transfer. *Isr. J. Chem.* **8**, 259-264 (1970).

Connelly, N. G. & Geiger, W. E. Chemical redox agents for organometallic chemistry. *Chem. Rev.* **96**, 877-910 (1996).

Ju, T. *et al.* Dicarboxylation of alkenes, alkenes and (hetero)arenes with CO₂ via visible-light photoredox catalysis. *Nat. Catal.* **4**, 304-311 (2021).

Huang, Q., Wu, J.-W. & Xu, H.-J. Biomimetic hydrogenation: A reusable nadh co-enzyme model for hydrogenation of α,β-epoxy ketones and 1,2-diketones. *Tetrahedron Lett.* **54**, 3877-3881 (2013).

Lo, H. C., Buriez, O., Kerr, J. B. & Fish, R. H. Regioselective reduction of NAD⁺ models with [Cp*Rh(bpy)H]⁺: Structure–activity relationships and mechanistic aspects in the formation of the 1,4-NADH derivatives. *Angew. Chem. Int. Ed.* **38**, 1429-1432 (1999).