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► **To cite this version:**

Vasilis Nikolaou, Chinju Govind, Evangelos Balanikas, Jaya Bharti, Stéphane Diring, et al.. Antenna Effect in Noble Metal-Free Dye-Sensitized Photocatalytic Systems Enhances CO₂-to-CO Conversion. *Angewandte Chemie International Edition*, 2024, 63 (13), pp.e202318299. 10.1002/anie.202318299 . hal-04676872

HAL Id: hal-04676872

<https://hal.science/hal-04676872v1>

Submitted on 24 Aug 2024

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Antenna Effect in Noble Metal-Free Dye-Sensitized Photocatalytic Systems Enhances CO₂-to-CO Conversion

Vasilis Nikolaou,* Chinju Govind, Evangelos Balanikas, Jaya Bharti, Stéphane Diring, Eric Vauthey,* Marc Robert,* and Fabrice Odobel*

Abstract: Dye-sensitized photocatalytic systems (DSPs) have been extensively investigated for solar-driven hydrogen (H₂) evolution. However, their application in carbon dioxide (CO₂) reduction remains limited. Furthermore, current solar-driven CO₂-to-CO DSPs typically employ rhenium complexes as catalysts. In this study, we have developed DSPs that incorporate noble metal-free components, specifically a zinc-porphyrin as photosensitizer (PS) and a cobalt-quaterpyridine as catalyst (CAT). Taking a significant stride forward, we have achieved an antenna effect for the first time in CO₂-to-CO DSPs by introducing a Bodipy as an additional chromophore to enhance light harvesting efficiency. The energy transfer from Bodipy to zinc porphyrin resulted in remarkable stability (turn over number (TON) = 759 vs. CAT), and high CO evolution activity (42 mmol g⁻¹ h⁻¹ vs. CAT).

Fossil fuels, such as natural gas, oil, and coal, constitute the universal primary energy sources.^[1] Their prolonged and intensive usage gave rise to global warming and climate change.^[2] Hence, there is an urgent need to establish a carbon-neutral and circular economy, by utilizing renewable energy sources to transform CO₂ into valuable fuels-chemicals.^[3] Indeed, CO₂ can be converted into useful products, namely formic acid, carbon monoxide, methane, methanol, ethanol, and ethylene.^[4] Even though the reduction of CO₂ into C₂⁺ products (ethylene, ethanol, etc.) is of great commercial interest, carbon monoxide (CO) is also a valuable product of CO₂ reduction reaction (CO₂RR); since it can be obtained with high selectivity and yield.^[5] Furthermore, CO production involves a 2e⁻/2H⁺ process (CO₂ + 2H⁺ + 2e⁻ → CO + H₂O, E^o = -0.53 V, vs. NHE, pH = 7) in contrast to ethanol and ethylene (12e⁻/12H⁺). In

addition, CO is a multipurpose feedstock in numerous industrial applications.^[3b,6]

Various strategies have been explored aiming at efficiently converting CO₂ into CO: i) electrocatalysis, ii) photocatalysis, iii) photoelectrocatalysis, iv) thermochemical, and v) biochemical conversion.^[7] Among all the above-mentioned approaches, solar-driven CO₂-to-CO reduction stands out as an auspicious approach since the abundant, clean, and renewable solar energy is utilized directly without any other additional energy supply.^[8] Over the last decades, numerous homogeneous, heterogeneous as well as hybrid systems combining molecular catalysts and solid/heterogeneous elements have been investigated,^[9] including noble-metal free molecular systems in water as well.^[10]

Dye-sensitized photocatalytic systems (DSPs) have great potential since they are extremely robust, highly tunable and potentially low-cost.^[11] In a typical CO₂-to-CO reducing DSP system, nanoparticles (NPs) of a semiconductor (e.g. TiO₂) are functionalized with a photosensitizer (PS), and a CO₂R catalyst (CAT) in order to form the heterogeneous photocatalyst. Upon light excitation, the PS injects electrons to the conduction band (CB) of TiO₂, which are subsequently transferred to the CO₂R CAT. Finally, CO₂ is being reduced to CO, whereas the oxidized PS (PS⁺) is regenerated by a sacrificial electron donor (SED). Interestingly, compared to the large number of DSPs for H₂ evolution in the literature,^[11a,12] only a few CO₂ reducing DSPs have been developed, notably by S.O. Kang and co-workers.^[13] However, in most of these examples, ReCl(L)(CO)₃ (L = 2,2'-bipyridine derivative) complex is the CO₂R CAT, containing one of the rarest elements in the earth's crust.^[14] One example of noble metal-free DSP system for CO₂ photo-reduction has been published, involving a Mn(I) catalyst for selective formate production (> 99 %) with a TON of 250.^[15]

Herein, we present the first noble metal-free DSPs for CO₂-to-CO conversion, by utilizing a zinc-porphyrin (ZnP) as PS and a cobalt-quaterpyridine (CoQP) as the CO₂R

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CAT. Moving one step forward, a Bodipy (**BDP**) was introduced as an additional light harvester to enhance photon capture. Thanks to energy transfer (EnT) from the **BDP** to the **ZnP**, antenna effect boosted the efficiency of DSP. Although this concept has been employed twice in DSPs for H₂ evolution,^[16] a similar approach for CO₂-to-CO reduction has not yet been reported. As illustrated in Figure 1, the advantages of this photocatalytic systems are:

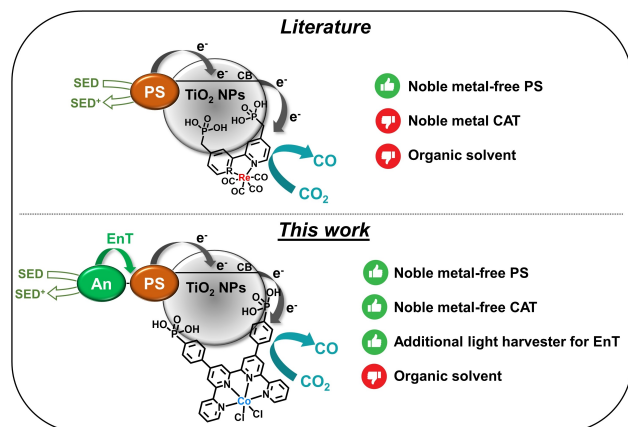
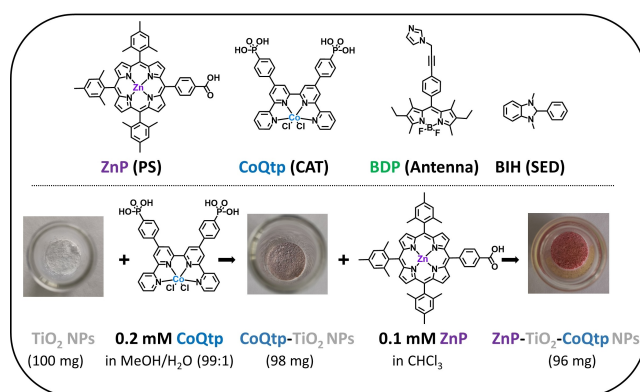


Figure 1. DSPs for CO₂-to-CO reduction: (upper panel) previous examples from literature; (lower panel) our strategy comprising a photo antenna component (An: BDP), a zinc porphyrin as sensitizer and a molecular cobalt catalyst.

i) the presence of a noble metal-free CAT and PS, and ii) the introduction of an additional chromophore (to enhance light harvesting efficiency and thereby the electron injection flux in TiO₂ nanoparticles) that may result in high efficiency for CO₂ reduction (in our case CO).

The preparations of Zinc-trimesitylporphyrin-benzoic acid (**ZnP**) and cobalt-quaterpyridine-bis phosphonic acid (**CoQPpy**), were carried out following procedures reported in the literature, (Schemes S1–S2, Figures S1–S7).^[16a,17] **ZnP** was selected as **PS**, not only because of its excellent properties in solar-harnessing application,^[18] but also because this porphyrin is a very efficient TiO₂ sensitizer (in terms of electron injection)^[19] and has been successfully tested as **PS** in homogeneous photocatalytic CO₂ and H⁺ reduction systems.^[18c,20] Concerning the CO₂ reduction part, we selected **CoQPpy** as **CAT**,^[17] because apart from being a noble metal-free catalyst, **CoQPpy** has been shown to be a very efficient CO₂-to-CO reducing **CAT** in both homogeneous and heterogeneous systems.^[9d,21] In addition, an imidazole-functionalized Bodipy (**BDP**)^[22] was connected to **ZnP** through metallo-supramolecular interaction, aiming to augment the light collection and the photoexcitation rate of **ZnP** via an EnT process, thereby enhancing the catalytic activity.^[23] In Scheme 1, the individual components of our DSPs, as well as the schematic representation of their preparation protocol are displayed (see ESI for experimental details). From absorption studies, atomic absorption, and infrared spectroscopy (IR) (Figure S8 and S9) the successful functionalization of TiO₂ surface was confirmed and the



Scheme 1. Components (upper panel), and protocol used for the preparation of the DSPs (lower panel); All the experimental details are given in the ESI.

loading of **ZnP** and **CoQPpy** was calculated (see ESI). In the final **ZnP-TiO₂-CoQPpy** NPs, the **CoQPpy** loading was 24 nmol/10 mg of TiO₂, while the **ZnP** amount was 0.22 μmol/10 mg of TiO₂, corresponding to the maximum loading in both cases.

The catalytic activity of our DSPs was evaluated by solar-driven CO₂ reduction measurements performed with LED light sources at different wavelengths. In a representative run, 10 mg of the **ZnP-TiO₂-CoQPpy** NPs were dispersed in 4 mL of acetonitrile (ACN) solution containing the sacrificial electron donor (SED). The green-LED irradiation (525 nm) was the most efficient one as compared to the respective white and purple ones (see ESI and Figure S10), resulting in the production of 4.4 μmol of CO and 0.4 μmol of H₂ (92:8 ratio, entry 7 in Table 1).

We explored the impact of SED by testing triethanolamine (TEOA) and 1,3-Dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole (BIH), respectively. As illustrated in Table 1 (compare entries 7 and 9, Table 1), BIH was more efficient than TEOA leading to 11.0 μmol of CO and 3.6 μmol of H₂ (76:24 ratio). BIH is a stronger reductant than TEOA and can serve as a two-electron donor.^[24] Upon adding water (entries 8 and 10, Table 1) the production of CO and H₂ decreased with both SEDs. This could be explained by the energy decrease of the TiO₂ CB, which diminishes the driving force to reduce **CoQPpy**, as already demonstrated.^[13a] Overall, the best results were obtained with BIH as SED and irradiation using a green-LED source (~525 nm). Control experiments showed no catalytic activity in the absence of any element of the system. From the data presented in Table 1, it is evident that neither CO nor H₂ was observed without: i) **PS** and **CAT** (entry 1), ii) **PS** (entry 2), iii) **CAT** (entry 3), iv) **SED** (entry 4), v) light irradiation (entry 5), and vi) TiO₂ (entry 6). Transient absorption spectroscopy (TAS) measurements were performed (see below and additional details in the ESI) to shed some light on the photocatalytic mechanism in our DSPs.

Different amounts of BIH were used to determine the optimal concentration of the SED (Figure 2a). The CO vs. H₂ ratio remained nearly the same (~75:25) at all SED concentration. The maximum amount of product was

Table 1: Photocatalysis results under different conditions. All experiments were conducted using a green-LED lamp (~525 nm), except entry 14.

Entry	NPs	Solvent	SED	CO ^[a]	H ₂ ^[a]	CO/H ₂
1	TiO ₂	ACN	0.05 M BIH	ND ^[b]	ND	–
2	CoQPy-TiO ₂	ACN	0.05 M BIH	ND	ND	–
3	ZnP-TiO ₂	ACN	0.05 M BIH	ND	ND	–
4	ZnP-TiO ₂ -CoQPy	ACN	–	ND	ND	–
5 ^[c]	ZnP-TiO ₂ -CoQPy	ACN	0.05 M BIH	ND	ND	–
6 ^[d]	ZnP-CoQPy	ACN	0.05 M BIH	ND	ND	–
7	ZnP-TiO ₂ -CoQPy	ACN	0.1 M TEOA	4.4	0.4	92/8
8 ^[e]	ZnP-TiO ₂ -CoQPy	ACN/H ₂ O	0.1 M TEOA	1.8	0.2	90/10
9	ZnP-TiO ₂ -CoQPy	ACN	0.05 M BIH	11.0	3.6	76/24
10 ^[e]	ZnP-TiO ₂ -CoQPy	ACN/H ₂ O	0.05 M BIH	4.4	1.6	74/26
11	ZnP-TiO ₂ -CoQPy	ACN	0.025 M BIH	10.1	3.4	75/25
12	ZnP-TiO ₂ -CoQPy	ACN	0.1 M BIH	13.4	4.8	76/24
13	BDP-ZnP-TiO ₂ -CoQPy	ACN	0.1 M BIH	8.8	3.3	67/33
14 ^[f]	BDP-ZnP-TiO ₂ -CoQPy	ACN	0.1 M BIH	18.2	9.3	66/34

[a] CO and H₂ quantities in μmol, upon reaching a production plateau. [b] ND: Not detected. [c] Without light irradiation. [d] Without TiO₂. [e] ACN + 3% H₂O. [f] Experiment performed using a white-LED lamp (400–700 nm).

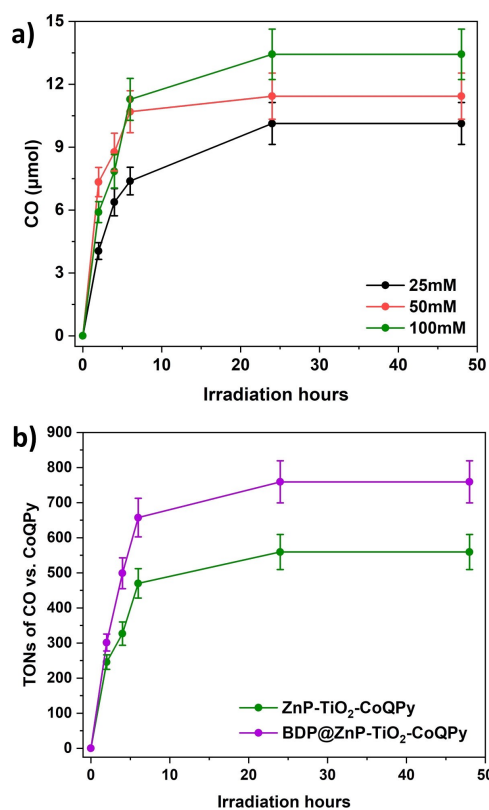


Figure 2. Photocatalytic CO₂-to-CO conversion activities of: a) ZnP-TiO₂-CoQPy DSPs (10 mg), in 4 mL of ACN solution with 25 mM (black), 50 mM (red), 100 mM (green) of BIH. b) ZnP-TiO₂-CoQPy (green line) versus BDP@ZnP-TiO₂-CoQPy DSPs (purple line). The reported CO quantities are the average of three independently repeated experiments.

obtained at 100 mM of SED, leading to the production of 13.4 μmol (CO) in 24 h of irradiation. Interestingly, by introducing **BDP** as a co-photosensitizer, the CO₂-to-CO production was significantly enhanced. Energy transfer (EnT) from Bodipy to ZnP is a well-established process, operating with an almost 100% quantum efficiency.^[22,25]

Remarkably, the CO evolution was significantly increased (from 13.4 to 18.2 μmol, compare entries 12 and 14 in Table 1), likely from the amplification of light harvesting efficiency. The BDP@ZnP-TiO₂-CoQPy DSPs were irradiated with two different light-sources, a green-LED (entry 13, Table 1) and a white-LED (entry 14, Table 1). Interestingly, the irradiation using the white-LED source led to higher-CO production. It may be ascribed to a better photon collection in the 450–550 nm window by **BDP**, before EnT to **ZnP** occurs. Indeed, **ZnP** exhibits an intense Soret band at 426 nm, and two Q-bands at 506 and 599 nm, whereas **BDP** has a sharp band at 526 nm (Figure S11) demonstrating complementary absorption features.^[16a,26] The observed redshift regarding the Q-bands of **ZnP** demonstrates that **BDP** binds onto the **ZnP** through the imidazole unit. However, **BDP** may also bind onto TiO₂ surface via *H*-bonding between the imidazole and the proton of TiO₂,^[16a,22] and possibly to the catalyst since cobalt loses its initial chloro ligands during catalysis (Figure S12).^[27] Overall, BDP-ZnP-TiO₂-CoQPy DSPs demonstrated high stability (759 TONs vs. **CoQPy**) and CO activity (42 mmol g⁻¹ h⁻¹ vs. **CoQPy**), outperforming the respective ZnP-TiO₂-CoQPy DSPs which resulted in 558 TONs and 31 mmol g⁻¹ h⁻¹, respectively.

Regardless of the different components (with/without **BDP**) and parameters (light source, amount of SED, etc.), deactivation of the system was observed after 24 h of irradiation. To elucidate the reason for this deactivation, a series of photocatalytic experiments were performed using ZnP-TiO₂-CoQPy DSPs (Figure S13). More precisely, after reaching a plateau for CO production (24 h), the DSP was relaunched by adding: a) **CoQPy**, b) **ZnP**, or c) **ZnP** + **CoQPy** respectively and by purging the suspension with CO₂. When **CoQPy** was added to the reaction vial (experiments a and c), the CO production was reactivated; whereas, by adding **ZnP** the system remained inactive. Consequently, the observed activity loss could most likely be attributed to **CoQPy**, which either leached from the TiO₂ NPs or was degraded; even though **CoQPy** has proven to be stable in

similar photocatalytic experiments.^[21a] As anticipated, the CO production in the relaunched experiment c (**ZnP** + **CoQPy**) slightly surpassed the amount obtained in the experiment a (**CoQPy**), due to the additional light harvesting contribution by the new **ZnP** molecules. The origin of carbon in the produced CO was confirmed by conducting ¹³CO₂-labeled experiments. As shown in Figure S14, ¹³CO was observed. It is worth mentioning that under N₂, no generation of carbon-containing product was observed. Collectively, all our results firmly demonstrate that the detected CO derives from CO₂.

To investigate the charge transfer dynamics of the photocatalytic system, we then carried out femtosecond transient absorption spectroscopy (fs TAS) measurements with **ZnP-TiO₂** and **ZnP-TiO₂-CoQPy** films, upon 550 nm photoexcitation (**ZnP** Q band). Such studies could reveal key parameters impacting the charge transfer dynamics between the PS, the CAT, and the TiO₂ NPs, and help elucidating the photocatalytic mechanism.^[28] As illustrated in Figure 3a, the early TA spectra were dominated by

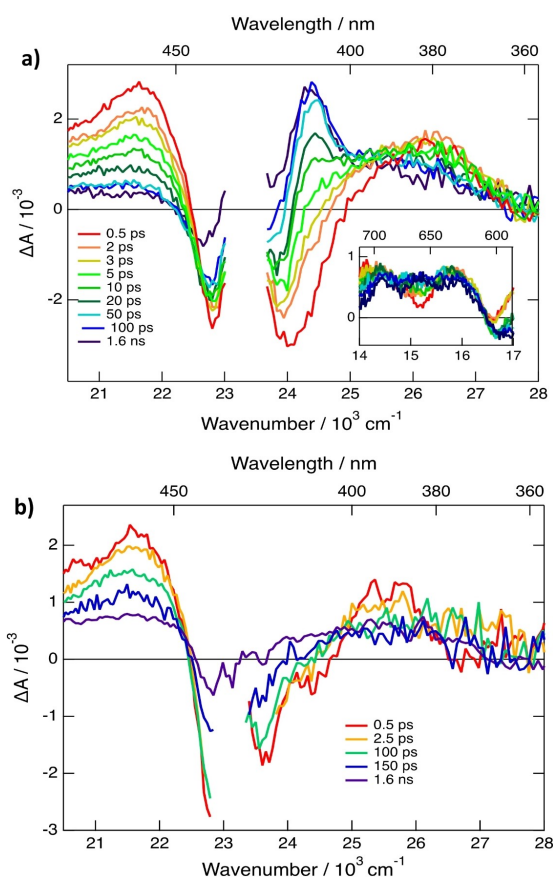


Figure 3. Transient absorption spectra recorded at various time delays after 550 nm excitation of **ZnP-TiO₂** film without (a) and with 0.04 M BIH (b).

excited-state absorption (ESA) bands above 620 nm and around 460 nm and 380 nm, which can be assigned to the local S₁ state of the excited **ZnP** (PS*). Additionally, stimulated emission (SE) as well as ground-state bleach

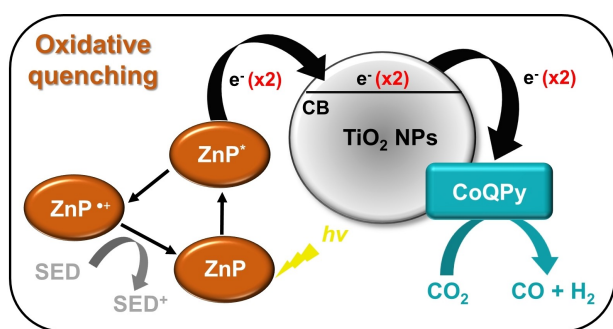
(GSB) features were visible at about 660 and 600 nm and in the 440–400 nm region.

Both the ESA and SE bands decayed in 11 ps, and a new band at 410 nm raised concurrently (Figure S15). This band can be assigned to the radical cation of the photosensitizer, PS*⁺, generated upon electron injection from PS* into TiO₂.^[29] Charge injection into TiO₂ was further supported by mid-IR TAS measurements at 4000 nm, which showed the rise of the absorbance typical of electrons in the conduction band of TiO₂ (Figure S16).^[30] The slower partial decay of the mid-IR absorbance can be attributed to charge recombination with PS*⁺.

In the presence of 0.04 M, the PS*⁺ band at 410 nm is hardly visible and the GSB was significantly reduced (Figure 3b). This difference can be attributed to a hole transfer from the radical cation of **ZnP** to BIH. The absence of the PS*⁺ band suggests that this hole transfer occurs on similar timescale as charge injection. As noted above, charge injection into TiO₂ was confirmed by mid-IR measurements. The decay of the TAS signal at 4000 nm was delayed in the presence of BIH. This effect is most probably due to the competition between hole transfer from PS*⁺ to BIH and charge recombination with the electron at the semiconductor surface. TA measurements with **ZnP** and 0.04 M BIH in acetonitrile indicated that reductive quenching of PS* by the SED is relatively inefficient and occurs with a rate constant well below the diffusion limit (Figures S17 and S18). Consequently, hole transfer from BIH to PS* is not competitive with electron injection into TiO₂. These two above-mentioned hole transfers are totally distinct processes. The first one is a hole transfer from PS*⁺ to BIH, whereas the second is a hole transfer from PS* to BIH. Both processes involve the oxidation of BIH, however the PS*⁺ is neutralized in the first one, while the PS* is reduced in the second one.

Finally, fs TA experiments with **ZnP-TiO₂-CoQPy** films in both the visible and the mid-IR pointed to the same dynamics as those found with **ZnP-TiO₂** films (Figures S19 and S16). This suggests that electron transfer from TiO₂ to the catalyst is too slow to be observed within the time window of the experiment. In summary, the TA experiments suggest an oxidative quenching mechanism for the photocatalytic activity of our DSPs. In detail, photoexcitation of **ZnP** gives rise to the population of **ZnP***, followed by ultrafast electron injection (11 ps) into TiO₂. The resulting **ZnP*⁺** is rapidly regenerated by the SED (**ZnP*⁺** → **ZnP**), whereas the electron diffuses in TiO₂ before being captured by the **CoQPy**. Given that two electrons (e⁻) are required to reduce CO₂-to-CO, these above-mentioned processes should, in principle, occur twice to generate a CO molecule (Scheme 2).

In our study, we successfully achieved CO₂-to-CO DSPs by combining noble metal-free PS (**ZnP**) and CAT (**CoQPy**) derivatives. The incorporation of an additional chromophore (**BDP**) introduced an antenna effect, significantly enhancing CO photoproduction. Table 2 presents the TONs and CO production data for both previous systems reported in the literature and our novel approach. It is crucial to note that various parameters exert significant influence on the



Scheme 2. Proposed photocatalytic mechanism for the two-electron reduction of CO_2 to CO in our DSPs.

Table 2: The TONs and the CO production rate of DSPs in the literature and in this work.

PS ^[a]	CAT ^[a]	TONs ^[b]	CO production ^[c]	Publication
2-H	Re-H	922	21.2	[13b]
SQ_{ca}	ReC	165	3.8	[31]
ZnP_{ca}	ReC	1028	39.4	[32]
Dye ₁	ReP	180	29.0	[33]
MOD	RePH	570	–	[34]
Dye ₂	ReC	435	–	[35]
BDP-ZnP	CoQPpy	759	42.1	this work
ZnP	CoQPpy	559	31.0	this work

[a] The molecular structures of all the different PSs and the CAT are shown in Figure S19. [b] TONs were calculated vs. CAT in all cases. [c] CO production is given in $\text{mmol g}^{-1} \text{h}^{-1}$ (g. of CAT). The CO production rates were calculated using the given data of each publication.

stability and production rate of such systems, including light intensity and source. In all prior reports, noble metal-free PSs were used in combination with $\text{ReCl}(\text{L})(\text{CO})_3$ ($\text{L} = 2,2'$ -bipyridine derivative) as the CO_2R CAT. Molecular structures of all the different PSs and the Re-CAT can be found in Figure S20. Our work yielded promising results, with the highest recorded CO production rate reaching $42.1 \text{ mmol g}^{-1} \text{h}^{-1}$ (per g. of CAT), TONs amounting to 759, and an apparent quantum yield efficiency (AQY) of 3.9% (see ESI). Building upon these encouraging findings, our ongoing research is now focusing on systems designed to operate in aqueous solutions without the need for sacrificial reagents—a crucial step towards the development of highly efficient CO_2 photocatalytic systems.

Supporting Information

Experimental details; synthesis and characterization; photocatalytic results; and transient absorption studies are provided. The authors have cited additional references within the Supporting Information.^[36–39]

Acknowledgements

This project was supported by HORIZON TMA MSCA Postdoctoral Fellowships - European Fellowships (HORIZON-TMA-MSCA-PF-EF) action program under the call MSCA Postdoctoral Fellowships 2021 (HORIZON-MSCA-2021-PF-01) to V.N., grant agreement No. 101064765, SOLAR-CAT. This study also received financial support under the EUR LUMOMAT project and the Investments for the Future program ANR-18-EURE-0012. Financial support from the Swiss National Science Foundation (grant 200020-184607) and the University of Geneva is also acknowledged. Partial financial support to M.R. from the Institut Universitaire de France (IUF) is warmly thanked.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: CO_2 reduction · dye-sensitized photocatalytic systems (DSPs) · porphyrin · quaterpyridine · antenna effect

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Manuscript received: November 29, 2023

Accepted manuscript online: February 5, 2024

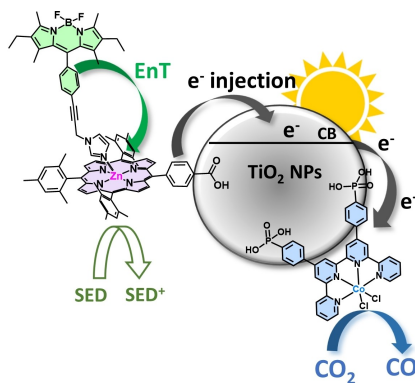
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Communications

CO₂ Reduction

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Antenna Effect in Noble Metal-Free Dye-Sensitized Photocatalytic Systems Enhances CO₂-to-CO Conversion



Efficient CO₂-to-CO dye-sensitized photocatalytic systems by utilizing noble metal-free photosensitizer (zinc-porphyrin) and catalyst (cobalt-quaterpyridine) derivatives. Upon introducing an additional chromophore (Bodipy), an antenna effect enhanced the photoproduction leading to 42.1 mmol g⁻¹ h⁻¹ of CO and 759 turn over numbers.