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Photocatalytic CO₂ reduction with a quantum efficiency exceeding 60%: time-resolved spectroscopic and X-ray studies on Cu(I) photosensitizers in coordinative interaction with Co(II) phthalocyanine catalysts

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Abstract

The utilization of a fully noble-metal-free system for photocatalytic CO₂ reduction remains a fundamental challenge, demanding the precise design of photosensitizers and catalysts, as well as the exploitation of their intermolecular interactions to facilitate electron delivery. Herein, we have implemented triple modulations on catalyst, photosensitizer and coordinative interaction between them for high-performance light-driven CO₂ reduction. In this study, heteroleptic copper and cobalt phthalocyanine complexes were selected as photosensitizers and catalysts, respectively. An over ten-fold improvement in light-driven reduction of CO₂ to CO is achieved for the catalysts with appending electron-withdrawing substituents for optimal CO-desorption ability. In addition, pyridine substituents were implanted at the backbone of the phenanthroline moiety of the Cu(I) photosensitizers and the effect of their axial coordinative interaction with the catalyst was tested. The combined results of ¹H NMR titration experiment, steady-state/transient photoluminescence, and transient absorption spectroscopy confirm the coordinative interaction and reductive quenching pathway in photocatalysis corroboratively. It has been found that the catalytic performances of the coordinatively interacted systems are unexpectedly reverse to those with the pyridine-free Cu(I) photosensitizers. Moreover, the latter system enables a very high quantum efficiency up to 63.5% at 425 nm with a high selectivity exceeding 99% for CO₂-to-CO conversion. As determined by time-resolved X-ray absorption spectroscopy and DFT calculation, the replacement of phenyl by pyridyl groups in the Cu(I) photosensitizer favors a stronger flattening and larger torsional angle change of the overall excited state geometry upon photoexcitation, which explains the decreased lifetime of the triplet excited state. Our work promotes the systematic multi-pathway optimizations on the catalyst, photosensitizer and their interactions for advanced CO₂ photoreduction.

Introduction

Sunlight-driven reduction of CO₂ continues to attract attention as a sustainable, carbon-neutral route to produce renewable fuels.^{1,2} Due to the sluggish multi-electron reaction kinetics and strong competition with H₂ evolution,^{3,4} considerable efforts have been dedicated to the development of efficient and selective systems for photocatalytic CO₂ reduction. Most examples, fully or in part, utilize metal complexes as molecular photosensitizers (PSs) or catalysts, which are highly optimizable via synthetic methods and easy to characterize for mechanistic investigations.⁵⁻⁷ Among them, noble-metal-based PSs, like Ru, Ir and Re complexes, are extensively applied to drive the catalysts.⁸⁻¹¹ However, the high expense and low abundance of 4d and 5d transition metals inevitably precludes large-scale applications of such systems and therefore earth-abundant molecular systems are of intensified interest.¹²⁻¹⁶ Organic dyes could serve as economical PSs due to their strong absorption and high redox potentials. An early example was contributed by Fujita *et al.*,¹⁷ in which the photocatalytic reduction of CO₂ to CO and HCOOH using Co macrocycles as catalysts was assisted by *p*-terphenyl, giving a quantum efficiency (Φ) of 25% at 313 nm. More recently, Robert and co-workers have exploited several organic dyes like 9-cyanoanthracene,¹⁸ purpurin¹⁹ or 3,7-di(4-biphenyl)-1-naphthalene-10-phenoxazine²⁰ in combination with iron porphyrin catalysts. These examples demonstrate the high catalytic efficiency and selectivity of organic dyes, while they may suffer from low photostability,²¹ demanding new alternatives for CO₂ reduction.

For instance, Cu(I) based PSs have shown great potential in photocatalysis caused by their versatile redox characteristics and highly variable ligand scaffolds for tunable redox and excited-state properties.²¹⁻²⁶ In terms of CO₂ reduction, Ishitani *et al.* have designed a diphosphine-tethered phenanthroline ligand to prepare a dimeric Cu(I) PS, which displayed notable stability during photocatalysis along with Fe^{27,28} or Mn²⁹ catalysts. The tetradentate nature of the applied ligand effectively prevents the dissociation of diphosphine donors around the Cu centers, achieving a maximum Φ of 57% for the co-production of CO and HCOOH. Beller and co-workers deployed the Cu(I) dyes *in situ* by directly mixing the Cu(I) precursor and respective ligands in the photocatalytic systems for CO₂ reduction, in conjunction with cyclopentadienone Fe complexes¹⁴ or Mn diamine complexes³⁰ respectively as catalysts. Furthermore, Sakai *et al.*^{13,31} prepared a sulphonated Cu(I) PS to work in fully aqueous solutions with water-soluble Co porphyrins, achieving good selectivity (near 90%) and turnover numbers (TONs, up to 4000).

The examples mentioned above have shown some promising catalytic performances and demonstrated that Cu(I) PS are suitable for light-driven CO₂ reduction. Nevertheless, there is still substantial room for improving the performances, as the noble-metal containing systems have demonstrated TON > 10⁷³² and Φ > 80%.³³ The anticipated improvement can be achieved by rationally

optimizing the catalysts and PSs and additionally by enhancing the essential electron transfer between PS and catalyst. Focusing on the latter issue, various strategies have been explored, including the covalent attachment,³⁴⁻³⁶ or H-bond interactions,³⁷ in addition to coordinative³⁸ interaction developed by us. However, most of these systems still rely on noble-metal-based PSs or catalysts. In contrast, fully noble-metal-free molecular systems applying weak interactions between PS and catalyst to improve electron transfer, to the best of our knowledge, have seldom been reported so far.

Herein, we have chosen heteroleptic diphosphine-diimine Cu(I) complexes, $[\text{Cu}(\text{P}^{\wedge}\text{P})(\text{N}^{\wedge}\text{N})]^+$, as PSs, and cobalt phthalocyanine (**CoPc**) derived complexes as catalysts, for optimizing photocatalytic CO₂ reduction. The three key factors, *i.e.* catalyst, PS and their interaction, are all considered for significant improvements in photocatalysis. In consequence, the optimal combination of $[\text{Cu}^{\text{I}}(\text{xantphos})(\text{bcp})]\text{PF}_6$ (**CuBCP**; xantphos = 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene, bcp = bathocuproine) and cobalt tetracarboxylphthalocyanine (**CoTCpC**) enables an extremely high maximum Φ of 63.5% at 425 nm for the CO₂-to-CO conversion with 99% selectivity. Further, the coordinative interaction between Cu(I) PS and **CoTCpC** has been constructed by using a pyridine-decorated 1,10-phenanthroline-derived ligand for the Cu(I) centers, which nonetheless led to a decreased efficiency. As evidenced through DFT calculations and time-resolved X-ray absorption spectroscopic measurements, the increased flattening of the overall excited state geometry and the larger torsional angle change of the photoexcited state impair the PS stability significantly in this case. This methodical study conducted is promising for future rational developments of both earth-abundant PSs and catalytic complexes for CO₂ reduction with additional interactions.

Results

Electronic structures of Co(II) catalysts

First, a systematic series of different Co(II) catalysts (see Figure 1) with different substituents for electronic modulation were selected, namely cobalt β -tetrasulphophthalocyanine (**CoTSPc**), **CoTCpC**, **CoPc**, cobalt β -tetraaminophthalocyanine (**CoTAPc**) and cobalt β -tetra(dimethylamino)phthalocyanine (**CoTDMAPc**). These catalysts, if not commercially available, were characterized by high-resolution mass spectrometry (HR-MS; Experimental section and Supplementary Figure 1-3 in Supporting Information), elemental analysis (Supplementary Table 1) and UV-vis spectroscopy (Supplementary Figure 4 in Supporting Information). As the structures of these β -substituted **CoPc** derivatives cannot be defined by single-crystal X-ray diffraction due to the different regioisomers arising from the synthesis with two random β -positions, DFT calculations were applied to analyze the structural and electronic effects of the different substituents by fixing them at the positions of 1, 5, 9 and 13. As can be seen from

Figure 1 and Table 1, the β -substituents result in negligible distortions on the phthalocyanine rings with the nearly 0° angles of plane distortion φ . According to the Hirshfeld population³⁹ listed in Table 1, the Co atomic charges in these molecules vary through incorporation of different substituents. All Co atomic charges are positive, which indicates that the electron density is transferred from cobalt to the phthalocyanine substituents. It is found that the Co atomic charges in the complexes with the $-N(CH_3)_2$, $-NH_2$, $-H$, $-COOH$, and $-HSO_3$ substituents are 0.1959, 0.1971, 0.2038, 0.2084, and 0.2122 e , respectively. This is in the exact order of the increasing ability of the β -substituents to attract electrons ($-N(CH_3)_2 < -NH_2 < -H < -COOH < -HSO_3$) and demonstrates the facile modulations of the electronic properties of these Co(II) catalysts.

Figure 1 | CoPc catalysts. **a** Chemical and **b** calculated structures (PBE0⁴⁰ functional and def2-SVP basis set; with top and side views) of the applied Co(II) catalysts, highlighting the electronic effects caused by the different β -substituents. The white, gray, blue, red and pink colors denote H, C, N, O, S and Co atoms, respectively.

Then cyclic voltammetric methods were utilized to examine their redox properties with respect to the different electron-withdrawing/donating substituents. NMP/TEA (NMP = *N*-methylpyrrolidone; TEA = triethylamine; v:v = 5:1) mixed solvent was chosen as the electrolyte solvent to fully dissolve the **CoPc** derivatives and mimic the alkaline conditions in subsequent photocatalysis. Studies of their cyclic voltammograms under N_2 revealed their first reduction waves at -0.83 to -1.46 V (vs. Fc^+/Fc^0 unless otherwise stated), mostly attributable to $Co^{II/I}$ reduction^{38,41} events. It has been found that the substituents with stronger electron-withdrawing ability enable the positive shifts of the first reduction wave (Supplementary Figure 5 and 6; Table 1), further manifesting the electronic effect. Meanwhile, the CVs of these complexes show enhanced currents in the presence of CO_2 and the addition of phenol as an additional proton source, displaying their catalytic capabilities under corresponding conditions in photocatalysis.

Table 1 Summary of the geometric parameters of the cobalt phthalocyanine catalysts presenting the Co-N bond length (Å), the angle of plane distortion (φ , °), Hirshfeld Co atomic charge (e) and the position of 1st reduction waves (V vs. Fc^+/Fc^0) in their CVs.

Molecules	$d(\text{Co-N})$	φ	Hirshfeld Co atomic charge	1st reduction wave
CoTDMAPc	1.9274	0.00	0.1959	-1.46
CoTAPc	1.9272	0.00	0.1971	-1.43
CoPc	1.9266	0.00	0.2038	-1.38
CoTCPc	1.9269	0.00	0.2084	-0.88
CoTSPc	1.9265	0.02	0.2122	-0.83

Structural and photophysical properties of Cu(I) PSs

Subsequently, four heteroleptic Cu(I) complexes of the type $[\text{Cu}(\text{P}^{\wedge}\text{P})(\text{N}^{\wedge}\text{N})]^+$ were prepared as PSs (Figure 2a). Two different $\text{P}^{\wedge}\text{P}$ ligands, namely DPEphos (= bis[(2-diphenylphosphino)phenyl]ether) and xantphos as well as two $\text{N}^{\wedge}\text{N}$ ligands, bcp (= bathocuproine) and pbcp (= 2,9-dimethyl-4,7-di(pyridin-4-yl)-1,10-phenanthroline), were employed in a pair-wise manner to afford four Cu(I) complexes. Two pendant pyridines were introduced at the 4,7-position of the phenanthroline moiety in **CuPBCP** and **CuPBCP'** with the aim to generate a coordinative interaction with the macrocyclic Co(II) catalysts. The purities and structures of these complexes were clarified by elemental analysis and ^1H NMR spectroscopy (Supplementary Table 1 and 2). The new Cu(I) dyes containing the pbcp ligand, *i.e.* $[\text{Cu}^{\text{I}}(\text{xantphos})(\text{pbcp})]\text{PF}_6$ (**CuPBCP**) and $[\text{Cu}^{\text{I}}(\text{DPEphos})(\text{pbcp})]\text{PF}_6$ (**CuPBCP'**), were further characterized by ^1H - ^1H NMR correlation spectroscopy (COSY; Supplementary Figure 7 and 8), HR-MS (Supplementary Figure 9 and 10) and single-crystal X-ray diffraction (Supplementary Figure 11 and 12, Supplementary Table 3) methods, respectively. Analysis of the crystal structures of $[\text{Cu}^{\text{I}}(\text{xantphos})(\text{bcp})]\text{PF}_6$ (**CuBCP**)⁴² and $[\text{Cu}^{\text{I}}(\text{DPEphos})(\text{bcp})]\text{PF}_6$ (**CuBCP'**)⁴³ and comparison with those the Cu(I) PSs with the same $\text{P}^{\wedge}\text{P}$ ligand reveal only negligible changes in the dihedral angles (Supplementary Table 4) between the $\text{P}^{\wedge}\text{P}$ and $\text{N}^{\wedge}\text{N}$ ligand planes, showing that the replacement of the bcp ligand with the pbcp ligand does not lead to significant configurational differences.

Figure 2 | Cu(I) PSs. **a** Chemical structures, **b** UV-vis absorption spectra and **c** steady-state fluorescent spectra of Cu(I) PSs, including **CuBCP** (pink), **CuBCP'** (azure), **CuPBCP** (orange) and **CuPBCP'** (turquoise). Deaerated 50 μM CH₃CN solutions were used. [Ru(bpy)₃](PF₆)₂ (gray) serves as the external reference for Φ_{em} determination.

We then applied various methods to investigate the photophysical and redox properties of the four Cu(I) PSs, which are summarized in Supplementary Table 4. The UV-vis and steady-state fluorescent spectra were measured in deaerated CH₃CN. The comparison of the UV-vis spectra (see Figure 2b) displays that the visible-light absorption of the four Cu(I) PSs are quite similar. More specifically, at about 380 nm, **CuPBCP** and **CuPBCP'** (both with pyridine moieties) have a lower absorbance than **CuBCP** and **CuBCP'**. The steady-state fluorescent spectra (see Figure 2c) show that the utilization of the bcp ligand induces stronger luminescence, attributed to the triplet states of metal-to-ligand charge transfer (³MLCT), under excitation at 450 nm compared to the complexes with the pbcp ligand. The electron-withdrawing effect of pyridine pendants in **CuPBCP** and **CuPBCP'** may lower the luminescent abilities. Due to the exciplex quenching effect posed by the CH₃CN coordination to the excited Cu dye,⁴⁴ the emission quantum yields (Φ_{em}) of all four Cu(I) complexes are relatively low. We thus calculated the Φ_{em} values with the reference of [Ru(bpy)₃](PF₆)₂ (Φ_{em} = 0.018 in ambient CH₃CN).⁴⁵ The following descending order of Φ_{em} values was found (Supplementary Table 4) to be **CuBCP'** (0.60%) > **CuBCP** (0.58%) > **CuPBCP'** (0.44%) > **CuPBCP** (0.23%). We further determined the excited state lifetimes by time-resolved fluorescent spectroscopy using time-correlated single photon counting (TCSPC; Supplementary Figure 13). The weighted average lifetimes of the Cu(I) PSs follow the same trends as their Φ_{em} with **CuBCP**, **CuBCP'**, **CuPBCP** and **CuPBCP'** displaying lifetimes of 280, 256.8, 74.2 and 63.8 ns, respectively (Table 4). The triexponential decay traces of the excited **CuPBCP** and **CuPBCP'** are consistent with markedly short lifetimes < 100 ns, which suggest the

presence of several decay pathways and will be further discussed later. To sum up, the Cu(I) PSs bearing the xantphos or bcp ligands display higher Φ_{em} values and excited state lifetimes than those with DPEphos or pbcp, respectively.

Furthermore, cyclic voltammetry in combination with the spectroscopic results discussed above was applied to evaluate the excited-state redox potentials^{46,47} of the Cu(I) PSs (Supplementary Figure 14 and Supplementary Table 4). It can be seen that the reductive quenching potentials ($E_{\text{q,red}}$) of the xantphos-based Cu(I) PSs are more positive than the two complexes with DPEphos (1.34/1.51 V vs. 1.26/1.21 V for **CuBCP/CuPBCP** vs. **CuBCP'/CuPBCP'**, Supplementary Table 4), indicative of the stronger driving force of reductive quenching pathway.^{27,30,31,48,49} As the reductive quenching is the preferred pathway using such Cu(I) PS,^{30,50} this should be favorable to drive the CO₂ reduction catalysis. With this knowledge of the four Cu(I) PSs, the correlation between photocatalytic performances and their properties will be examined by the following catalytic experiments.

Modulation on catalysts for photocatalytic CO₂ reduction

With basic understanding of the above Cu(I) PSs and Co(II) catalysts, they were then used for the visible-light-driven reduction of CO₂ using a mixture CH₃CN/TEA and BIH (1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[*d*]imidazole) as the sacrificial electron donor. As photo-induced dissociation of the diphosphine ligand is a commonly observed drawback of heteroleptic [Cu(P[^]P)(N[^]N)]⁺ complexes,^{51,52} a general protocol was followed,⁵³ where 1.0 mM diphosphine ligand (2.0 eq. of PS) was added to the catalytic mixture to inhibit its dissociation during photocatalysis. We first screened the Co(II) catalysts together with **CuBCP** as the PS (Table 2, entries 1-5) under 450 nm irradiation. All five Co(II) catalysts enabled the selective formation of CO with only trace amounts of H₂ and no liquid products, providing CO selectivity over 97%. **CoTCpC** showed the highest catalytic performance in terms of CO yield, followed by **CoTSPc**, **CoPc**, **CoTAPc** and **CoTDMAPc** (Figure 3a). As a result, an impressive increase of more than ten-fold in catalytic efficiency is achieved from **CoTDMAPc** to **CoTCpC**. Hence, the usage of electron-withdrawing β -substituents tend to increase the catalytic performances of Co(II) catalysts, with **CoTCpC** as the optimal one, while the more electron-withdrawing **CoTSPc** shows a lower activity.

It should be noted that all components are necessary to afford a substantial amount of CO in the representative **CuBCP/CoTCpC** system (Supplementary Table 5), and some factors were further considered for a systematic optimization of the photocatalytic system applying the best catalyst, *i.e.* **CoTCpC**. As depicted by Figure 3b and S15, a decreasing concentration of **CoTCpC** can significantly increase the TON with a maximum of 2950 at 0.2 μM within 1 h (Table 3, entry 6). Conversely, the CO yield (ca. 110 μmol when deactivated; Supplementary Figure 15) reached a plateau at catalytic

concentrations over 100 μM **CoTCPc**. This is most likely because the increasing **CoTCPc** concentration leads to a stronger absorption of irradiated light at 450 nm and thus precludes the excitation of PS, as indicated by their partially overlapped UV-vis spectra (Supplementary Figure 16). Beside catalyst concentration, the addition of a proton source, like phenol, H_2O or 2,2',2''-trifluoroethanol, can significantly promote the catalytic activity (Supplementary Figure 17). This can be explained by the facilitation of proton-dependent chemical steps in CO_2 reduction.^{54,55} More impressively, by varying the irradiation wavelengths (*i.e.* 405, 425 and 450 nm) and impairing the intensity to 40 mW cm^{-2} , a maximum quantum efficiency (Φ) of 63.5% can be obtained at 425 nm (Figure 3c and 3d). This Φ is comparable to state-of-the-art molecular systems for photocatalytic CO_2 reduction and even better than some noble-metal-based ones like *fac*-[Re{4,4'-(MeO)₂bpy}(CO)₃{P(OEt)₃}]/*fac*-[Re(bpy)(CO)₃(CH₃CN)]⁺⁵⁶ (Φ_{CO} = 59% at 365 nm), a Ru-Re dyad (Φ_{CO} = 45% at 480 nm),⁵⁷ etc. Most important, this Φ value is the highest value among the noble-metal-free systems, including Cu-purpurin/FeTDHPP⁵⁸ (Φ_{CO} = 6% at 450 nm; FeTDHPP = chloroiron(III) 5,10,15,20-tetrakis (2',6'-dihydroxyphenyl)-porphyrin), *p*-terphenyl/Co-cyclam¹⁷ ($\Phi_{\text{HCOOH+CO}}$ = 25% at 313 nm; cyclam = 1,4,8,11-tetraazacyclotetradecane), [Cu₂(P₂bph)₂]²⁺/*fac*-Mn(4,4'-(OMe)₂bpy)(CO)₃Br²⁹ ($\Phi_{\text{HCOOH+CO}}$ = 57% at 436 nm; P₂bph = 4,7-diphenyl-2,9-di(diphenylphosphinotetramethylene)-1,10-phenanthroline), etc. The CO production of the **CuBCP/CoTCPc** system ceased after 2 h of reaction, most presumably due to the decomposition of the Cu PS,^{50,51} whereas the high Φ of this photocatalytic system is still impressive. On the other hand, the reaction with ¹³CO₂ atmosphere exhibited the significant formation of ¹³CO (m/z = 29; Supplementary Figure 18), evidencing that the CO was produced from the reduction of CO₂ rather than from the decomposition of organic components. Overall, the above photocatalytic results demonstrate the extraordinary performance of the **CuBCP/CoTCPc** system for photocatalytic CO₂-to-CO conversion.

Table 2. Results of photocatalytic CO₂ reduction experiments.*

Entry	PS	Catalyst	n(CO) (μmol)	n(H ₂) (μmol)	TON(CO)	CO%
1	CuBCP	CoTDMAPc	8.4	0.23	42	97
2	CuBCP	CoTAPc	23.9	0.56	120	98
3	CuBCP	CoPc	37.0	0.79	185	98
4	CuBCP	CoTSPc	51.5	0.95	258	98
5	CuBCP	CoTCPc	86.8	0.62	456	99
6 ^b	CuBCP	CoTCPc	2.16	0.07	2950	97
7	CuBCP'	CoTCPc	57.2	0.52	286	99
8	CuPBCP	CoTCPc	4.2	0.55	21	88
9	CuPBCP'	CoTCPc	3.3	0.48	16	87

*Standard condition: Cu(I) PS (0.5 mM), diphosphine ligand (1.0 mM), Co(II) catalyst (0.05 mM), phenol (5.0 v%),

and BIH (20 mM) in 4 mL CH₃CN/TEA (v:v = 5:1) within 1 h of 450-nm irradiation (100 mW cm⁻²) under 1 atm CO₂.

Figure 3 | Photocatalytic CO₂ reduction. **a** Time profiles of photocatalytic CO (star) and H₂ (circle) formation using 0.5 mM CuBCP and 50 μM CoTCpC (red), CoTSPc (orange), CoPc (violet), CoTAPc (blue) or CoTDMAPc (green) under 450 nm irradiation (100 mW cm⁻²). **b** TON comparison for CO and H₂ formation at varying concentrations of CoTCpC with CuBCP. **c** Wavelength dependency of the time profiles of photocatalytic CO (star) and H₂ (circle) formation with 0.5 mM CuBCP and 50 μM CoTCpC at 450 (blue), 425 (red) or 405 (green) nm light irradiation (40 mW cm⁻²). **d** Φ values for CO and H₂ formation at 5 min of 450, 425 or 405 nm light irradiation (40 mW cm⁻²) from CuBCP/CoTCpC system. **e** Time profiles of photocatalytic CO (star) and H₂ (circle) formation with 50 μM CoTCpC and 0.5 mM CuBCP (pink), CuBCP' (azure), CuPBCP (orange) and CuPBCP' (turquoise).

Modulations on PSs and interaction for photocatalytic CO₂ reduction

Next, the four different Cu(I) PSs were tested with the best CoTCpC catalyst under the same optimized catalytic conditions (Figure 3e and Table 2, entries 5, 7-9). The activity was found to follow a descending order of CuBCP > CuBCP' > CuPBCP > CuPBCP'. It is obvious, that the two Cu(I) PSs bearing the xantphos ligand exhibit higher performances than their counterparts with DPEphos. The differences can be ascribed to the bulkier and more rigid nature of xantphos than DPEphos. The bulky xantphos ligand can protect the copper center against undesired exciplex quenching by solvent molecules or counter ions. Moreover, xantphos is less flexible, which prevents the unwanted flattening in the excited state. Accordingly, it has been reported that in terms of photocatalytic hydrogen

evolution, the replacement of the DPEphos ligand by the xantphos not only enhanced the (photo)stability, but also improved the photophysical properties (*e.g.* excited-state lifetimes).^{24,59} Here we also observed that the photophysical properties of **CuBCP**, including Φ_{em} and lifetimes, are better than those of **CuBCP'**, which are consistent with the observed activity order, demonstrating that the photophysical properties of Cu(I) PSs play a key role in CO₂ photoreduction.

The most notable observation is that the use of the pyridine-containing pbcp ligand does not result in an improved reduction of CO₂, which is most possibly caused by the much shorter excited state lifetimes of **CuPBCP** and **CuPBCP'**. Nevertheless, our previous studies indicate that a slightly inferior PS can be compensated by reinforcing the intermolecular electron transfer via coordinative interaction.³⁸ As a type of covalent bonds, the labile coordinate bond not only endows the dynamic stability in the coordinatively interacted system, but also additionally facilitates the electron transfer processes in a manner of inner-sphere electron transfer (ISET) via the coordinative interaction⁶⁰ as either a stable adduct or a transition state, potentially circumventing the diffusion limit.⁶¹ Therefore, we also examined the coordinative interaction by ¹H NMR titration experiments. Prior to titration, the proton assignment for **CuPBCP** was carried out in *d*₇-DMF (Supplementary Table 2 and Supplementary Figure 19), because this solvent was suited to prepare highly concentrated **CoTCPc** solutions essential for titration. Then the addition of **CoTCPc** into the *d*₇-DMF solution of **CuPBCP** induced notable shifts and a broadening of the proton signals responsible for the pbcp ligand, indicating the interaction between **CoTCPc** and **CuPBCP** via the pbcp ligand, most possibly by the desired coordination interaction (Supplementary Figure 20). The binding constant^{38,62} can be calculated on the basis of the proton shifts in binding fit, which is estimated as a 1:1 binding constant (K_{11}) of $3795 \pm 118 \text{ M}^{-1}$ in non-cooperative 1:2 model (see detailed analysis in Experimental section and Supplementary Table 6). The K_{11} value is of the same order of 10^3 M^{-1} as the measured value from the coordinative interaction between a pyridine-appended Ir(III) PS and **CoPc**,³⁸ supporting the presence of a dynamic coordinative interaction between **CuPBCP** and **CoTCPc**. This optimal non-cooperative 1:2 model suggests each of the two pyridine pendants in **CuPBCP** can coordinate to a **CoTCPc** molecule without interference. In contrast, the parallel titration between **CuBCP** and **CoTCPc** yielded only negligible shift for all proton signals (Supplementary Figure 21), supporting the absence of interaction without the pbcp ligand. The above comparison demonstrates well the coordinative

interaction between **CoTCpC** and **CuPBCP**. Furthermore, the ^1H NMR titration between **CuPBCP** and **CoTCpC** was carried out in the presence of excess TEA (5%). This investigation aims at estimating the competitive coordination between **CuPBCP** and TEA toward **CoTCpC**, because TEA can also axially coordinate to **CoTCpC**,^{38,63} as herein revealed by UV-vis spectra in the absence and presence of TEA (Supplementary Figure 22). During the ^1H NMR titration in the **CuPBCP/CoTCpC/TEA** system, the shifts were still visible (Supplementary Figure 23), and the binding constant was calculated as $1611 \pm 45 \text{ M}^{-1}$ in non-cooperative 1:2 model (Supplementary Table 7). This value is in the same order of magnitude and in the same binding model as the TEA-free system, demonstrating the tolerance of coordinative interaction against competitive TEA coordination. According to the above results, substantial coordinative interaction has been achieved between **CuPBCP** and **CoTCpC**, but this cannot compensate for the impaired photophysical properties caused by the replacement of bcp with pbcp, leading to diminished activity. The further reasons for the loss of activity caused only by the replacement of two C atoms by N atoms should be investigated in detail for the rational design of Cu(I) PSs, which will be discussed later.

Catalytic mechanism of **CoTCpC**

A mechanistic understanding of the best **CoTCpC** catalyst from the sequence of **CoPc** derivatives is meaningful for further optimization of this family of catalysts. First, the CVs of **CoTCpC** can provide some redox catalytic insights (Supplementary Figure 5). Under N_2 , three reduction events appeared in the CV of **CoTCpC** in NMP/TEA medium. The first reversible one should be attributed to $\text{Co}^{\text{II/I}}$ reduction, while the subsequent reduction waves may be induced by the reduction on the Pc ring.⁶⁴ The introduction of CO_2 induces a current enhancement at the second reduction wave, indicating that the two-electron reduced species is able to initiate the catalytic reduction of CO_2 . Further, an additional catalytic wave appeared at the $\text{Co}^{\text{II/I}}$ reduction wave in the CV upon the addition of phenol under CO_2 , showing the decreased overpotential required for effective catalysis by enabling the proton-dependent transfer.^{54,65} The quite positive catalytic potential for CO_2 reduction should contribute to the high catalytic activity of **CoTCpC** in photocatalysis. With the above clues, a catalytic cycle for **CoTCpC** can be proposed (Supplementary Figure 24), in which the one-electron reduced catalyst, the Co(I) species, can bind and reduce CO_2 with protonation to yield Co-COOH intermediate, followed by the

cleave of C-OH bond to release CO.

Structure-activity relationship

Aforementioned electrochemical results have illustrated that the electron-withdrawing effects effectively impose positive shifts of $\text{Co}^{\text{II/I}}$ redox couple, which is amenable for photocatalysis at lower overpotentials.⁵⁴ However, **CoTSPc**, with the most electron-withdrawing sulfonic-acid substituents, gave a minor performance than **CoTCPc**. To preliminarily decipher the structure-activity relationship, additional DFT calculations (PBE0⁴⁰ functional and def2-SVP basis set) based on the above proposed mechanism were carried out. The calculated reactions involve the rate-determining generation of *COOH intermediate from the adsorption and reduction of CO_2 at the Co site. The *COOH intermediate then undergoes a proton-coupled electron transfer step to cleave C-OH bond and evolves *CO, which is ultimately desorbed to recover the free Co center. We have obtained the calculated structures derived from the used Co(II) catalysts that adsorb CO and COOH with corresponding Gibbs free energies, most importantly the $\Delta G(\text{*COOH})$ and $\Delta G(\text{*CO})$ (Supplementary Table 8). It can be seen that the values of $\Delta G(\text{*COOH})$ for all **CoPc** molecules are close, showing a negligible correlation with the order of catalytic activity. In contrast, the order of the $\Delta G(\text{*CO})$ values is more consistent with the order of catalytic activity (Figure 4), which suggests that the CO desorption step plays a crucial role for the catalytic performance. The key contribution of CO desorption ability in CO_2 reduction has been extensively documented.^{66,67} This DFT-calculated volcano-type plot computationally indicates **CoTCPc** as the best catalyst in our case, while this primary observation demands more **CoPc** derivatives as well as more detailed theoretical/experimental works, which are on the progress, for further confirmation.

Figure 4 | Structure-activity relationship. Plots of $\Delta G(*CO)$ (red diamond) and CO production rate (blue pentagon) of five Co(II) catalysts versus their Hirshfeld Co atomic charges, showing the correlations between $\Delta G(*CO)$ and catalytic activity as well as the volcano-like trend of electronic effects.

Photo-induced electron transfer

The proposed catalytic mechanism and the observed structure-activity relationship were further supported by verifying the underlying photo-induced electron transfer processes. For this purpose, we focused on the investigation of the excited states of **CuBCP** and **CuPBCP** to also analyze the low performances caused by the pyridine pendants. Firstly, quenching experiments with the excited state of the Cu(I) PSs were carried out by steady-state fluorescent spectroscopy (Figure 5 and Table 3). On one hand, both **CuBCP** and **CuPBCP** can be effectively quenched by BIH (Figure 5a and 5b), which suggests a reductive quenching pathway (see Equation 1, 2 and 3). On the other hand, the reductive quenching constant for BIH ($k_{q(\text{BIH})}$), as determined by Stern-Volmer (S-V; Equation 4) plots, is higher for **CuBCP** than for **CuPBCP** (5.23 vs. $3.27 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$; Figure 5c). This is contradictory to the more positive $E_{q,\text{red}}$ value of **CuPBCP** compared to **CuBCP** (1.51 vs. 1.34 V), inferring that other factors, most presumably the short-lived excited state, induce the lethargic quenching between **CuPBCP** and BIH. The reductive quenching belongs to dynamic quenching,³⁰ as the lifetime of **CuBCP** can also be reduced upon the addition of BIH with a comparable quenching constant, $k_{q(\text{BIH})}' = 8.95 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Supplementary Figure 25). On the other hand, we also observed significant quenching by the addition of **CoTCPc** in both steady-state (Figure 5d-5f) and transient fluorescent spectra (Supplementary Figure 26). However, the slopes in S-V plots with **CoTCPc** for both **CuBCP** and **CuPBCP** are not linear with shifted emission peaks. These observations are consistent with the absorption of excitation light and excited luminescence (Supplementary Figure 16) rather than

oxidative quenching (Equation 1, 5 and 6) by **CoTCPc**.

$$\frac{I_0}{I} = 1 + k_q \tau_0 [\text{Q}] \quad (4)$$

$$\frac{\tau_1}{\tau} = 1 + k_r \tau_1 [\text{Q}] \quad (7)$$

We then implemented transient absorption (TA; Figure 6 and Table 3 with Experimental details in SI) spectroscopy to further verify the electron transfer pathway and analyze the different states of the Cu(I) PSs. First, for **CuBCP**, the excitation at 420 nm can induce significant absorption changes peaking at 330 and 530 nm, in which the latter can be attributed to the absorption of the ³MLCT species (Figure 6a). The excited species has a lifetime (τ_0') of 301.6 ns, which is close to the result of time-resolved fluorescent lifetime $\tau_0 = 280.0$ ns). The addition of an excess of BIH (60 equivalents) induces a long-lived species ($\tau_1 = 75.8$ μs ; Figure 6b) with a new absorption spectrum with a main absorption at 350 nm, indicative of the formation of a reduced state, **CuBCP⁻**, and accordingly the reductive quenching pathway (Equation 2). In contrast, negligible changes occur in the shape of TA spectra upon the addition of **CoTCPc**, proving the absence of oxidative quenching pathway (equation 5). Further, the spectral intensity was markedly reduced and the lifetime was slightly reduced in a non-linear manner (Supplementary Figure 26a-26b), which can be attributed to the significant absorption of **CoTCPc** rather than the oxidative quenching. Subsequently, an increasing concentration of **CoTCPc** decreased the longevity of **CuBCP⁻** and a second-order reaction constant, $k_r = 4.73 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ can be calculated via equation 7.³⁸

The TA spectral evolution of **CuPBCP** upon excitation (Figure 6e) and the addition of BIH (Figure 6f) or **CoTCPc** (Supplementary Figure 26c-26d) are similar to those of **CuBCP** with analogous conclusions. It can be noticed that the lifetime of **CuPBCP⁻** is much longer than that of **CuBCP⁻** (470.8 vs. 75.8 μs), which could be related to the different electron localization in the varied diimine

ligands. Moreover, the further reaction between **CuPBCP** and **CoTCpC** at increasing concentrations gave rise to a higher $k_r = 6.91 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ than that of **CuBCP**. Considering that their reducing abilities are nearly identical (-1.36 V for **CuBCP** and -1.37 V for **CuPBCP**) and that the influence of the different lifetimes of their reduced states is eliminated via equation 7, the faster k_r of **CuPBCP** should be mainly attributed to the coordinative interaction between the pyridine substituents and the macrocyclic **CoTCpC**.

From the numerous results of the different spectroscopic methods discussed above, several conclusions can be drawn. First, the photocatalytic reduction of CO_2 to CO using the system of Cu(I) PS and **CoTCpC** follows the reductive quenching pathway. Second, the light absorption of **CoTCpC** induces the apparent fluorescent quenching, and the oxidative quenching pathway has been excluded by characteristic TA spectra. Last and importantly, despite the very short-lived excited state of **CuPBCP** which impedes photocatalysis, the coordinative interaction between **CuPBCP** and **CoTCpC** still reinforces their intermolecular electron transfer. Hence, the principal strategy of designing a diimine ligand enabling a molecular interaction between PS and catalyst is very promising for future research.

Figure 5 | Steady-state emission quenching. Emission spectra of a CH_3CN solution containing 0.2 mM Cu(I) PS (**CuBCP** or **CuPBCP**), in the absence and presence of varying concentrations of quencher (BIH or **CoTCpC**), respectively. **a** **CuBCP**/BIH; **b** **CuPBCP**/BIH; **d** **CuBCP**/**CoTCpC**; **e** **CuPBCP**/**CoTCpC**. Linear fitting of ratio of luminescence intensity versus **c** [BIH] or **f** [**CoTCpC**].

Table 3 Related data and calculated reaction constants from steady-state fluorescent quenching and TA experiments in degassed CH₃CN solutions.

PS	Steady-state fluorescent quenching		TA		
	τ_0 (ns)	$k_{q(\text{BIH})} (\times 10^9 \text{ M}^{-1} \text{ s}^{-1})$	τ_0' (ns)	τ_1 (μs)	$k_r (\times 10^8 \text{ M}^{-1} \text{ s}^{-1})$
CuBCP	280.0	5.23	301.6	75.8	4.73
CuPBCP	74.2	3.27	53.3	470.2	6.91

Figure 6 | Nanosecond TA spectroscopy. Nanosecond TA spectroscopic results of (a-d) **CuBCP** and (e-h) **CuPBCP**.

TA spectra of **a** 0.03 mM **CuBCP** or **b** 0.03 mM **CuBCP** with 0.20 mM BIH. **c** Kinetic traces of 0.03 mM **CuBCP** with 0.20 mM BIH and 0~18 μM **CoTCPc**. **d** Plot of $(\tau_1 / \tau - 1)$ versus $[\text{CoTCPc}]$ with linear fitting for the **CuBCP** system with BIH. TA spectra of **e** 0.05 mM **CuPBCP** or **f** 0.05 mM **CuPBCP** with 0.30 mM BIH. **g** Kinetic traces of 0.05 mM **CuPBCP** with 0.30 mM BIH and 0~20 μM **CoTCPc**. **h** Plot of $(\tau_1 / \tau - 1)$ versus $[\text{CoTCPc}]$ with linear fitting for the **CuPBCP** system with BIH. The data were collected by following the spectra at 360 nm in Ar-saturated CH₃CN upon excitation at 420 nm.

Photocatalytic CO₂ reduction with other molecular catalysts

Besides the catalytic properties and mechanisms, the above systematic studies also reveal that the short-lived excited state of **CuPBCP** (analogous for **CuPBCP'**) should be the main reason to induce a low activity in light-driven CO₂ reduction. To unfold this mystery, the electronic and structural properties of the ground- and excited-state conformations of **CuBCP** and **CuPBCP** were studied

through steady-state and time-resolved X-ray absorption near-edge (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopies (Supplementary Figure 27). The ground-state XANES spectra of **CuBCP** and **CuPBCP** (Supplementary Figure 27a) display identical features in the rising edge and main edge regions from 8980-9020 eV, indicating similar local coordination spheres, and geometrical conformations. A main peak was further observed at 8984 eV in the XANES spectra reflecting the nature of the 4p_z orbital in the pseudo-tetrahedral coordination environments⁶⁸⁻⁷¹ of these Cu(I) complexes (Supplementary Figure 27a). The **CuBCP** and **CuPBCP** EXAFS spectra reveal a prominent peak (Peak I) corresponding to the averaged Cu-N and Cu-P bond distances (Supplementary Figure 27b). The EXAFS fits for the extraction of the actual bond distances are shown in Supplementary Figure 28, Table 4 and Supplementary Table 9. Analysis of the EXAFS spectra of **CuBCP** and **CuPBCP** clearly resolved two Cu-N and Cu-P distances at 2.08/2.09 and 2.30 Å, respectively (Table 4 and Supplementary S9, Supplementary Figure 27). The observed trends in the experimental EXAFS are in good agreement with structural parameters from XRD analysis and DFT optimized coordinates (Supplementary Figure 27c, Supplementary Table 9-11), confirming the suitability of the theoretical method to account for the main structural trends in the Cu(I) PSs.

Following the above steady-state XANES and EXAFS measurements, picosecond time-resolved X-ray absorption (tr-XAS) spectroscopy was employed to capture snapshots of the excited state conformations of the **CuBCP** and **CuPBCP** complexes. In this scenario, a laser pulse (pump) initiates a photophysical process within the molecules under study and an X-ray pulse (probe) is used to interrogate its evolving optical response at varying delays.⁷²⁻⁷⁷ The solutions of the Cu(I) PSs were pumped at 400 nm wavelength. The tr-XAS spectra were collected before (laser-off) and after (laser-on) the laser excitation (Figure 7). In particular, by subtracting the laser-off from the laser-on spectrum, a transient signal is obtained for each pump-probe delay and provides information on the photoinduced dynamics. The transient signal monitored at 100 ps features two intense bleach transitions at 8982 and 8988 eV together with a broad positive peak at ~ 9000 eV (Figure 7), corresponding to the ground state bleaching of the Cu(I) PSs and formation of the formally oxidized Cu(II) and ³MLCT excited state. Interestingly, clear changes were not only observed in the oxidation state of Cu but also in its electronic configuration and coordination geometry. MLCT transition causes a 3d electron to be promoted to the low-lying π^* orbital of the ligand upon excitation, thus leading to a d level

occupational change from $3d^{10}$ to $3d^9$. A pre-edge feature corresponding to the $1s$ to $3d$ quadrupole transition which gains intensity due to $4p$ mixing^{78,79} into the Cu $3d$ shell is thus observed at low photon energies at 8979 eV (Figure 7).

Figure 7 | Time-resolved XAS. Time-resolved XAS spectra (laser on/off) corresponding to the excited states of 0.8 mM **CuBCP** (magenta) and **CuPBCP** (green) owing to MLCT transitions at a delay of 100 ps between laser and X-ray pulses. The inset shows the pump-probe delay scans recorded at 9000 eV, corresponding to the decay of the excited-state species with the fittings of **CuBCP** (magenta) and **CuPBCP** (green).

Figure 8 | XAS. Normalized Cu K-edge XANES of the laser-off spectrum (black), laser-on (in magenta) and reconstructed excited state spectra (in dotted magenta) of **CuBCP** assuming 35% excited state. (b) Experimental Fourier transforms of k^2 -weighted Cu EXAFS of the laser-off (in black) and reconstructed excited state (in dotted magenta) of **CuBCP**. The inset shows the back Fourier transformed experimental (solid line) and fitted (dashed lines)

$k^2[\chi(k)]$ of the laser off and reconstructed spectra of **CuBCP**. Experimental spectra for the reconstructed spectra were calculated for k values of 2-10 Å⁻¹. (c) Normalized Cu K-edge XANES of the laser-off (in red), laser-on (green) and reconstructed excited state spectra (dotted green) of **CuPBCP** assuming 27% excited state. (d) Experimental Fourier transforms of k^2 -weighted Cu EXAFS of the laser off (red) and reconstructed excited state (dotted green) of **CuPBCP**. The inset shows the back Fourier transformed experimental (solid lines) and fitted (dashed lines) $k^2[\chi(k)]$ of the laser off and reconstructed excited state of **CuPBCP**.

Table 4. Comparison of structural parameters obtained from DFT calculations and EXAFS analysis for **CuBCP** and **CuPBCP**. Bond lengths are given in Å.

Complex	EXAFS fits	DFT ground state (Å)	DFT excited state (Å)
CuBCP	Ground state:	Cu-N: 2.07, 2.06	Cu-N: 2.01, 2.07
	Cu-N: 2 × 2.08	Cu-N _{avg} : 2.07	Cu-N _{avg} : 2.04
	Cu-P: 2 × 2.30	Cu-P: 2.23, 2.26	Cu-P: 2.31, 2.35
	Excited state:	Cu-P _{avg} : 2.25	Cu-P _{avg} : 2.33
	Cu-N: 2 × 2.01	Cu-O: 3.17	Cu-O: 3.29
	Cu-P: 2 × 2.39	Torsional angle: 86.5 °	Torsional angle: 79.6°
			ΔTorsional angle: -6.84°
CuPBCP	Ground state:	Cu-N: 2.07, 2.07	Cu-N: 2.02, 2.05
	Cu-N: 2 × 2.09	Cu-N _{avg} : 2.07	Cu-N _{avg} : 2.04
	Cu-P: 2 × 2.30	Cu-P: 2.23, 2.26	Cu-P: 2.31, 2.36
	Excited state:	Cu-P _{avg} : 2.25	Cu-P _{avg} : 2.34
	Cu-N: 2 × 1.99	Cu-O: 3.16	Cu-O: 3.29
	Cu-P: 2 × 2.43	Cu-N: 9.13, 9.15	Cu-N: 9.13, 9.17
		Torsional angle: 86.4°	Torsional angle: 78.5°
			ΔTorsional angle: -7.89°

The kinetics of the decay of the ³MLCT excited state were additionally monitored by fixing the X-ray photon energy at 9000 eV and varying the time delay between the laser and X-ray pulses (Figure 7 inset and Supplementary Figure 29). The ³MLCT states of **CuBCP** and **CuPBCP** form promptly in less than the ~100 ps pulse duration of the X-rays and decay within 287 ± 63 and 64.3 ± 22.1 ns, respectively, in agreement with the previous time-resolved fluorescent experiments (Supplementary Table 4 and Supplementary Figure 13). The excited state fractions of **CuBCP** and **CuPBCP** were

determined by comparing their laser-off and laser-on XANES spectra (Figure 8a and 8c) to those of previous reported heteroleptic Cu complexes⁸⁰ with similar coordination environments. A relative chemical shift in energy of 2 eV was typically observed between Cu(I) and Cu(II) reference complexes, such that the proportions of excited state of 35% and 27% were estimated in the laser on spectra of **CuBCP** and **CuPBCP**, respectively, and used to plot the actual or reconstructed XANES spectra of the excited states (Figure 8a and 8c).

The formation of a flattened geometry within the ³MLCT state has been well known to enable nucleophilic attack by solvent molecules or counterions thus promoting the formation of a low-energy excited state known as an “exciplex”, which subsequently decays to the ground state.^{70,71} Alternatively, the nature of the solvent can also modify triplet lifetimes without a direct coordination to the metal centre by tuning charge transfer excited state energies.⁸¹ The shortened excited-state lifetime of **CuPBCP** versus **CuBCP** reflects the effect of the pyridine decoration instead of benzene. That is, the pendant pyridine rings in **CuPBCP** seem to account for the decreased stability and lifetime of its ³MLCT state, as they can favour a stronger flattening of the overall excited-state geometry and a larger torsional angle change, as evidenced through DFT geometry optimization calculations and experimental EXAFS fits (Table 4 and Supplementary Table 11). DFT optimization calculations of the excited-state conformation of **CuPBCP** further display a larger torsion of the pendant pyridine rings of -0.729° and -0.229° in comparison to **CuBCP** which display decreased torsions of -0.117° and -0.160° (Supplementary Table 12). The larger torsions in the pyridine rings of **CuPBCP** are consequently presumed to lead to the decreased steric hindrance and enhanced solvent accessibility in its excited-state conformation, namely a stronger exciplex effect.

Discussion

In summary, triple modulations, in terms of catalyst, PS and additional coordinative interactions, have been employed in this work to accomplish high-performance photocatalytic CO₂ reduction to CO, using earth-abundant elements only. An excellent quantum efficiency of 63.5% has been achieved with complete selectivity by the optimal selection of Cu(I) PSs and **CoPc** derivatives. Even more intriguing, the structure-activity relationships for both the catalysts and the PSs have been well verified by combined experimental and theoretical investigations. For the **CoPc** catalysts, the electron-

withdrawing substituents show a promotive effect on the photocatalysis, which are correlated with CO desorption tendencies during catalysis. For the $[\text{Cu}(\text{P}^{\wedge}\text{P})(\text{N}^{\wedge}\text{N})]^+$ PSs, on one hand, in terms of the diphosphine $\text{P}^{\wedge}\text{P}$ ligand, a stronger rigidity of the diphosphine $\text{P}^{\wedge}\text{P}$ ligand (xantphos *vs.* DPEphos) favors the luminescent properties and thus the photocatalytic activity. On the other hand, the results of the time-resolved X-ray absorption spectroscopy and the DFT calculations indicate for the diimine $\text{N}^{\wedge}\text{N}$ ligand that the replacement of phenyl by pyridyl groups enhances exciplex quenching and thus induces short-lived triplet excited states. As a proof-of-concept, the intended coordinative interaction between the pendant pyridine rings in the Cu(I) PSs and the axial sites of **CoTCPC** has been established, which can facilitate the electron transfer between the above two components. Interestingly, the presence of such an interaction does not lead to an increase in catalytic activity, because the performance is still limited by the unstable excited state of the pyridine-decorated PS, noting the impact of delicate ligand modifications. Based on the above merits, we believe that our work opens new avenues to the development of highly cost-efficient molecular systems for CO₂ photoreduction. The above-described experiments on the optimization of photocatalytic systems can serve as an inspiring and systematic guide to improve catalytic performances.

Methods

Materials

5 **CuBCP**,⁸² **CuBCP'**,⁸² **BIH**,⁸³ **CoTSPc**,⁸⁴ **CoTCPC**,^{85,86} and pbcp ligand⁸⁷ were prepared following the
6 previously reported methods. Milli-Q ultrapure water ($> 18 \text{ M}\Omega$) was utilized unless otherwise stated.
7 $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ (97%, Innochem), bis[(2-diphenyl-phosphino)phenyl]ether (DPEphos; 97%,
8 Innochem), 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene (xantphos; 97%, Innochem), 2,9-
9 dimethyl-4,7-diphenyl-1,10-phenanthroline (bathocuproine, bcp; 97%, Innochem), **CoPc** (97%, β -form,
10 Aldrich), **CoTAPc** (95%, Jilin Chinese Academy of Sciences-Yanshen Technology Co., Ltd.), and
11 other chemicals were commercially available and used without further purification.

Instruments

¹H NMR and ¹H-¹H 2D NMR correlation spectroscopy (COSY) spectra were obtained on a Bruker advance III instrument (400 MHz). Electrochemical measurements were carried out using an

electrochemical workstation (CHI 620E). Gas chromatographic analysis was conducted on an Agilent 7820A gas chromatography. The isotopic labeling experiment was conducted under $^{13}\text{CO}_2$ 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) to detect the presence of formate. UV-vis spectra were collected on a Shimadzu UV-3600 spectrophotometer. The emission experiments were conducted on a modular fluorescent life and steady-state fluorescence spectrometer (FLSP1000, Edinburgh Instruments LTD.). The TA spectroscopy was carried out on a laser flash photolysis instrument (LP980, Edinburgh Instruments LTD.). All experiments were operated at room temperature (24~25 °C) unless otherwise stated.

Data availability

Experimental details, Supplementary figures and tables, and computational data are available from the authors. Most data generated in this study are provided in the Supplementary Information/Source Data file. Source data are provided with this paper. The data with CCDC number, **CuPBCP** (2092595) and **CuPBCP'** (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/>.

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Author contributions

J.W.W. conceived and designed this project, J.W.W. and Z.M.L. synthesized the complexes, J.W.W., Z.M.L., Z.L. and Y.H. performed the photocatalytic experiments and luminescence spectroscopies, J.W.W. and M.K. analyzed and discussed the spectroscopic data, J.W.W. conducted the transient absorption spectroscopy and analyzed the data, X.Z. and D.M. carried out the DFT calculations, J.Y., W.H., X.Z. and D.M. operated the time-resolved X-ray absorption spectroscopy and analyzed the data, J.W.W., D.M. and O.G. analyzed the bulk data and provided the funding, J.W.W. organized the collaborations. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Competing Interests

The authors declare no competing interests.

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