CHEMISTRY

Improving photosensitization for photochemical CO₂-to-CO conversion

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ABSTRACT

Inspired by nature, improving photosensitization represents a vital direction for the development of artificial photosynthesis. The sensitization ability of photosensitizers (PSs) reflects in their electron-transfer ability, which highly depends on their excited-state lifetime and redox potential. Herein, for the first time, we put forward a facile strategy to improve sensitizing ability via finely tuning the excited state of Ru(II)-PSs (Ru-1–Ru-4) for efficient CO₂ reduction. Remarkably, [Ru(Phen)₂(3-pyrenylPhen)]²⁺ (Ru-3) exhibits the best sensitizing ability among Ru-1–Ru-4, over 17 times higher than that of typical Ru(Phen)₃²⁺. It can efficiently sensitize a dinuclear cobalt catalyst for CO₂-to-CO conversion with a maximum turnover number of 66 480. Systematic investigations demonstrate that its long-lived excited state and suitable redox driving force greatly contributed to this superior sensitizing ability. This work provides a new insight into dramatically boosting photocatalytic CO₂ reduction via improving photosensitization.

Keywords: photosensitization, photocatalysis, CO₂ reduction, excited state, Ru(II) complexes

INTRODUCTION

Solar-driven reduction of CO₂ into energy-rich fuels, such as CO, HCOOH and CH₃OH, has been conceived of as a highly promising approach to solve the energy crisis and environmental pollution [1–6]. In the past decades, great efforts have long been devoted to improving the photocatalytic activity and selectivity for efficient CO₂ conversion. Throughout the molecular photocatalytic systems, numerous catalysts, such as complexes of Re, Ru, Fe, Co and Ni, have been developed [7–13] with detailed study of their catalytic mechanism [14–17]. In light of their being relatively comprehensively studied, more and more attention has begun to shift to accelerate electron transfer between catalyst and antenna molecules to promote CO₂ reduction. For example, Ishitani and several groups have explored efficient photocatalytic systems through combining photosensitizers (PSs) with catalysts via covalent bonds [8,9,18–20]. These systems exhibited enhanced catalytic ability compared to that of separated systems owing to their more efficient electron transfer via intramolecular process. However, this strategy was limited by the complex synthesis and lack of flexibility in investigating different PSs and catalysts. Very recently, Cheung et al. discovered that the hydrogen-bonding interaction between PSs and catalysts can improve the catalytic performance [21]. Nevertheless, these H-bonds can be easily disrupted by external factors, e.g. temperature and the solvents of N,N-Dimethylformamide (DMF) and H₂O. Accordingly, it is highly necessary yet remains greatly challenging to develop an alternative strategy for dramatically boosting photocatalytic CO₂ reduction (Fig. 1).

PSs, as the light-harvesting main body, have been widely used as a key mediator for efficient electron transfer between catalysts and electron donors in both natural and artificial photosynthetic systems [3,9,22–24]. Currently, improving the photosensitization ability of PSs for enhancing photocatalytic performance for CO₂ reduction is still in its infancy [24,25]. In this field, the frequently used PSs were confined to prototypical metal-to-ligand charge-transfer complexes [24,26–30], such as Ru(bpy)₃²⁺ [31–34] and Ru(Phen)₃²⁺ (Phen = 1,10-phenanthroline) [35–37], where their
Figure 1. Evolution process of the photocatalytic system for CO$_2$ reduction. (A) The study was mainly focused on the development of highly active catalysts (CATs) during this period. (B) Non-covalent/covalent supramolecular assembly has been developed over the past decades. (C) In this work, we open a new way to boost photocatalytic CO$_2$ reduction by improving the photosensitization ability of photosensitizers (PSs).

excited-state lifetime was usually <1 $\mu$s ($\tau = 600$ ns for Ru(bpy)$_3^{2+}$ and 360 ns for Ru(Phen)$_3^{2+}$ in CH$_3$CN) [36,38,39]. It will be a promising way to boost CO$_2$ reduction via adjusting the excited-state population and lifetime of these PSs to improve their sensitizing ability. In the past decades, decreasing the energy level of organic ligands by implanting a conjugated group has been used as a common strategy for achieving a long-lived excited state, which can realize a transition from 3MLCT state to 3IL state (intragrid triplet excited state) [40–45]. In this field, we have first introduced 3IL-type PSs with a long-lived excited state into photocatalytic systems for efficient H$_2$ production [43,45]. Unfortunately, the excited oxidation potentials of PSs usually become more positive in this process. This will greatly weaken the driving force for electron transfer from excited PSs to catalysts in thermodynamic catalytic processes [44,45]. As a result, how to substantially improve the sensitizing ability of molecular antenna whilst balancing its excited-state lifetime and redox driving force represents a key role in enhancing photoconversion efficiency, although it still remains a great challenge.

In this contribution, we put forward a new strategy to greatly boost photocatalytic CO$_2$ reduction by improving the photosensitization ability of PSs. A family of Ru(II)-based PSs Ru-2, Ru-3 and Ru-4 were prepared by the selective addition of pyrene/pyrenyl ethynylene to the 3- and 5-positions of Phen in Ru(Phen)$_3^{2+}$ (Ru-1) (Supplementary Figs 1–18). The triplet lifetimes of these complexes were gradually prolonged and their excited-state oxidation potentials became less negative with fine-tuning the excited state from Ru-1 with the 3MLCT state to Ru-4 with the 3IL state, which provided a platform to compare the effect of PSs with different sensitizing abilities on photocatalytic CO$_2$ reduction. Remarkably, the most efficient PS Ru-3 simultaneously possesses a long triplet lifetime (68.2 $\mu$s), $\sim$189 times longer than that of Ru(Phen)$_3^{2+}$, and a suitable excited-state oxidation potential (−0.92 V vs Saturated Calomel Electrode (SCE)). Impressively, the sensitizing ability of Ru-3 is $>17$ times higher than that of typical Ru-1 and it can efficiently sensitize the dinuclear cobalt catalyst (C-1) for photochemical CO$_2$-to-CO conversion with an extremely high TON of 66 480.

RESULTS

Molecular design and optical properties

In order to achieve a more rational molecular design, Gaussian calculations were carefully performed to predict the energy level of the triplet states and molecular geometries of the pyrene–phen ligands L-2–L-4 and Ru-1–Ru-4 (Fig. 2, Supplementary Figs 19 and 20, and Supplementary Table 1). As shown in Fig. 2A, the triplet energy levels of these ligands
Figure 2. Fine-tuning the excited state of PSs to improve photosensitization for photochemical CO$_2$-to-CO conversion. (A) Molecular structure of Ru-1–Ru-4 (up). Energy diagram of triplet states of Ru-1 and L-2–L-4, calculated at the B3LYP/6-31 G/genecp/LanL2DZ level with Gaussian 09 W (down). (B) UV-vis absorption and emission spectra of Ru-1–Ru-4 under the same condition, $\lambda_{ex} = 450$ nm, $c$ = 5.0 $\mu$M in deaerated CH$_3$CN. (C) Emission spectra of Ru(II) complexes at RT and 77 K: Ru-1, $\lambda_{ex} = 450$ nm; Ru-2, $\lambda_{ex} = 450$ nm; Ru-3, $\lambda_{ex} = 450$ nm; Ru-4, $\lambda_{ex} = 450$ nm.

were in the order of L-2 $>$ L-3 $>$ L-4, which was proportional to the dihedral angle between phen and pyrene (71° for L-2 $>$ 55° for L-3 $>$ 0° for L-4) (Supplementary Figs 19 and 20, and Supplementary Table 1). Meanwhile, the energy level of the $^3$IL states of these ligands was lower than that of the $^3$MLCT state of Ru(Phen)$_3^{2+}$, indicating that the triplet states of pyrene-functionalized Ru(II) complexes will be mainly localized on the pyrene-phen ligands ($^3$IL states). Hence, fine-tuning the excited states is promising to be achieved by adjusting the position of pyrenyl on Phen of Ru(II) complexes.

According to Density Functional Theory (DFT) calculations, Ru-2–Ru-4 were predicted as ideal models to determine the effect of the excited states on their sensitizing ability due to their well-proportioned energy-level gradient. All these complexes were synthesized according to the modified literature methods described in Supplementary Scheme 1 [42,46]. In this synthetic process, the precursors L-2, L-3 and L-4 were prepared by selective bromination of phen and subsequent coupling with pyrenylboronic acid and ethynyl pyrene, which were used to coordinate with Ru$^{3+}$ to generate corresponding Ru-2–Ru-4 via a one-pot reaction, respectively. These complexes and intermediates were fully characterized by $^1$H NMR, $^{13}$C NMR and MS spectroscopy (Supplementary Figs 1–18).

The UV-vis absorption spectra of Ru-1–Ru-4 are presented in Fig. 2B. Ru-1 exhibits an absorption band of between 400 and 500 nm, corresponding to $S_0 \rightarrow$ $^1$MLCT transition. For pyrene, a dual peak was observed at 319 and 334 nm, respectively, arising from $\pi \rightarrow \pi^*$ transition (Supplementary Fig. 21). The absorption spectrum of Ru-2 is almost a superposition of that of Ru-1 and pyrene, indicating a weak electron communication between Ru(Phen)$_3^{2+}$ and pyrenyl at the ground state [45]. In contrast to the absorption of Ru-1 and Ru-2, a new peak at around 380 and 400 nm emerged in the absorption spectra of Ru-3 and Ru-4, respectively, which resulted from the strong electronic interaction between the Ru center and pyrenyl. Interestingly, Ru-3 and Ru-4 exhibit a stronger
visible-light-absorption ability than that of Ru-1 and Ru-2. As a result, molecular regulation can gradually enhance the electron communication between Ru(Phen)\textsuperscript{2+} and pyrenyl from Ru-2 to Ru-4. Moreover, the absorption spectra of Ru-1–Ru-4 in the presence of C-1 or TEOA were almost similar to that of PSs alone (Supplementary Fig. 22). These results reveal that there is no intermolecular electronic interaction between the PSs under ground state and C-1 (or TEOA)\cite{45,47}.

The photoluminescence (PL) spectra of Ru-1–Ru-4 were carried out to investigate their excited-state properties (Fig. 2B and Supplementary Fig. 23). As shown in Supplementary Fig. 23, all the peaks in the PL spectra of Ru-1–Ru-4 that emerged under the Ar atmosphere were significantly quenched as exposed to air, indicating the phosphorescence emission process, which mainly derived from the triplet state \cite{48,49}. The PL spectrum of Ru-1 showed a typical 3MLCT emission at 595 nm and a similar emission peak at 595 nm was also observed in the PL spectrum of Ru-2, manifesting that its 3MLCT characteristic in Ru-2 partially remained after molecular regulation. In the PL spectra of Ru-3 and Ru-4, a redshift and much broader phosphorescence emission at around 632 and 668 nm was presented in comparison with that of Ru-1. Especially for Ru-4, its emission reveals a fine structure and an obvious shoulder peak at 735 nm, indicating the existence of an 3IL emissive state. The emissive state of Ru-3 should stand between those of Ru-2 and Ru-4. All the above results were further illuminated by 77 K emission and nanosecond transient absorption spectra.

The emission spectra of Ru-1–Ru-4 at 77 and 298 K were compared for clarifying their emissive state (Fig. 2C). A large hypochromic shift between 77 and 298 K spectra was observed for Ru-1 (\(\Delta E\), 665.7 cm\(^{-1}\)), indicating a typical 3MLCT emissive state \cite{48,50}. By contrast, Ru-4 showed a small hypochromic shift at 670 nm (148.7 cm\(^{-1}\)), suggesting an 3IL emissive state. For Ru-2, an emission band between 600 and 800 nm was observed at 77 K, which matched well with the phosphorescence of pyrene \cite{51}. Thus, this indicated a pyrenyl localized emissive state. Interestingly, the PL spectrum of Ru-3 exhibits multiple emission peaks at 77 K. Two weak peaks at around 600 and 660 nm close to the pyrenyl localized emissive state of Ru-2 were detected in the PL spectrum of Ru-3 and a strong dual emission around 750 nm that corresponded to the 3IL emissive state was also observed. This dual emission also emerged in the PL spectrum of Ru-4. As a result, it can be proposed that the emissive state of Ru-3 was between those of Ru-2 and Ru-4, but was dominated by the 3IL emissive state.

To further decipher their excited-state properties, nanosecond transient absorption spectra were performed on these four PSs, Ru-1–Ru-4 (Fig. 3A–D). The transient spectrum of Ru-1 showed a bleaching band at around 450 nm corresponding to the depletion of the ground state, which was a typical characteristic of the 3MLCT state. In the transient spectra of Ru-2–Ru-4, there was some superposition between the bleaching band and the excited-state absorption band \cite{48}. Ru-2 only afforded a transient absorption band between 380 and 700 nm, along with its 3MLCT emission at 595 nm; thus, its excited state could be ascribed to a mix of 3MLCT and the pyrenyl localized excited state. The transient spectrum of Ru-3 shows a positive absorption above 400 nm and a bleaching peak at 371 nm, manifesting a feature of the 3IL state. For Ru-4, a strong bleaching band at around 400 nm was observed, which matched well with its steady absorption to re-affirm its 3IL state.

Spin-density surfaces of these Ru(II) complexes (Ru-1–Ru-4) were calculated at B3LYP/6–31 G\textsuperscript{*}/genecp/LanL2DZ level with Gaussian 09, which can rationalize the population of their triplet states. As shown in Fig. 3, the spin density of Ru-1 was primarily localized on the Ru-Phen coordination center, indicative of a 3MLCT state. For Ru-2–Ru-4, their spin densities were mainly distributed on the Phen and pyrene owing to the lower triplet energy level of pyrenyl-Phen than that of the 3MLCT state. These results supported that the excited states of Ru-2–Ru-4 were largely populated on the ligands, which matched well with the experimental results. Therefore, we proposed that the redox center should be localized at pyrenyl functionalized ligands. All the photophysical data are summarized in Table 1 and the combination of these data with these calculated results can illustrate that fine-tuning of the excited state of these PSs from 3MLCT state to the 3IL state was realized. This provided a platform on which to compare the effect of PSs with different sensitizing abilities on photocatalytic CO\(_2\) reduction.

**Photocatalytic CO\(_2\) reduction**

Further, to reveal the influence of different sensitizing abilities on CO\(_2\) reduction, photocatalytic activities of these Ru(II) complexes (Ru-1–Ru-4) were investigated in 5 mL CO\(_2\)-saturated CH\(_3\)CN/H\(_2\)O (v/v = 9/1) solution containing C-1 as the catalyst and TEOA as the electron sacrificial agent under the illumination of a 450 nm LED (Fig. 4 and Supplementary Tables 2–4). As shown in Fig. 4A, the TON of C-1 with Ru-3 was up to 1120, 17 times higher
than that with Ru-1. In the Ru-3-containing photocatalytic system, the TON towards C-1 can reach as high as 66 480 under the optimized condition, which substantially exceeds our previously reported results with Ru-1 as the PS (TON = 16 896, Supplementary Table 3) [35]. In addition, no or a trace amount of CO was detected in the absence of PS, TEOA, C-1, light or CO₂, manifesting that all the above factors are indispensable for efficient photocatalytic CO₂ reduction (Supplementary Table 4).

The photocatalytic mechanism was studied by steady and transient quenching experiments (Fig. 4). Phosphorescence quenching experiments of Ru-1–Ru-4 reveal that their excited states can be efficiently quenched by C-1; nevertheless, no change on their photoluminescence spectra was observed in the presence of TEOA (Supplementary Figs 24 and 25). We therefore proposed that the photocatalytic process was dominated by the oxidation mechanism for Ru-1–Ru-4-containing systems [35,36], which was further confirmed by nanosecond transient absorption. The triplet lifetimes of Ru-1–Ru-4 remained before and after adding to TEOA, but became shorter in the presence of C-1, confirming that the initial step for electron transfer should be from excited PSs to C-1 (Fig. 4B and Supplementary Fig. 26). As a result, all these photocatalytic systems could be determined as oxidation mechanisms (Fig. 4C).

With the above results in mind, both triplet excited-state lifetimes and the excited-state oxidation potentials of PSs are key factors affecting electron-transfer efficiency in photocatalytic systems. From the view of kinetics, the long-lived triplet state of PSs greatly contributed to intermolecular electron transfer/energy transfer. Thus, Stern–Volmer-quenching constants of PSs by C-1 were in the order of 4.4 × 10³ M⁻¹ for Ru-4 > 3.2 ×

Table 1. Summary of photophysical data of Ru-1–Ru-4.

|       | λₓₒₓ/ nm | λₓₑₑ/ nm | ε/(M⁻¹ cm⁻¹) | τ/μs | K₁/(M⁻¹) |
|-------|----------|-----------|--------------|------|----------|
| Ru-1  | 447      | 595       | 20 914       | 0.4  | 375      |
| Ru-2  | 447      | 595       | 19 824       | 32.0 | 957      |
| Ru-3  | 391      | 632       | 33 318       | 68.2 | 3239     |
| Ru-4  | 415      | 668       | 49 808       | 118.7| 4419     |

¹5.0 μM Ru-1–Ru-4 in CH₃CN. ²Triplet excited-state lifetime measured by transient absorption. ³Stern–Volmer-quenching constants with C-1 as the quenchers.
Figure 4. Photocatalytic CO₂ reduction and photocatalytic mechanism. (A) Photocatalytic CO₂ reduction with Ru-1–Ru-4 under irradiation of a LED light (450 nm, 100 mW cm⁻², irradiation area, 0.8 cm²) in the presence of PS (20 μM), C-1 (1.0 μM) and TEOA (0.3 M) in 5 mL CO₂-saturated CH₃CN/H₂O (v/v = 9/1) solution. Each photocatalytic reaction was repeated at least three times. (B) Nanosecond transient absorption spectra of kinetic decay trace of Ru-3 (black), Ru-3 with 0.4 mM TEOA (green), and Ru-3 with 0.5 μM C-1 (blue). (C) Photocatalytic process with Ru-3 as PS. ET, electron transfer; ISC, intersystem crossing. (D) Kinetic traces of Ru-1–Ru-4 followed at 450 nm. (E) Stern–Volmer plot of Ru-1–Ru-4. λₑₓ = 450 nm, cₚₛ = 5.0 μM. (F) Energy diagram depicting the excited-state oxidation potential (†Ox) of Ru-1–Ru-4 and the onset reduction potential of C-1 in the catalytic system.

10³ M⁻¹ for Ru-3 > 9.6 × 10² M⁻¹ for Ru-2 > 3.8 × 10² M⁻¹ for Ru-1, which was proportional to their excited-state lifetimes (Fig. 4D and E). From the thermodynamics viewpoint, the excited-state oxidation potentials of PSs determine the driven force of electron transfer from excited PSs to C-1 (Supplementary Table 5). As shown in Fig. 4F, the absolute value of the excited-state oxidation potential was in the order of Ru-4 < C-1 < Ru-3 < Ru-2 < Ru-1, indicating that excited Ru-1–Ru-3 can provide a sufficient driven force for delivering the electron to C-1 but the driven force from excited Ru-4 to C-1 was humble. Notably, the triple bond in Ru-4 makes greater delocalization than Ru-2 and Ru-3, indicating a lower excited-state energy level of the ligand in Ru-4. This delocalization can contribute to obtaining a long-lived excited state. However, the oxidizing ability of excited Ru-4 becomes weaker, which is disadvantageous for electron transfer from excited Ru-4 to C-1 and will further decrease the photocatalytic activity. As a result, Ru-3, as a trade-off PS, possesses a long-lived triplet state and a suitable excited-state oxidation potential simultaneously, highlighting its great potential for efficient CO₂ reduction.

CONCLUSION

In summary, we have developed a novel strategy to boost photocatalytic CO₂ reduction via improving photosensitization. In this work, four Ru-based complexes (Ru-1–Ru-4) were prepared and they presented a gradual variable excited state from Ru-1 with the 3MLCT state to Ru-4 with the 3IL state, which provides a platform on which to compare the effect of PSs with different sensitizing abilities on photocatalytic CO₂ reduction. Remarkably, the catalytic activity of Ru-3 was >17 times higher than that of Ru-1 and the TON towards C-1 can reach 66 480. The outstanding photocatalytic activity of Ru-3 was chiefly ascribed to its long-lived excited...
state and suitable excited-state oxidation potential. This work provides a new insight into substantially improving visible-light-driven CO\textsubscript{2} reduction performance through fine-tuning the excited states of PSs on a molecular level.

**METHODS**

**Materials and instrumentation**

All the reactions were performed in argon unless otherwise mentioned. All the solvents were of analytical grade and distilled before use. The dichloro(p-cymene)ruthenium(II) dimer and 1,10-Phenanthroline were purchased from Sigma-Aldrich. The 1-pyrenylboronic acid, NH\textsubscript{4}PF\textsubscript{6} and K\textsubscript{2}CO\textsubscript{3} were purchased from HEOWNS. The Tetrakis(triphenylphosphine)palladium(0) and CuI were purchased from Adamas-beta. Chromatographic-grade acetonitrile was purchased from Adamas Reagent. The synthetic scheme of Ru\textsubscript{1}–Ru\textsubscript{4} is presented in Supplementary Scheme 1. The synthetic intermediates and target complexes were evidenced by \textsuperscript{1}H NMR, \textsuperscript{13}C NMR and mass spectroscopy. Elemental analysis was performed as C/H/N analyses on the Vario EL Cube (Elementar, Germany).

Electrochemical measurements were carried out on a CHI 760E electrochemical workstation at room temperature. The amount of CO product was analysed by gas chromatography (Shimadzu GC-2014+ AT230C, TDX-01 column, TCD, argon carrier). UV-vis absorption spectra were recorded on a LAMBDA750 UV-vis spectrophotometer. Fluorescence spectra were taken on a Hitachi F4600 spectrofluorometer. Transient absorption spectra were measured on the LP980 laser flash photolysis instrument (Edinburgh, UK).

**Photocatalytic CO\textsubscript{2} reduction**

Photocatalytic CO\textsubscript{2} reduction was conducted under 1 atm of CO\textsubscript{2} at 25°C in 5 mL reactor containing PS (20.0 \(\mu\)M), catalyst (1.0 \(\mu\)M), TEOA (0.3 M), 0.5 mL H\textsubscript{2}O and 4.5 mL CH\textsubscript{3}CN. The photocatalytic system was bubbled with CO\textsubscript{2} for 30 min. The mixture was continuously stirred and irradiated under a LED (\(\lambda = 450\) nm, 100 mW cm\textsuperscript{-2}).

**DFT calculation**

The geometries and the spin-density surfaces of the complexes (Ru\textsubscript{1}–Ru\textsubscript{4}) were performed at the B3LYP/6–31 G/LanL2DZ level. There are no imaginary frequencies for all optimized structures of L-1–L-4 and Ru\textsubscript{1}–Ru\textsubscript{4}. The triplet-state energy levels were carried out with the time-dependent DFT (TDDFT) method. All these calculations were performed with Gaussian 09 W.

**DATA AND SOFTWARE AVAILABILITY**

All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

**SUPPLEMENTARY DATA**

Supplementary data are available at NSR online.

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**AUTHOR CONTRIBUTIONS**

S.G. and Z.M.Z. conceived of and designed this project, P.W. and R.D. performed the experiments, S.G. and J.Z. carried out the DFT calculation, P.W., S.G. and Z.M.Z. analysed the data, and P.W., S.G., J.Z., Z.M.Z. and T.B.L. wrote and revised the article.

Conflict of interest statement. None declared.

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