Rapid electron transfer via dynamic coordinative interaction boosts quantum efficiency for photocatalytic CO₂ reduction

Jia-Wei Wang

Sun Yat-sen University

Long Jiang

Sun Yat-sen University <https://orcid.org/0000-0002-3230-4522>

Hai-Hua Huang

Sun Yat-Sen University <https://orcid.org/0000-0002-1873-6871>

Zhiji Han

Sun Yat-sen University <https://orcid.org/0000-0001-9349-1571>

Gangfeng Ouyang (✉ cesoygf@mail.sysu.edu.cn)

Sun Yat-sen University

Article

Keywords: photocatalytic CO₂ reduction, rapid electron transfer

Posted Date: February 10th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-192163/v1>

License: This work is licensed under a Creative Commons Attribution 4.0 International License. [Read Full License](#)

Version of Record: A version of this preprint was published at Nature Communications on July 13th, 2021. See the published version at <https://doi.org/10.1038/s41467-021-24647-y>.

Abstract

The fulfilment of a high quantum efficiency for photocatalytic CO₂ reduction presents a key challenge, which can be overcome by developing new strategies for dynamic attachment between photosensitizer and catalyst. In this context, we have for the first time exploited the use of coordinate bond to connect a pyridine-appended iridium photosensitizer (IrQPY) and molecular catalysts for CO₂ reduction, which has been systematically demonstrated by ¹H NMR titration, theoretical calculations, electrochemistry, and spectroscopic measurements. The mechanistic investigations reveal that the coordinative interaction between IrQPY and an unmodified cobalt phthalocyanine significantly accelerates the electron transfer and thus realizes a remarkable quantum efficiency of 10.2%±0.5% at 450 nm for photocatalytic CO₂-to-CO conversion with nearly complete selectivity, over 4 times higher than a comparative system with no additional interaction (2.4%±0.2%). Moreover, the decoration of electron-donating amino groups on cobalt phthalocyanine has optimized the quantum efficiency up to 27.9%±0.8% at 425 nm, which is more attributable to the enhanced coordinative interaction rather than the intrinsic activity. The control experiments have indicated that the dynamic feature of coordinative interaction is important to prevent the coordination occupancy of labile sites and back electron transfer, also enabling the wide applicability on diverse non-noble-metal catalysts.

Introduction

Harvesting sunlight for reductive transformation of CO₂ into carbonaceous fuels has been regarded as a sustainable pathway to manufacture carbon-neutral energy, as well as the promising mitigation of greenhouse gas. With the advantages of well-defined and highly modifiable molecular structures, many chemists have devoted to the design of molecular systems of light-stimulated CO₂ reduction with transition metal complexes, which can function as either photosensitizers (PSs) to transporting electrons upon light excitation, or catalysts to accept electrons for catalytic CO₂ reduction.¹⁻⁶ Extensive efforts have been dedicated to achieving high catalytic rates,⁷⁻¹¹ i.e. turn-over frequency (TOF) or turn-over number (TON), while quantum efficiency (QE) also deserves significant attention as it has been considered as the prominent, intrinsic parameter to evaluate the photon-to-product efficiency for a photocatalytic system.¹² The accomplishment of a high QE is challenging as it is limited by multiple factors in a photocatalytic system, including the catalytic performance of catalyst, the photophysical properties of PS, and also importantly, the electron transfer between PS and catalyst.¹³ As a representative example to attain considerable QEs, Kojima et al designed a Ni catalyst featuring a bio-mimic S₂N₂-type tetradentate ligand to couple with [Ru(bpy)₃]²⁺ (bpy = 2,2'-bipyridine) PS, achieving TONs > 700 and a good QE of 1.42% at 450 nm.¹⁴ Afterwards, they further decorated the above Ni catalyst with pyridine arms, obtaining Ni(bpepy)₂²⁺ (bpepy₂ = bis(2-pyridyl-3-pyridylmethyl)-1,2-ethanedithiol), which can stabilize a Mg²⁺ ion as a Lewis acid to enhance the fixation of CO₂ for further catalysis, reaching a much higher QE of 11.1% at 450 nm for CO₂ reduction to CO,¹⁵ a record high value to our knowledge among the molecular systems for photocatalytic CO₂-to-CO conversion employing noble-metal PSs and earth-abundant catalysts (Supplementary Table 1). Besides the labors in catalyst design, the optimization of PSs also attracts much attention, which can be exemplified by a ring-shape Re trinuclear complex prepared from Ishitani and co-workers.¹⁶ This Re compound can be utilized as a potent PS to promote the catalytic activity of a Re catalyst, fac-[Re(bpy)(CO)₃(CH₃CN)]⁺, ultimately accomplishing an extremely high QE of 82% of CO formation from CO₂ photoreduction at 436 nm. Consequently, the above documents demonstrate that major progress has been made in improving the QEs of molecular systems for CO₂ reduction by rational design of catalysts or PSs, based on which, presumably, the QE can be further optimized by strengthening the electron transfer between PS and catalyst.

In this context, the effective strategies to accelerate the electron transfer between PS and catalyst are highly desirable. Recently, the construction of supramolecular photocatalytic systems by connecting PS and catalyst via covalent bonds has been exploited (Figure 1).¹⁷⁻²¹ Pioneering instances include the covalent attachments between Re-/Ru-bpy catalysts and diverse PS moieties by Ishitani et al, generally showing rapid intramolecular charge transfer and accomplishing high QEs.^{17-19,22} Additionally, a very recent example reports the synthesis a Zn-porphyrin PS dangling with a Re-phen catalytic module, which displays TONs > 1300 and a QE of 8% at 420 nm for highly selective CO₂-to-CO photo-conversion.²¹ However, substantial synthetic efforts are required to prepare such dyad molecules. Moreover, the possibly vulnerable covalent linkers (like acetylene or amide bonds)^{23,24} and back electron transfer via covalent connection²⁵ may lead to irreversible losses of stability and activity.

Compared with traditional covalent strategies, a dynamic binding between PS and catalyst may offer an elastic endurance and ultimately a stable performance, as the reversible character of dynamic interaction may enable a self-correction behavior.²⁶⁻²⁹ Nevertheless, the documented dynamic assembly for photocatalytic CO₂ reduction is rare, except a H-bond-interacted system from Kubiak et al³⁰ in which a remarkable QE of 23.3%±0.8% and a TON of 100±4 were achieved (Figure 1). In addition, the detailed characterizations on the dynamic interaction and mechanistic studies on the facilitated intermolecular electron transfer are elusive, which is worthy of in-depth investigations to provide insights for further optimization on such systems. Consequently, the exploration of novel strategies to bridge dynamic interaction between PS and catalyst is in urgent need.

As a type of covalent bonds, coordinate bond can be an ideal intermolecular force to attach PS and catalyst, of which the labile feature will endow the dynamic stability while facilitating the intermolecular electron transfer. Herein, we have designed a combination between an pyridine-pendented iridium PS, [Ir(ppy)₂(qpy)](BF₄) (IrQPY; ppy = 2-phenylpyridine; qpy = 4,4':2',2'':4'',4'''-quaterpyridine), and a pristine cobalt phthalocyanine (CoPc) catalyst (Figure 1). The pyridine pendants of IrQPY can serve as the binding sites to axially coordinate to CoPc, a molecular catalyst seldom utilized in photocatalytic CO₂ reduction but extensively employed in electrocatalysis.³¹⁻³⁵ As expected, the dynamic coordinative interaction between IrQPY and CoPc has achieved an impressive performance in photocatalytic CO₂ reduction, affording a QE of 10.2%±0.5% at 450 nm for CO production, with a TON of 391±7 and a high selectivity of 98%, far superior to the IrBPY/CoPc (IrBPY = [Ir(ppy)₂(bpy)](BF₄)) system which has no coordinative interaction. Moreover, the coordinative interaction strategy is highly applicable to other molecular catalysts with varying configurations. The selection of an anion-appended CoPc catalyst has further achieved an exceptionally high QE of 27.9%±0.8% at 425 nm, where the stronger coordinative binding essentially accounts for the enhanced activity. The above advantages strongly recommend the coordinative interaction as a versatile strategy to improve photocatalytic performance. To our knowledge, such coordinative interaction has been utilized in molecular systems for hydrogen evolution^{27,29,36-38} or immobilizing molecular catalysts on heterogeneous materials,³⁹⁻⁴² while it is the first time to employ this concept in a fully molecular photocatalytic system for CO₂ reduction.

Results And Discussion

¹H NMR titration for coordinative interaction

The synthetic methods of IrQPY and IrBPY are shown in the Supplementary Information, and CoPc is commercially available. We investigated the interaction between IrQPY and CoPc by ¹H NMR titration in DMF-d₇. The ¹H NMR spectrum of IrQPY (Fig. 2) reveals a local C₂ symmetry around the iridium center, consistent with the structure obtained from single-crystal X-ray diffraction (Supplementary Fig. 1). The spectrum of CoPc shows no apparent signal < 20 ppm due to the paramagnetic Co^{II}. Notably, the titration of CoPc into IrQPY induced slightly shifted, broadened peaks, and faded peak splitting, where the relatively differentiable shifts appeared at the pendant pyridyl protons of IrQPY. A binding constant of 276 M⁻¹ based on 1:2 non-cooperative binding mode was calculated (see Supplementary Fig. 2 and Experimental details).⁴³ These observations suggest that IrQPY interacts with the paramagnetic CoPc via a dynamic interaction with the two pendent pyridyl moieties.^{27,30} In contrast, the ¹H NMR spectra of IrBPY do not change when titrated with CoPc (Supplementary Fig. 3), which demonstrates negligible interaction between IrBPY and CoPc and indicates that the pyridine pendants in IrQPY are indispensable to interact with CoPc. Moreover, to preclude the interference of paramagnetic additive that may also cause the shifts without coordination, we further utilized the diamagnetic zinc phthalocyanine, ZnPc, to replace CoPc in titration. Similar shifted signals are observed in the IrQPY/ZnPc titration, with no peak broadening and splitting (Supplementary Fig. 4), which gives a binding constant of 252 M⁻¹ (Supplementary Fig. 5), a value close to that of IrQPY/CoPc. This parallel outcome can exclude the magnetic interference in estimating the binding constant of the IrQPY/CoPc system. Therefore, the above ¹H NMR titration results demonstrate the coordinative interaction between metal phthalocyanines and IrQPY via pendant pyridine groups.

DFT Calculation

We further employed DFT calculation to mimic the coordinative interaction between IrQPY and CoPc at the M06⁴⁴/BSI level (see Supplementary Information for details). The DFT-simulated structures of IrQPY, CoPc, and their two combinations, IrQPY-CoPc and IrQPY-(CoPc)₂, were taken into consideration. The calculation results are shown in Appendix in the Supplementary

Information. As indicated by Fig. 2b, the Co-N_{py} bond lengths are approximately 2.26–2.29 Å in IrQPY-CoPc and IrQPY-(CoPc)₂, respectively, which are longer than those of equatorial Co-N_{Pc} bonds (ca. 1.92–1.93 Å), showing the presence of weak axial coordination in both adducts. We also analyzed the Mayer bond orders⁴⁵ of Co-N bonds and found that the bond order of Co-N_{py} (0.24 ~ 0.25) are only ca. half of that of Co-N_{Pc} (0.48), which further indicate the weak coordinate bonds. Presumably, the low-spin *d*⁷ Co^{II} center in CoPc molecules owns a half-filled *d*_{z²} orbital which will weaken the axial coordination from the z-direction, while the *d*_{x²-y²} is vacant for strong equatorial coordination. In addition, the relatively labile axial coordinate bond can be partially attributed to the cationic nature of IrQPY, which makes the pyridine less electron-donating.

Besides geometry, IrQPY-CoPc and IrQPY-(CoPc)₂ adducts display calculated energy changes of + 1.9 and – 0.8 kcal mol^{–1} relative to the free energies of isolated IrQPY and CoPc. Considering the computational error here is ± 2.0 kcal mol^{–1}, the energy changes indicate the coordinative interaction between IrQPY and CoPc should be relatively reversible. As the free energy of IrQPY-(CoPc)₂ even slightly decreases with the coordination of one more CoPc, the coordination of two CoPc molecules is not markedly interfered by each other. Consequently, the energy results of coordinative interaction are in good accordance with the outcome of ¹H NMR titration which manifests the dynamic, reversible interaction between IrQPY and CoPc, as well as the 1:2 non-cooperative binding mode.

Cyclic Voltammetry

Cyclic voltammetry was applied to investigate the redox properties of Ir PSs and CoPc and their interaction. Potentials are footnoted versus Fc⁺/Fc (Fc = ferrocene) unless otherwise noted. Initially, the cyclic voltammogram (CV) of CoPc displays a quasi-reversible couple at *E*_{1/2} = -1.28 V under N₂, assignable to a 1e Co^{II/I} reduction (Fig. 3a). Upon the introduction of CO₂, a large catalytic wave appeared at ca. -1.03 V with enhanced current initiated at an onset potential of ca. -0.87 V, which suggests catalytic CO₂ reduction (Fig. 3b). The addition of phenol (PhOH) led to a more positive onset potential (ca. -0.68 V; Supplementary Fig. 6) and a higher catalytic current, indicating that the presence of PhOH as proton source can facilitate CO₂-reduction catalysis.⁴⁶

On the other hand, both CVs of IrQPY and IrBPY in CH₃CN exhibit three successive cathodic waves (Fig. 3a and Supplementary Fig. 7–9). The first cathodic wave is attributed to the reduction of bpy-based ligands, and latter two waves may originate from the reduction of ppy ligands.^{19,47} Interestingly, the addition of CoPc into the solution of IrQPY induced positive shifts of the first two cathodic waves of IrQPY (Fig. 3a and Table 1), suggesting the interaction between IrQPY and CoPc. The cathodic direction of the shift indicates the electron-withdrawing nature of CoPc when attached to IrQPY. In contrast, the CV of IrBPY/CoPc shows no significant shift of the cathodic waves in contrast to that of IrBPY (Supplementary Fig. 9), indicative of negligible interaction.

Next, the CV of IrQPY/CoPc mixture under CO₂ reveals the characteristic catalytic wave of CoPc at ca. -1.02 V (Fig. 3b). At more negative potentials, a two-wave feature appears in this CV, which presumably indicates the “total catalysis” situation, showing total consumption of substrate (CO₂) at the electrode surface followed by the reversible wave of catalyst reduction.⁴⁸ However, the axial coordination of ppy ligand from IrQPY to CoPc caused a relatively low catalytic current in contrast to the CV of bare CoPc, which suggests that the coordination may not favor the electrocatalytic CO₂ reduction, possibly due to the inhibited binding of CO₂. Consequently, the axial coordination of IrQPY at CoPc did not improve the intrinsic catalytic activity of CoPc, in contrast to the reported positive effect by pyridine coordination at CoPc-based heterogeneous electrode.^{42,49} At this stage, we have successfully evidenced the coordinative interaction between IrQPY and CoPc by corroborated experimental and theoretical results.

Table 1
Redox properties and photophysical properties of Ir PSs.

Complex	$E_{\text{red},1}$ (V)	$E_{\text{red},2}$ (V)	$E_{\text{red},3}$ (V)	E_{ox} (V)	ϵ_{450} (L mol ⁻¹ cm ⁻¹)	Φ_{450} (%)	τ_0 (ns)	Isosbestic point (nm)	$E_0 -$ ₀ (V)	$E_{\text{q,red}}$ (V)	$E_{\text{q,ox}}$ (V)	$k_{\text{q,red}}$ ($\times 10^9$ M ⁻¹ s ⁻¹)	$k_{\text{q,ox}}$ ($\times 10^9$ M ⁻¹ s ⁻¹)
IrQPY	-1.37 -1.33 ^[a]	-1.65 -1.59 ^[a]	-2.11 -2.09 ^[a]	0.96	1500	6.86	152	510	2.43	1.06	-1.47	13.3	33.3
IrBPY	-1.34 -1.36 ^[a]	-1.78 -1.79 ^[a]	-2.46 -2.46 ^[a]	0.93	700	11.89	193	470	2.64	1.30	-1.72	18.1	20.3
[a] 1 equivalent of CoPc was added to the solution.													

Photocatalytic CO Reduction With COPC

To verify the merits of coordinative interaction in photocatalysis, visible-light-driven CO₂ reduction was carried out with IrQPY or IrBPY as the PS (0.1 mM), CoPc as the catalyst (0.1 mM), PhOH (6.0 v%) as the optimized proton source, triethylamine (TEA; 2.5 v%), and 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole (BIH; 80 mM) in dry CH₃CN, irradiated by 450 nm monochromic light. As shown in Fig. 4a, the IrQPY/CoPc system afforded a TON of 391 ± 7 and a 98% selectivity for CO production within 4 h, while the IrBPY/CoPc pair yielded a lower TON of 152 ± 6 and a decreased CO selectivity of 91%. More importantly, the maximum QE (see Fig. 4b and Methods) was calculated to 10.2%±0.5% in the IrQPY/CoPc system within the first hour of photocatalysis, which is more than 4 times higher than that of IrBPY/CoPc (2.4%±0.2%). The above comparison demonstrates the remarkable performance of coordination-interacted IrQPY/CoPc system for photocatalytic CO₂ reduction.

Although the IrQPY/CoPc system produced no CO after 4 h of reaction, addition of fresh BIH instead of PS or catalyst could reinitiate the CO production with retention of most activity (Fig. 4c), manifesting that the ceased CO formation is mainly attributed to the consumption of BIH rather than PS or catalyst. Additionally, the photocatalysis under ¹³CO₂ atmosphere combined with mass spectroscopy showed the bare production of ¹³CO (*m/z* = 29; Supplementary Fig. 10), indicating that the evolved CO originates from the reduction of CO₂ rather than the decomposition of organic compounds in the IrQPY/CoPc system. The above results strongly confirm the robustness of IrQPY/CoPc system.

Each component is crucial to achieve the high catalytic activity. Foremost, the absence of Ir PS, CoPc, CO₂ and light could not trigger the formation of CO (Supplementary Table 2, entry 1–4), while the use of low-concentration CO₂, a simulated flue gas (10% CO₂/argon), is sufficient to initiate a substantial amount of CO, showing its potency to work under a low concentration of CO₂ (Supplementary Table 2, entry 5). Additionally, the addition of proton sources like PhOH, H₂O or 2,2,2-trifluoroethanol (TFE), greatly improves the CO yields compared to the one under anhydrous system (Fig. 4d, Supplementary Table 3 and Supplementary Fig. 11–12), which is consistent with the CV of CoPc with PhOH (Supplementary Fig. 6). These enhancements by protons are attributable to the facilitated proton-coupled electron transfer during catalytic CO₂ reduction.^{46,50} It should be noted that the CO selectivity of IrQPY/CoPc system can be impressively maintained at over 90% even upon the addition of water up to 25 v% volume (Fig. 4d and Supplementary Table 3), presumably endowed by the high selectivity of CoPc. However, further increasing the water ratio will lead to the severe precipitation of BIH and CoPc, leading to vanished activity. Thus, the use of water-soluble electron donor and catalyst to develop this coordinatively interacted CO₂ reduction system is promising to attain high selectivity in purely aqueous solution, which is a warranted work in the future.

$$\frac{I_0}{I} = 1 + K[Q] = 1 + k_q\tau_0[Q] \quad (1)$$

Further, two potential sacrificial electron donors, TEA and BIH, are also important to drive the photocatalysis. As exhibited in Supplementary Table 3, In the absence of TEA, the TON for CO production decreased significantly to 167 ± 2 within 4 h. BIH is more indispensable as no CO formation took place without BIH. By measuring the fluorescent intensity and lifetimes with a fluorescent spectrometer (Supplementary Figure 13), the Stern-Volmer (S-V) plots between IrQPY and BIH or TEA can be obtained via Equation 1,⁸ demonstrating a much higher quenching constant (k_q) for BIH than that of TEA (1.33×10^{10} vs. $3.50 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$; Supplementary Figure 14 and 15), possibly due to the greater ease of BIH over TEA toward oxidation.⁶ Rather than a sacrificial electron donor, TEA here should act as a base to deprotonate the oxidized BIH and thus accelerate an irreversible electron transfer.⁵¹

Optimization for higher QEs

We further tried to optimize the conditions to obtain higher QEs. We noticed that the significant consumption of BIH took place after 1 h of reaction, thus more BIH and shorter time were applied (Supplementary Table 4). The LED lights with different wavelengths, including 450, 425 and 405 nm, were also utilized for trials, showing that 425 nm is the optimal light source in our case, which gave a $19.2\% \pm 0.4\%$ QE for IrQPY/CoPc system. The higher yield at 425 nm can be attributed to the relatively high emission quantum yield (ϕ) of IrQPY at this wavelength (Supplementary Table 5). More intriguingly, when a derivative of CoPc, cobalt(II) tetraamino-phthalocyanine (CoTAPc), was used instead under the above-optimized conditions, a high QE of $27.9\% \pm 0.8\%$ could be attained under a solar-simulated light intensity of 100 mW cm^{-2} at 425 nm (Fig. 4e). Remarkably, this QE value is record high among the molecular systems for photocatalytic CO_2 -to-CO conversion employing noble-metal PSs and earth-abundant catalysts, surpassing $\text{Ru}(\text{bpy})_3^{2+}/\text{Fe}(\text{qpy})^{2+}$ (qpy', 2,2':6',2'':6'',2'''-quaterpyridine; QE = 8.8% at 450 nm),⁵² $\text{Ru}(\text{bpy})_3^{2+}/\text{Ni}(\text{beptpy})_2^{2+}$ (QE = 11.1% at 450 nm),¹⁵ $\text{Ru}(\text{phen})_3^{2+}/[\text{CoZn}(\text{OH})\text{L1}]^{3+}$ ($\text{L1} = \text{N}[(\text{CH}_2)_2\text{NHCH}_2(m\text{-C}_6\text{H}_4)\text{CH}_2\text{NH}(\text{CH}_2)_2]_3\text{N}$; QE = 4.9% at 450 nm)¹⁰ and other pioneering systems listed in Supplementary Table 1.

To elucidate the origins of improvement, we first operated cyclic voltammetry to compare the redox properties of CoPc and CoTAPc. The comparison reveals that for CoTAPc, both its $\text{Co}^{\text{II/I}}$ reduction potential under N_2 (Fig. 4f) and its onset catalytic potential under CO_2 (Supplementary Fig. 16) are more negative than those of CoPc, attributable to the electron-donating amino groups. The more negative potentials indicate the higher overpotentials for catalysis, implying the disfavored photocatalysis.⁵³ The above electrochemical results are in agreement with the photocatalysis with IrBPY, where CoTAPc displayed a lower QE than CoPc under identical conditions (Fig. 4e). In sharp contrast, CoTAPc gave a higher performance than CoPc in the presence of IrQPY. This contradiction indicates that other factor remains to facilitate the photocatalysis with IrQPY rather than the altered intrinsic activity of catalyst. Then we conducted the ^1H NMR titration between IrQPY and CoTAPc to study if the intermolecular affinity is the more important factor (Fig. 5). Interestingly, the ^1H NMR spectra of IrQPY displayed more notable shifts upon the addition of CoTAPc instead of CoPc, and achieved a higher binding constant of 450 M^{-1} (Supplementary Fig. 17), demonstrating a stronger coordinative interaction, which can be explained that the coordinate bond is reinforced by sharing more electron density from the electron-donating amino groups. Based on the above results, we propose that the electron-rich amino groups of CoTAPc result in a higher overpotential for catalysis and a stronger binding with IrQPY. The latter feature can in turn overcome the negative influence of the former one, demonstrating that the coordinative interaction plays a more important role in promoting the photocatalysis over the capability of catalyst.

Photocatalytic CO_2 reduction with other molecular catalysts

More excitingly, this coordinative interaction strategy is widely applicable to other molecular catalysts with different metal centers and coordination modes. As a proof-of-concept, we then utilized a commercially available chloro iron(III) tetraphenylporphyrin (denoted as FePor; Fig. 6a) as another catalyst with a similar macrocyclic configuration and a varied metal center to CoPc, to cooperate with IrQPY in light-induced CO_2 reduction. As shown in Fig. 6b, under optimized conditions, the IrQPY/FePor system

accomplished a TON of 253 ± 10 , a selectivity of 99.8% and a QE of 1.7% for CO production. In contrast, the use of IrBPY only afforded a TON of 65 ± 5 , one-fourth of the TON of IrQPY/FePor system under identical conditions. Also, the deactivation took place earlier than IrBPY/FePor system (4 vs. 7 h). The comparative results further demonstrate that the coordinative interaction strategy is versatile toward different molecular catalysts to promote their catalytic performances. Notably, the above performances of IrQPY/FePor system are superior to the reported photocatalytic systems with FePor, like g-C₃N₄/FePor (6 TONs, 99% selectivity)⁵⁴ and *fac*-Ir(ppy)₃/FePor systems (84 TONs, 79% selectivity),⁵⁵ displaying the boosted performance of FePor in cooperation with IrQPY.

Next, we envisioned that the use of a molecular catalyst with only one labile site, [Co(tpa)Cl]ClO₄ (CoTPA; tpa = tris(2-pyridylmethyl)amine; Fig. 6c)^{50,56} as the example, may be not applicable to the coordinative interaction method, as the only vacant site may possibly be seized by IrQPY to prevent CO₂ binding and catalysis. Unexpectedly, similar enhancement in CO₂ reduction over H₂ evolution could also be observed in IrQPY/CoTPA in contrast to IrBPY/CoTPA combination (Fig. 6d), showing the successful application of coordinative interaction on the complex with only one accessible site. Meanwhile, the results also infer that during photocatalysis, the coordination is highly dynamic to avoid the stable occupancy at the labile sites, and merely serves a bridge to accelerate the electron transfer from IrQPY to various types of catalysts, which is schematically proposed in Fig. 6e.

To verify the hypothesis, we added 0.1 M pyridine in the photocatalytic systems with IrQPY and IrBPY. Pyridine should be a stronger axial ligand relative to IrQPY due to its smaller size and neutral feature. Compared to the unperturbed IrQPY/CoPc system (Fig. 4a), the CO evolution rate and final yield were significantly inhibited by pyridine (Fig. 6f). In contrast, the pyridine-added IrBPY/CoPc system was not markedly affected, showing a similar CO yield of ca. 60 μmol to the one with no pyridine (Fig. 4a). Eventually, an even lower activity of IrQPY/CoPc than that of IrBPY/CoPc was observed in the presence of pyridine. That is, the pyridine coordination severely diminished the activity of IrQPY/CoPc, but not affected IrBPY/CoPc. This difference is most likely due to the pyridine-impeded coordination between IrQPY and CoPc, which further proves the positive contribution of the elastic coordinative interaction between IrQPY and catalyst, and supports the hypothesis proposed in Fig. 6e. That is, the dynamic coordinative interaction with suitable affinity prevents the occupancy at the labile sites and barely serves a facile electron delivery to accelerate photocatalytic CO₂ reduction. This dynamic and reversible character should be able to prevent the back electron transfer for high-performance photocatalysis.

Photo-induced electron transfer pathway

Finally, the photo-induced electron transfer pathway by quenching experiments was studied to verify the role of coordinative interaction in intermolecular electron transfer. Compared to the one with BIH, the S-V plot between IrQPY and CoPc reveals an even steeper slope, resulting in a significantly higher quenching constant of $3.33 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ (Supplementary Figure 18). This observation suggests that CoPc quenched the fluorescence of excited IrQPY more markedly than BIH. Thus the oxidative quenching pathway should be more accessible (equation 2, 3 and 4) than the reductive quenching pathway (equation 2, 5 and 6).⁵⁷ The same conclusion can be drawn in the case of IrBPY according to the evaluation outcome of its quenching constants with BIH (Supplementary Figure 19) or CoPc (Supplementary Figure 20), respectively. It cannot be neglected that the reductive quenching pathway may also be viable, as both the oxidative/reductive quenching constants are at the same magnitude ($\times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$). However, the reducing abilities of IrQPY^{•-} and IrBPY^{•-} are both significantly weaker than their photo-excited species ($E_{\text{red},1}$ vs. $E_{\text{q,ox}}$, Table 1), respectively, manifesting that the oxidative quenching should serve as a major driving force for the reduction of CO₂. Although the light absorption by CoPc in quenching experiments should also be taken into consideration,⁵⁸ but this factor can be excluded by the negligible shift of emission band and the good linear fitting along with titration.

Following the oxidative quenching pathway, two main factors related to Ir PSs are responsible for the QE of photocatalysis, including the emission quantum yields of Ir PSs (ϕ , eq 2), and the oxidative quenching rates, namely the electron transfer rates from the excited Ir PS to CoPc ($k_{q,ox}$, eq 3). Therefore the ϕ and $k_{q,ox}$ values were measured to verify the varied performances between IrQPY and IrBPY. First, although the UV-Vis spectra show that the absorption at 450 nm of IrQPY is higher than that of IrBPY (1500 vs. 700 L mol⁻¹ cm⁻¹; Supplementary Figure 21), the ϕ_{450} of IrQPY is lower than that of IrBPY (6.86% vs. 11.89%, Table 1), which are attributable to the more conjugated qpy ligand.⁵⁹ Second, the quenching rates between the excited Ir PSs and CoPc have been estimated by the S-V plots with CoPc titration, and it was found that the $k_{q,ox}$ value of IrQPY (3.33×10^{10} M⁻¹ s⁻¹) is higher than that of IrBPY (2.03×10^{10} M⁻¹ s⁻¹). However, the reducing ability of IrQPY* is significantly weaker than that of IrBPY* (-1.49 vs. -1.72 V, Table 1), thus the reaction rate between IrQPY and CoPc should be slower than the one between IrBPY and CoPc if no additional interaction exists. The contradiction indicates that an additional interaction between PS and catalyst, most possibly the coordinative interaction, plays the key role in facilitating the electron transfer from the photoexcited IrQPY to CoPc. Overall, the above results validate that although IrQPY possesses a lower ϕ and a less reducing excited state in comparison with those of IrBPY, the coordinative interaction between IrQPY and CoPc enables a much faster intermolecular electron transfer and thus achieves considerable QEs for photocatalytic CO₂ reduction.

Conclusion

In conclusion, for the first time, a coordinative interaction between PS and catalyst has been employed in a purely molecular system for photocatalytic CO₂ reduction. The redox properties, molecule dynamics and photo-induced electron delivery were carefully studied to reveal the role of coordination interaction in the photocatalytic mechanism. The results manifest that the dynamic coordinative interaction in our case not only accelerates the intermolecular electron transfer, but also avoids the stable occupancy at the labile sites which induces back electron transfer and impeded substrate binding. Eventually, the coordinative interaction between the optimized PS and catalyst have boosted the QE from 2.4–27.9% for selective CO₂-to-CO conversion, an over 11-times improvement. Our studies demonstrate that in contrast to the documented covalent strategies, the application of coordinate bond has multiple advantages, including its dynamic feature, suitable affinity, extensive applicability, strong tolerance to conditional changes, etc. We believe that our work provides a versatile method to facilitate the electron transfer and readily improve the photocatalytic efficiency of CO₂ reduction. It is also notable that we have utilized multiple earth-abundant molecular catalysts to lower the expense, and further cost down will be facilitated by the use of Cu-based or organic PSs instead of Ir PSs. Consequently, a novel pyridine-appended Cu PS, [Cu(DPEphos)(pbcp)](PF₆) (DPEphos = bis[(2-diphenyl-phosphino)phenyl]ether, pbcp = 2,9-dimethyl-4,7-di(pyridin-4-yl)-1,10-phenanthroline), has been synthesized (see Supplementary Fig. 22 and Methods for details) for the next noble-metal-free system to apply the concept of coordinative interaction.

Methods

Materials

IrBPY⁵⁹, BIH⁶⁰, CoTPA⁵⁰ and pbcp ligand⁶¹ were synthesized according to the literature methods, Milli-Q ultrapure water (> 18 MΩ) was utilized unless otherwise stated. Bis[(2-diphenyl-phosphino)phenyl]ether (DPEphos; 97%, Innochem), 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (bathocuproine, bcp; 97%, Innochem), CoPc (97%, β -form, Aldrich), FePor (97%, Shanghai Tensus Biotech Co.,Ltd), CoTAPc (95%, Jilin Chinese Academy of Sciences-Yanshen Technology Co., Ltd.), PhOH (99.5%, Aladdin), TFE

(99.5%, Aladdin), pyridine (99.5%, Aladdin), CO₂ (99.999%), N₂ (99.999%), ¹³CO₂ (99.9%), DMF-*d*₇ (99.5%, Acros) and other chemicals were commercially available and used without further purification.

Instruments

¹H NMR spectra were obtained on a Bruker advance III instrument (400 MHz). The electron spray ionization mass spectra of metal complexes were collected on an Ion Mobility-Q-TOF High Resolution LC-MS (Waters Corporation, Synapt G2-Si). Single-crystal X-ray diffraction data were collected at 150 K on an Agilent Technologies Supernova system with Cu/*Kα* ($\lambda = 1.54178 \text{ \AA}$) radiation. Electrochemical measurements were carried out using an electrochemical workstation (CHI 620E). The irradiation experiments were carried out with a blue LED light (Zolix, MLED4). Gas chromatographic analysis was conducted on an Agilent 7820A gas chromatography equipped with a thermal conductivity detector (TCD) and a TDX-01 packed column, where the oven temperature was held constant at 60°C, the inlet and detector temperature were set at 80°C and 200°C, respectively. The isotopic labeling experiment was conducted under ¹³CO₂ atmosphere and the gas in the headspace was analyzed by a quantitative mass spectrometer attached Agilent 7890A gas chromatography. The liquid phase of the reaction system was analyzed by an ion chromatograph (Metrohm, 930 Compact IC Flex, Supp 5 anion column, Na₂CO₃/NaHCO₃ aqueous eluent) to detect the presence of formate. UV-vis spectra were collected on a Shimadzu UV-3600 spectrophotometer. The quantum yields of Ir PSs were carried out on a fluorescence spectrometer (F-7000, Hitachi, Japan) equipped with an integrating sphere, which were also reproduced on another fluorescence spectrometer (FLS 1000, Edinburgh Instruments LTD.). The quenching experiments were conducted on a modular fluorescent life and steady-state fluorescence spectrometer (FLS 980, Edinburgh Instruments LTD.). All experiments were operated at room temperature (24 ~ 25°C).

Data Availability

Experimental details, supplementary figures and data are available from the authors. The data with CCDC number, IrQPY (2043015) and [Cu(DPEphos)(pbcp)](PF₆) (2043973), contain the supplementary crystallographic information for this paper. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk/>.

Declarations

Acknowledgments

We are grateful for the expertise in NMR titration from Dr. Kai Wu from Faculty of Chemistry and Chemical Biology, TU Dortmund University. This work was financially supported by National Natural Science Foundation of China (21737006, 22076222 and 22036003), Guangdong Basic and Applied Basic Research Foundation (2020A1515110017), China Postdoctoral Science Foundation (2020M683020), Guangdong Provincial Key R&D Programme (2020B1111350002) and the Fundamental Research Funds for the Central Universities (201gpy87).

Author contributions

J.W.W. and G.O. conceived and designed this project, J.W.W. and L.J. performed the experiments, H.H.H. carried out the DFT calculation, J.W.W. and O.G. analyzed the data, J.W.W., H.Z. and O.G. wrote and revised the article. All authors participated in drafting the paper, and gave approval to the final version of the manuscript.

Competing Interests

The authors declare no competing interests.

References

1. Dalle, K. E., Warnan, J., Leung, J. J., Reuillard, B., Karmel, I. S. & Reisner, E. Electro- and solar-driven fuel synthesis with first row transition metal complexes. *Chem. Rev.* **119**, 2752-2875 (2019).

2. Wang, J. W., Liu, W. J., Zhong, D. C. & Lu, T. B. Nickel complexes as molecular catalysts for water splitting and CO₂ reduction. *Coord. Chem. Rev.* **378**, 237-261 (2019).
3. Wang, J.-W., Zhong, D.-C. & Lu, T.-B. Artificial photosynthesis: Catalytic water oxidation and CO₂ reduction by dinuclear non-noble-metal molecular catalysts. *Coord. Chem. Rev.* **377**, 225-236 (2018).
4. Elgrishi, N., Chambers, M. B., Wang, X. & Fontecave, M. Molecular polypyridine-based metal complexes as catalysts for the reduction of CO₂. *Chem. Soc. Rev.* **46**, 761-796 (2017).
5. Takeda, H., Cometto, C., Ishitani, O. & Robert, M. Electrons, photons, protons and earth-abundant metal complexes for molecular catalysis of CO₂ reduction. *ACS Catal.* **7**, 70-88 (2016).
6. Yamazaki, Y., Takeda, H. & Ishitani, O. Photocatalytic reduction of CO₂ using metal complexes. *J. Photochem. Photobiol., C* **25**, 106-137 (2015).
7. Shirley, H., Su, X., Sanjanwala, H., Talukdar, K., Jurss, J. W. & Delcamp, J. H. Durable solar-powered systems with ni-catalysts for conversion of CO₂ or CO to CH₄. *J. Am. Chem. Soc.* **141**, 6617-6622 (2019).
8. Thoi, V. S., Kornienko, N., Margarit, C. G., Yang, P. & Chang, C. J. Visible-light photoredox catalysis: Selective reduction of carbon dioxide to carbon monoxide by a nickel N-heterocyclic carbene-isoquinoline complex. *J. Am. Chem. Soc.* **135**, 14413-14424 (2013).
9. Ouyang, T., Huang, H.-H., Wang, J.-W., Zhong, D.-C. & Lu, T.-B. A dinuclear cobalt cryptate as a homogeneous photocatalyst for highly selective and efficient visible-light driven CO₂ reduction to CO in CH₃CN/H₂O solution. *Angew. Chem. Int. Ed.* **56**, 738-743 (2017).
10. Ouyang, T., *et al.* Dinuclear metal synergistic catalysis boosts photochemical CO₂-to-CO conversion. *Angew. Chem. Int. Ed.* **57**, 16480-16485 (2018).
11. Hu, Y., *et al.* Tracking mechanistic pathway of photocatalytic CO₂ reaction at Ni sites using operando, time-resolved spectroscopy. *J. Am. Chem. Soc.* **142**, 5618-5626 (2020).
12. Of best practice in catalysis. *Nat. Catal.* **3**, 471-472 (2020).
13. Kisch, H. Semiconductor photocatalysis—mechanistic and synthetic aspects. *Angew. Chem. Int. Ed.* **52**, 812-847 (2013).
14. Hong, D., Tsukakoshi, Y., Kotani, H., Ishizuka, T. & Kojima, T. Visible-light-driven photocatalytic CO₂ reduction by a Ni(II) complex bearing a bioinspired tetradentate ligand for selective CO production. *J. Am. Chem. Soc.* **139**, 6538-6541 (2017).
15. Hong, D., Kawanishi, T., Tsukakoshi, Y., Kotani, H., Ishizuka, T. & Kojima, T. Efficient photocatalytic CO₂ reduction by a Ni(II) complex having pyridine pendants through capturing a Mg(2+) ion as a lewis-acid cocatalyst. *J. Am. Chem. Soc.* **141**, 20309-20317 (2019).
16. Morimoto, T., *et al.* Ring-shaped Re(I) multinuclear complexes with unique photofunctional properties. *J. Am. Chem. Soc.* **135**, 13266-13269 (2013).
17. Yamazaki, Y. & Ishitani, O. Synthesis of Os(II)-Re(I)-Ru(II) hetero-trinuclear complexes and their photophysical properties and photocatalytic abilities. *Chem. Sci.* **9**, 1031-1041 (2018).
18. Nakada, A., Koike, K., Nakashima, T., Morimoto, T. & Ishitani, O. Photocatalytic CO₂ reduction to formic acid using a Ru(II)-Re(I) supramolecular complex in an aqueous solution. *Inorg. Chem.* **54**, 1800-1807 (2015).
19. Kuramochi, Y. & Ishitani, O. Iridium(III) 1-phenylisoquinoline complexes as a photosensitizer for photocatalytic CO₂ reduction: A mixed system with a Re(I) catalyst and a supramolecular photocatalyst. *Inorg. Chem.* **55**, 5702-5709 (2016).
20. Nakada, A., Koike, K., Maeda, K. & Ishitani, O. Highly efficient visible-light-driven CO₂ reduction to CO using a Ru(II)-Re(I) supramolecular photocatalyst in an aqueous solution. *Green Chem.* **18**, 139-143 (2016).
21. Kuramochi, Y., Fujisawa, Y. & Satake, A. Photocatalytic CO₂ reduction mediated by electron transfer via the excited triplet state of Zn(II) porphyrin. *J. Am. Chem. Soc.* **142**, 705-709 (2020).
22. Tamaki, Y., Morimoto, T., Koike, K. & Ishitani, O. Photocatalytic CO₂ reduction with high turnover frequency and selectivity of formic acid formation using Ru(II) multinuclear complexes. *Proc. Natl. Acad. Sci. U. S. A.* **109**, 15673-15678 (2012).

23. Windle, C. D., George, M. W., Perutz, R. N., Summers, P. A., Sun, X. Z. & Whitwood, A. C. Comparison of rhenium–porphyrin dyads for CO₂ photoreduction: Photocatalytic studies and charge separation dynamics studied by time-resolved ir spectroscopy. *Chem. Sci.* **6**, 6847-6864 (2015).
24. Li, F., Jiang, Y., Zhang, B., Huang, F., Gao, Y. & Sun, L. Towards a solar fuel device: Light-driven water oxidation catalyzed by a supramolecular assembly. *Angew. Chem. Int. Ed.* **51**, 2417-2420 (2012).
25. Gholamkhass, B., Mametsuka, H., Koike, K., Tanabe, T., Furue, M. & Ishitani, O. Architecture of supramolecular metal complexes for photocatalytic CO₂ reduction: Ruthenium-Rhenium bi- and tetranuclear complexes. *Inorg. Chem.* **44**, 2326-2336 (2005).
26. Li, H., Li, F., Zhang, B., Zhou, X., Yu, F. & Sun, L. Visible light-driven water oxidation promoted by host-guest interaction between photosensitizer and catalyst with a high quantum efficiency. *J. Am. Chem. Soc.* **137**, 4332-4335 (2015).
27. Li, X., *et al.* Noncovalent assembly of a metalloporphyrin and an iron hydrogenase active-site model: Photo-induced electron transfer and hydrogen generation. *J. Phys. Chem. B* **112**, 8198-8202 (2008).
28. Schulz, M., Karnahl, M., Schwalbe, M. & Vos, J. G. The role of the bridging ligand in photocatalytic supramolecular assemblies for the reduction of protons and carbon dioxide. *Coord. Chem. Rev.* **256**, 1682-1705 (2012).
29. Kluwer, A. M., *et al.* Molecular recognition and self-assembly special feature: Self-assembled biomimetic [2Fe2S]-hydrogenase-based photocatalyst for molecular hydrogen evolution. *Proc. Natl. Acad. Sci. U. S. A.* **106**, 10460-10465 (2009).
30. Cheung, P. L., Kapper, S. C., Zeng, T., Thompson, M. E. & Kubiak, C. P. Improving photocatalysis for the reduction of CO₂ through non-covalent supramolecular assembly. *J. Am. Chem. Soc.* **141**, 14961-14965 (2019).
31. Choi, J., *et al.* Steric modification of a cobalt phthalocyanine/graphene catalyst to give enhanced and stable electrochemical CO₂ reduction to CO. *ACS Energy Lett.*, 10.1021/acsenerylett.8b02355, 666-672 (2019).
32. Ren, S., *et al.* Molecular electrocatalysts can mediate fast, selective CO₂ reduction in a flow cell. *Science* **365**, 367-369 (2019).
33. Wang, M., *et al.* CO₂ electrochemical catalytic reduction with a highly active cobalt phthalocyanine. *Nat. Commun.* **10**, 3602 (2019).
34. Wu, Y., Jiang, Z., Lu, X., Liang, Y. & Wang, H. Domino electroreduction of CO₂ to methanol on a molecular catalyst. *Nature* **575**, 639-642 (2019).
35. Su, J., *et al.* Building a stable cationic molecule/electrode interface for highly efficient and durable CO₂ reduction at an industrially relevant current. *Energy Environ. Sci.*, 10.1039/d0ee02535f, (2021).
36. Fihri, A., Artero, V., Pereira, A. & Fontecave, M. Efficient H₂-producing photocatalytic systems based on cyclometalated iridium- and tricarbonylrhenium-diimine photosensitizers and cobaloxime catalysts. *Dalton. Trans.*, 2008, 5567-5569 (2008).
37. Fihri, A., Artero, V., Razavet, M., Baffert, C., Leibl, W. & Fontecave, M. Cobaloxime-based photocatalytic devices for hydrogen production. *Angew. Chem. Int. Ed.* **47**, 564-567 (2008).
38. Zhang, P., Wang, M., Li, C., Li, X., Dong, J. & Sun, L. Photochemical H₂ with noble-metal-free molecular devices comprising a porphyrin photosensitizer and a cobaloxime catalyst. *Chem. Commun.* **46**, 8806-8808 (2010).
39. Wang, J., *et al.* Linkage effect in the heterogenization of cobalt complexes by doped graphene for electrocatalytic CO₂ reduction. *Angew. Chem. Int. Ed.* **58**, 13532-13539 (2019).
40. Wang, J., Huang, X., Xi, S., Xu, H. & Wang, X. Axial modification of cobalt complexes on heterogeneous surface with enhanced electron transfer for carbon dioxide reduction. *Angew. Chem. Int. Ed.* **59**, 19162-19167 (2020).
41. Reuillard, B., Warnan, J., Leung, J. J., Wakerley, D. W. & Reisner, E. A poly(cobaloxime)/carbon nanotube electrode: Freestanding buckypaper with polymer-enhanced H₂-evolution performance. *Angew. Chem. Int. Ed.* **55**, 3952-3957 (2016).
42. Pan, Y., *et al.* Design of single-atom CO-N5 catalytic site: A robust electrocatalyst for CO₂ reduction with nearly 100% CO selectivity and remarkable stability. *J. Am. Chem. Soc.* **140**, 4218-4221 (2018).
43. Thordarson, P. Determining association constants from titration experiments in supramolecular chemistry. *Chem. Soc. Rev.* **40**, 1305-1323 (2011).

44. Zhao, Y. & Truhlar, D. G. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: Two new functionals and systematic testing of four M06-class functionals and I_2 other functionals. *Theor. Chem. Acc.* **120**, 215-241 (2007).
45. Lu, T. & Chen, F. Multiwfn: A multifunctional wavefunction analyzer. *J. Comput. Chem.* **33**, 580-592 (2012).
46. Wang, J.-W., Huang, H.-H., Sun, J.-K., Zhong, D.-C. & Lu, T.-B. Syngas production with a highly-robust nickel(II) homogeneous electrocatalyst in a water-containing system. *ACS Catal.* **8**, 7612-7620 (2018).
47. Wang, P., *et al.* A broadband and strong visible-light-absorbing photosensitizer boosts hydrogen evolution. *Nat. Commun.* **10**, 3155 (2019).
48. Saveant, J. M. Molecular catalysis of electrochemical reactions. Mechanistic aspects. *Chem. Rev.* **108**, 2348-2378 (2008).
49. Kramer, W. W. & McCrory, C. C. L. Polymer coordination promotes selective CO_2 reduction by cobalt phthalocyanine. *Chem. Sci.* **7**, 2506-2515 (2016).
50. Wang, J.-W., Huang, H.-H., Sun, J.-K., Ouyang, T., Zhong, D.-C. & Lu, T.-B. Electrocatalytic and photocatalytic reduction of CO_2 to CO by cobalt(II) tripodal complexes: Low overpotentials, high efficiency and selectivity. *ChemSusChem* **11**, 1025-1031 (2018).
51. Burks, D. B., *et al.* Nickel(II) pincer complexes demonstrate that the remote substituent controls catalytic carbon dioxide reduction. *Chem. Commun.* **54**, 3819-3822 (2018).
52. Guo, Z., *et al.* Highly efficient and selective photocatalytic CO_2 reduction by iron and cobalt quaterpyridine complexes. *J. Am. Chem. Soc.* **138**, 9413-9416 (2016).
53. Liu, D.-C., *et al.* Conjugation effect contributes to the CO_2 -to-CO conversion driven by visible-light. *ACS Appl. Energy Mater.* **1**, 2452-2459 (2018).
54. Lin, L., Hou, C., Zhang, X., Wang, Y., Chen, Y. & He, T. Highly efficient visible-light driven photocatalytic reduction of CO_2 over $\text{g-C}_3\text{N}_4$ nanosheets/tetra(4-carboxyphenyl)porphyrin iron(III) chloride heterogeneous catalysts. *Appl. Catal. B-Environ* **221**, 312-319 (2018).
55. Rao, H., Schmidt, L. C., Bonin, J. & Robert, M. Visible-light-driven methane formation from CO_2 with a molecular iron catalyst. *Nature* **548**, 74-77 (2017).
56. Chan, S. L., Lam, T. L., Yang, C., Yan, S. C. & Cheng, N. M. A robust and efficient cobalt molecular catalyst for CO_2 reduction. *Chem. Commun.* **51**, 7799-7801 (2015).
57. Rao, H., Bonin, J. & Robert, M. Toward visible-light photochemical CO_2 -to- CH_4 conversion in aqueous solutions using sensitized molecular catalysis. *J. Phys. Chem. C* **122**, 13834-13839 (2018).
58. Bonin, J., Robert, M. & Routier, M. Selective and efficient photocatalytic CO_2 reduction to CO using visible light and an iron-based homogeneous catalyst. *J. Am. Chem. Soc.* **136**, 16768-16771 (2014).
59. DiSalle, B. F. & Bernhard, S. Orchestrated photocatalytic water reduction using surface-adsorbing iridium photosensitizers. *J. Am. Chem. Soc.* **133**, 11819-11821 (2011).
60. Zhu, X. Q., Zhang, M. T., Yu, A., Wang, C. H. & Cheng, J. P. Hydride, hydrogen atom, proton, and electron transfer driving forces of various five-membered heterocyclic organic hydrides and their reaction intermediates in acetonitrile. *J. Am. Chem. Soc.* **130**, 2501-2516 (2008).
61. Li, C., *et al.* A phenanthroline derivative as exciton blocking material for organic solar cells. *Dyes and Pigments* **97**, 258-261 (2013).

Figures

Figure 1

Comparison of different methods to bridge PS and catalyst.

Figure 2

Characterization of coordinative interaction. a ¹H NMR titration with CoPc into a 1.0 mM DMF-d₇ solution of IrQPY, highlighting the pendent pyridyl proton signals. b DFT-calculated structures of IrQPY-CoPc and IrQPY-(CoPc)₂. Counter anions are omitted for clarity. The Co-N bond lengths, bond orders and spin states of Co(II) are noted.

Figure 3

Cyclic voltammetry. a Comparison among CVs under N_2 with 0.5 mM IrQPY (red), 0.5 mM CoPc (orange), as well as 0.5 mM CoPc and 0.5 mM IrQPY (blue). b Comparison among CVs of 0.5 mM CoPc and 0.5 mM IrQPY under N_2 (blue) or CO_2 (pink), as well as the one with 0.5 mM CoPc under CO_2 (brown).

Figure 4

Photocatalytic CO₂ reduction. a Time profiles of photocatalytic CO (star) and H₂ (pentagon) formation with IrQPY/CoPc (red) or IrBPY/CoPc (blue) system. b QEs for CO and H₂ formation from IrQPY/CoPc (red) and IrBPY/CoPc (blue) systems. c Time profiles of photocatalytic CO (star) and H₂ (pentagon) formation from IrQPY/CoPc (red) system. After 4 h, fresh CoPc (0.4 μmol, orange), IrQPY (0.4 μmol, green), or BIH (32 μmol, blue) was dispersed in 0.5 mL CO₂-saturated CH₃CN and injected in the solution, respectively. d Photocatalytic CO and H₂ yields with IrQPY/CoPc and varying volumes of H₂O, and corresponding CO% are shown. e QEs for CO and H₂ formation from IrQPY/CoPc, IrBPY/CoPc, IrQPY/CoTAPc and IrBPY/CoTAPc systems with 150 mM BIH and 425 nm light within 30 min. f CVs of CoPc (orange) and CoTAPc (violet) under N₂.

Figure 5

a

Chemical structure of FePor (Iron Porphyrin) showing two axial labile sites (indicated by blue arrows).

b

Plot of Yield (μmol) and TON (Turnover Number) versus Time (h) for Ir and Co complexes with FePor. The legend indicates: IrQPY/FePor, CO (blue circles); IrQPY/FePor, H_2 (blue squares); IrBPY/FePor, CO (magenta circles); IrBPY/FePor, H_2 (magenta squares).

c

Chemical structure of CoTPA (Cobalt Tetraphenylporphyrin) showing only one labile site (indicated by an orange arrow).

d

Plot of Yield (μmol) and TON (Turnover Number) versus Time (h) for Ir and Co complexes with CoTPA. The legend indicates: IrQPY/CoTPA, CO (orange circles); IrQPY/CoTPA, H_2 (orange squares); IrBPY/CoTPA, CO (green circles); IrBPY/CoTPA, H_2 (green squares).

e

Proposed mechanism for the catalytic activity of Ir and Co complexes with CoPc. The mechanism involves electron transfer (e^-) from the Ir or Co complex to the CoPc, leading to the formation of a radical cation ($\text{CoPc}^{\cdot+}$). This radical cation then reacts with CO_2 to form a radical anion ($\text{CoPc}^{\cdot-}$), which is then converted to a cobalt complex (CoPc) and releases CO . The cobalt complex is then re-oxidized to the Ir or Co complex, completing the cycle.

f

Plot of Yield (μmol) versus Time (h) for Ir and Co complexes with CoPc in 0.1 M pyridine. The legend indicates: IrQPY/CoPc, CO (pink circles); IrQPY/CoPc, H_2 (pink squares); IrBPY/CoPc, CO (blue circles); IrBPY/CoPc, H_2 (blue squares).

Wide applicability of dynamic coordination interaction. a Structures of FePor. b Time profiles of photocatalytic CO (diamond) and H₂ (square) formation from a mixture of FePor (0.1 mM), IrQPY (blue, 0.1 mM) or IrBPY (magenta, 0.1 mM), TEA (2.5 v%) and BIH (80 mM). c Structures of CoTPA. d Time profiles of photocatalytic CO (diamond) and H₂ (square) formation from a mixture of CoTPA (0.1 mM), IrQPY (orange, 0.1 mM) or IrBPY (green, 0.1 mM), PhOH (5.0 v%), TEA (2.5 v%) and BIH (80 mM). e Proposed reaction mechanism for the relative states of IrQPY and CoPc during electron transfer and CO₂ reduction. f Time profiles of photocatalytic CO (diamond) and H₂ (square) formation from a mixture of pyridine (0.1 M), CoPc (0.1 mM), IrQPY (pink, 0.1 mM) or IrBPY (navy, 0.1 mM), TEA (2.5 v%), PhOH (6.0 v%) and BIH (80 mM).

This is a list of supplementary files associated with this preprint. Click to download.

- Page 17/17