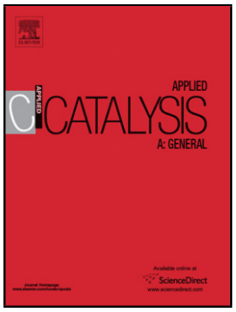

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Author: Jun-Xiao Zhang Chang-Ying Hu Wei Wang Hui Wang Zhao-Yong Bian

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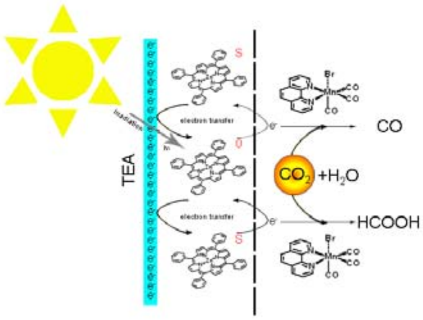
Visible light driven reduction of CO_2 catalyzed by an abundant manganese catalyst with zinc porphyrin photosensitizer

Jun-Xiao Zhang[a], Chang-Ying Hu[a], Wei Wang[b], Hui Wang[b,**], Zhao-Yong Bian[a,*]
[1]*College of Water Sciences, Beijing Normal University, Beijing 100875, PR China*
[2]*College of Environmental Science and Engineering, Beijing Forestry University, Beijing 100083, PR China*

[*]Corresponding author. Tel.: +86 10 58802736; Fax: +86 10 58802739
E-mail address: bian@bnu.edu.cn
[**] Corresponding author. Tel.: +86 10 62336615; Fax: +86 10 62336596
E-mail address: wanghui@bjfu.edu.cn

Graphical abstract



Highlights

(1) We investigated the visible light driven reduction of CO_2 using an abundant metal system containing tricarbonyl manganese catalyst with zinc porphyrin.
(2) Abundant and cheap metal manganese and zinc complexes were used in this study to replace novel rare metal complexes.
(3) In the aqueous acetonitrile reaction solution, carbon monoxide and formic acid were efficiently produced as the gas and liquid products.

Visible light driven photocatalytic CO_2 conversion has been investigated using abundant metal complexes catalyst *fac*-[Mn(phen)$(CO)_3$Br] and photosensitizer ZnTPP, which efficiently produced carbon monoxide and formic acid in an aqueous acetonitrile solution. The photochemical and electrochemical properties of the catalysis system proved the good ability of the light utilization and the reduction. During the 180-min irradiation experiments with the Mn/Zn ratio of 2:1, the TONs reached 64 for the CO formation and 16 for the formic acid formation, respectively. An integrated mechanism was proposed for the CO_2 reduction in this system. This photocatalyst system not only shows environmental friendly and sustainability, but also retains the product selectivity in the CO_2 photoreduction system.

Keywords: Visible light catalysis; CO2 reduction; abundant catalyst; Mn; Zn

Introduction

In recent years, photocatalytic CO_2 conversion has attracted significant attention because of a couple of serious problems such as global warming and shortage of energy sources. Many attempts have been taken to design a system to convert CO_2 to useful fuel with the help of novel methods, such as electrochemistry as well as photochemistry methods.[1] In 1979, Inoue and his coworkers first announced that TiO_2 has the ability to catalyze the reduction of CO_2, which induced the research of photocatalytic reduction of CO_2.[2] Since then, researchers continued to looking for new efficient catalysts for the CO_2 conversion, in which various kinds of macrocyclic complexes have been designed and synthesized, which are capable for the absorption of visible light. For instance, Hawecker and his coworkers firstly used [Re(bpy)$(CO)_3$Cl] (bpy=2,2'-bipyridine) as both photocatalyst and photosensitizer for the CO_2 reduction in a homogeneous system with the turnover number (TON_{CO})=48 in a four-hour photoreaction.[3] Beyond that, more Ru and Re macrocycle complexes showed good photocatalytic ability and were used as the catalyst for CO_2 photo-reduction.[4] Recently, Kuramochi and his coworkers found that *trans*-[Ru(bpy)$(CO)_2Cl_2$] achieved an unexpected production of CO and formic acid in a photocatalysis, in which $[Ru(bpy)_3]^{2+}$ served as a photosensitizer.[5]

Although these systems with such catalysts loaded with precious rare metals get efficiencies in the CO_2 photocatalysis, their applications are limited by the low concentration in earth and high price of the noble metals. Hence, abundant metals have more advantages for broader application because of their easier achievement and the lower cost. Therefore, researchers have always been trying to look for suitable abundant metals for the load for photo-catalyst, while for decades rhenium has always been regarded as one of the best one.[6] For example, Liu and his co-workers used a copper porphyrin based metal organic framework in chemical adsorption capture and photoreduction of CO_2.[7] In recent years, researchers began to explore manganese catalysts, because manganese, which shares the same family as rhenium, has similar properties in some aspects. As for the catalytic reduction of CO_2, manganese compounds could act like Rhenium complexes. For example, Mukhopadhyay and his coworkers used a bis(imino)pyridine manganese electrocatalyst realizing the promotion of H^+ reduction by the addition of CO_2.[8] It was also found that manganese have the ability to substitute rhenium in the electrocatalyst system.[9] In order to make the extensive study of the manganese catalyst, researchers began to study the similarities and differences between materials loaded with these two elements. Smieja and his coworkers found that the addition of Brønsted acid to CO_2-sturated solutions of Mn complexes and subsequent reduction of the complexes could lead to the stable and efficient production of CO from CO_2.[10] Riplinger and his coworkers have also studied the characters of the two elements and found that with the weak Brønsted acid manganese compound can act well in the electronic CO_2 reduction.[11] Furthermore, researchers also began to study the effect of manganese catalysts in both electrocatalytic and photocatalytic reduction of CO_2. Agarwal and his coworkers has found manganese complexes electrocatalyzed the CO_2 reduction with a turnover frequency (TOF) = 0.14 s^{-1}.[12] Zeng and his coworkers used a manganese(I) tricarbonyl complex containing a nonaromatic α-diimine ligand in the electrocatalytic reduction of CO_2.[13] Using $[Ru(dmb)_3]^{2+}$ as the photosensitizer, Takeda and his coworkers has reported a carbonyl manganese complex acted as a photocatalyst for the CO_2 reduction and formed CO with TON_{CO} = 13.[14] However, many Mn compounds do not get the good ability in the using of visible light. Thus there is a necessity to looking for a suitable photosensitizer helping to absorb the visible light in this research.

Researchers have used precious metal complexes, such as ruthenium complexes, as the photosensitizer for a long time. There are enormous types of macrocycle photosensitizers applied loaded with precious and abundant metals during past years. Among these compounds ruthenium complexes have been used in plenty of photocatalysis systems both as photocatalyst and photosensitizer, for which it is also regarded as one of the most efficient materials. For instance, Shakeri and his co-workers used ruthenium(II) complex as a photosensitizer in a rhenium photocatalytic system.[3d] However, despite the high absorbing efficiency, ruthenium complex costs too much so that it makes an unsustainable system, which could not be widely used. It is necessary to replace the precious metal with abundant metal as the coordinated metal for sustainable application, for which transitional metals, such as zinc and copper, have come into the sight of researchers. In a research done by Li and Diau showed that the power conversion efficiency of porphyrin dyes has grown a lot to 12% from the year of 1991 to 2012 in excess of Ru-based complexes and organic dyes.[15] This result illustrates the trend of the research of porphyrins in recent years, because of the low cost and likely efficiency, especially for porphyrins loaded with transition metals. For instance, Amao and his coworkers reported a photocatalytic system containing zinc tetraphenyl porphyrin (ZnTPP), serving as a photosensitizer, MV^{2+}, FDH (formate dehydrogenase), AldDH (aldehyde dehydrogenase), ADH (aldehyde), TEOA, and $NaHCO_3$ in potassium phosphate buffer solution (pH 8), in which methanol as product was found after three hours of irradiation.[16]

In this research, we reported a homogeneous photochemical system using *fac*-[Mn(phen)$(CO)_3$Br] (phen

=1,10-phenanthroline) as a precursor of the catalyst and [ZnTPP] as a photosensitizer. In this system, CO_2 could be reduced to CO as gas product and formic acid as liquid product. In this experiment, the use of ZnTPP prevented the generation of hydrogen from the reduction of proton, which showed high product selectivity to the non-H_2 products of the CO_2 reduction.

Experimental Section

Reactions were performed in oven-dried round-bottomed flasks unless otherwise noted. Reactions that required an inert atmosphere were conducted under pressure of N_2. Air and moisture sensitive reagents were transferred using standard syringe or cannula techniques. Reagents and solvents were of reagent grade and used as received.

Tetraphenyl porphyrin (TPP) was synthesized by a method modified from the classical Adler method.[17] 9.6 g of aluminum chloride anhydrous was dissolved in 165 mL N,N-dimethylformamide (DMF) in a three-necked, round-bottomed flask containing a stirring bar. When the solution was heated to reflux, 6.4 g of pyrrole and 7.7 g of benzaldehyde were added into the flask. The reaction was stopped after heating for additional 2 hours. A certain volume of absolute ethyl alcohol was added into the device after cooled to room temperature. After overnight standing, a large amount of solid precipitated and was filtrated out. The purple crystals were achieved after washed by ethanol and hot water in sequence for at least two times. The crude product was then purified by column chromatography (eluent: dichloromethane). The compound was characterized by NMR and elemental analysis. ^1H NMR ($CDCl_3$) δ: -2.70 (N-H); 7.71-7.85 (othor- and para- H); 8.97 (meta-H). Element analysis: TPP: Found: C, 86.0; H, 5.1; N, 9.7. $C_{44}H_{30}N_4$ requires C, 85.9; H, 4.9; N, 9.2%.

Zinc tetraphenyl porphyrin (ZnTPP) was synthesized following the reported method[11] and purified by recrystallization and centrifugation. The compound was characterized by ESI-MS and elemental analysis. Through the ESI-MS analysis, it could be seen that peaks at 677.5 got the highest value. According to the molecular weight of ZnTPP (676), the values in the picture could prove that the zinc element was loaded successfully to TPP. From element analysis of ZnTPP (Found: C, 77.9; H, 4.1; N, 8.4. $C_{44}H_{30}N_4$ requires C, 78.1; H, 4.1; N, 8.3%), it could be easily found that the sum of the percentage of the three elements is 90.4%, which is much fewer than 100%, while the difference stands for the existence of zinc.

fac-[Mn(phen)$(CO)_3$Br] was synthesized by a reflux-condensation method and purified by recrystallization and filtration. The material was characterized by ESI-MS, which showed the molecular weight was 335, which is the same as the theoretical value calculated by taking away the Br and adding the CH_3CN radical, which leads to the formation of [Mn(phen)$(CO)_3CH_3CN$] structure. Therefore, the result matched the exact calculating value well.

^1H NMR spectra were recorded using BRUKER AVANCE 500Hz and Mass spectrometry was recorded using Quattro Micro API from Waters Micromass. Electrochemistry was performed using a CHI-660 electrochemical workstation. Cyclic voltammetry (CV) was performed using a standard three-electrode configuration. The working electrode was a polished glassy carbon electrode and a piece of platinum wire was used as the counter electrode, while a saturated calomel electrode (SCE) was used as the reference electrode. Prior to electrolysis the solution was dissolved by MeCN bubbled with nitrogen and CO_2 gas for 40 min, respectively. With all these steps, the cell was sealed and electrolysis initiated. UV-vis absorption spectra were acquired by UV-3600 from Shimazu Corporation. All absorption spectra were recorded at room temperature and all samples were prepared in dichloromethane (DCM). Samples for fluorescence analysis were prepared in an analogous method to that described above for the preparation of samples for UV-vis spectroscopy. For ZnTPP, samples were excited at λ_{ex}=499 nm and emission was monitored from 509 nm to 800 nm with a step size of 1 nm. The experiment began with the addition of 120 mL MeCN into a 250 mL flask, which was bubbled with nitrogen for 1 h. The ZnTPP was resolved in bubbled acetonitrile solution and prepared as a 0.1 mM MeCN solution. The ZnTPP solution was quenched using the 0.1M TEA-MeCN solution bubbled by nitrogen for 40 min. The quenching experiment was also done using the TEA solution.

fac-[Mn(phen)$(CO)_3$Br], ZnTPP and TEA of certain quantities are added into tube shaped reactor containing 25 mL solvent of the mixture of MeCN and deionized water(v/v=20:1). The solution is bubbled by nitrogen for 40 min to wipe off oxygen and then by CO_2 for 40 min to make sure the solution is saturated with CO_2. The tubes of solution with magnetic rotors are sealed up to make sure that the gas inside would never come out and put into an equipment installed with a lamp to do the experiment. After a certain period, samples are taken out and placed in a dark container, followed by the detection of products, including gas chromatograph and ion chromatograph. The turnover numbers are the average of at least three individual acquisitions.

Results and Discussion

Electrochemical properties

The catalysis material *fac*-[Mn(phen)(CO)$_3$Br] was analyzed by electrochemical cyclic voltammetry. It could be easily seen that there are three reduction peaks in the CV spectrum under the nitrogen pressure (as shown in Fig 1). The first peak appeared at -1.2V vs. SCE, while the second occured at -1.5 V and the third at -1.75 V, respectively. Under CO$_2$ (red trace), the current enhancement of peaks, relative to the nitrogen scan at each peak, were 1.98×, 1.88×, and 4.58×, respectively. These three peaks stood for the three reaction processes of *fac*-[Mn(phen)(CO)$_3$Br] under different potentials. And the considerable current enhancement illustrated that there were reactions between CO$_2$ and *fac*-[Mn(phen)(CO)$_3$Br] in the system. The first peak stood for the protonation of [Mn(phen)(CO)$_3$(MeCN)], which could be observed that the current difference was not big. Under the potential of -1.5 V vs. SCE, [Mn(phen)(CO)$_3$]$_2$, the key compound in the whole reaction, was formed. However, it quickly received energy from the electrode and then transformed to [Mn(phen)(CO)$_3^-$]. It was also declared in Bourrez's research that for this kind of manganese compounds, lower potential could lead to the decrease of selectivity because of the production of a small amount of hydrogen in a process of electrocatalytic reduction.[9] In this research, the electrolysis producing CO was done under a potential of -1.70 V vs. Ag/Ag$^+$, obtaining the TON$_{CO}$=13. However, it was also found that when the potential becomes more negative than -2.1 V vs. Ag/Ag$^+$, there would be hydrogen generated from the system. That is to say, in order to increase the selectivity of the catalytic reduction, less negative reduction potential is needed.

In an electroreaction, the driving force and energy were given by the applied potential. However, in a photoreaction, the irradiation energy absorbed by a photocatalyst will motivate the proposed reaction. If the potential was no more negative than -2.1 V vs. Ag/Ag$^+$ (-1.8 V vs. SCE), there would be no hydrogen generated. As shown in Fig 2, it could be observed that there were two obvious reduction peaks, one at -1.05 V vs. SCE and the other at -1.65 V vs. SCE. The first peak (-1.05 V vs. SCE) stood for the reduction of ZnTPP to an excited state of ZnTPP (ZnTPP E$_1$), which was a transition form of the ZnTPP complex. The second state (-1.65 V vs. SCE) stood for the reduction of ZnTPP E$_1$ to ZnTPP$^-$. In a typical electroreaction, when the potential was between these two state (not more negative -1.8 V vs SCE), there would be no hydrogen generated. However, in a typical photoreaction, the energy was got from the irradiation and electrons were provided by the electron donor. The energy transferred from excited ZnTPP should be between -1.65 V and -1.05 V vs. SCE which was positive than -1.8 V vs. SCE. Therefore, the use of ZnTPP as a photosensitizer could prevent the production of hydrogen.

With the comparison of the current peaks under the two reduction potentials, it could be found that the peak currents and the square roots of the scan rate match better the linear relationship (R^2=0.983). It means that the electron transfer process of ZnTPP was controlled by the diffusion process in the solution.

In addition, ZnTPP is one of excellent materials for the visible light utilization, due to the good ability of absorbing visible light. As shown in Fig 3, there were three absorption peaks, appearing at 424 nm, 556 nm and 593 nm. According to the former research, the Soret-band of ZnTPP appeared at 425 nm, while Q-bands appeared at 559 nm and 599 nm.[17b] This indicated the good absorption ability of ZnTPP sample in this research. In the fluorescence spectrum of ZnTPP, it could be easily seen that there are two strong emission peaks, one at 600 nm and another at 650 nm. It indicated that ZnTPP could transform the absorbed light energy into other kinds of light and the excited state of ZnTPP had a lifetime long enough for the energy utilization.

Quenching Experiment

In order to use ZnTPP as a photosensitizer in this research, a quenching experiment was done to confirm the sacrificial reductant. Triethylamine (TEA) is regarded as one of the most efficient reductant, also known as electron donor. Fluorescence quenching measurements in the acetonitrile solutions containing ZnTPP with increasing concentrations of TEA were analyzed by the Sterm-Volmer equation:

$$\frac{I_0}{I} = 1 + k_q \tau_0 [Q]$$

In this equation, I$_0$ and I stand for the fluorescence intensity without and with the quencher, respectively. k_q is the quenching rate constant and [Q] is the quencher concentration. τ_0 is the excited-state lifetime of ZnTPP without the quencher which was 2ns in a acetonitrile solution.[18]

According to spectrums above, it could be figured out that the evolution of the fluorescence ratio with the concentration of TEA was linear. The quenching rate constant k_q could be calculated as $2.7*10^{10}$ L mol^{-1} s^{-1}. The conclusion could be made that the reductive electron transfers between ZnTPP and TEA was efficient.

Photoreaction

The molar ratio of the catalyst and photosensitizer in a photocatalysis system is important for the photocatalysis operation. A group of experiments was set to determine the suitable ratio of the concentration of the catalyst and the photosensitizer. In a typical photoreaction experiment, a 20:1 mixed solution of acetonitrile and deionized water (v/v) containing the catalyst *fac*-[Mn(phen)(CO)$_3$Br], photosensitizer ZnTPP, and reductant TEA was irradiated using xenon lamp under a CO_2 atmosphere. The concentration of catalyst *fac*-[Mn(phen)(CO)$_3$Br] was 0.5 mM, while different concentrations of the photosensitizer were set to investigate the effect of ratio of catalyst and photosensitizer on the photocatalytic ability to the CO_2 reduction.

Table 1 summarized catalytic reduction efficiencies under different operation conditions. In these photoreaction experiments, the main reduction products were CO as a gas product and formic acid as a liquid product. There was no hydrogen gas could be determined. From the control experiment (No. 6), the catalyst *fac*-[Mn(phen)(CO)$_3$Br] formed little products without the photosensitizer ZnTPP under the same conditions. Because the catalyst *fac*-[Mn(phen)(CO)$_3$Br] had weak absorption in the visible light region and could not efficiently utilize the visible light energy. It indicated that the visible light was the main driving force for this CO_2 conversion. Additionally, in experiment 7, there was no products detected in the reaction system without catalyst *fac*-[Mn(phen)(CO)$_3$Br]. It indicated that both the catalyst and photosensitizer played vital roles in this CO_2 conversion. The whole experiments could be divided into two parts with controlling variable method. On the one hand, the concentration of ZnTPP was set as a constant (0.5mM), while the concentration of *fac*-[Mn(phen)(CO)$_3$Br] was changed from 0.5mM to 2mM (Group 1, 2 and 4). In this series of experiment, it could be seen that with the increase of the concentration of *fac*-[Mn(phen)(CO)$_3$Br], the production of both CO and formic acid was enhanced. Specifically, when the concentration ratio of catalyst *fac*-[Mn(phen)(CO)$_3$Br] and the photosensitizer ZnTPP increased from 1:1 to 3:1 and ultimately 4:1, the TON_{CO} increased from 12 to 97 and finally 119, while TON_{HCOOH} rose from 10 to 18 and finally 19. On the other hand, in the other series of experiments, the concentration of *fac*-[Mn(phen)(CO)$_3$Br] was the constant, while the concentration of ZnTPP changed from 0.25mM to 1mM (Group 3, 4 and 5). It could also be found that with the concentration ratio increased, the TON of the formed products became bigger. For the gas product CO, TON increased from 8 to 64 when the Mn/Zn ratio changed from 1:2 to 2:1. Meanwhile, TON of formed liquid product formic acid increased from 6 to 16. It illustrated that the combination of *fac*-[Mn(phen)(CO)$_3$Br] and ZnTPP in this system favored a high selectivity as well as a high productivity in the catalytic reduction of CO_2.

Group 3 was chosen as the research target to study the formation of the two products during the whole reaction. Fig.6 shows the production of CO and formic acid with the irradiation time. It could be obviously seen that formic acid generated quickly during the first one hour of the reaction (TON_{HCOOH} quickly changed to 7 and then 11), and then the production slowed down during the three hours irradiation (TON_{HCOOH} ultimately reached 16). Additionally, a dramatic amount of CO was produced with TON_{CO}=64, which was the main product in this reaction. During this progress CO generated with a surprising speed in the first one hour and then slowed down gradually until TON_{CO} reached 64 during the experiment period.

According to the table above, there are two kinds of products detected in the reaction, in which the main one is CO while the minor one is formic acid. Some mechanisms were reported to describe the solo product formation process. For example, both manganese and rhenium compounds were reported to reduce CO_2 into formic acid when combined with protons in the first place, while leaded to the CO product if combined with CO_2 firstly[3d]. In some other systems using manganese compounds, the mechanisms show that certain electron donors, such as TEOA, could take part in reactions of Mn catalyst, to make a combination of proton and the catalyst.[6] And some Mn species existing in the system could control the product selectivity.[14] Herein, an integrated photocatalysis mechanism was proposed to discuss the CO_2 conversion (shown in Scheme 1). As discussed in the former part of this article, ZnTPP could successfully transfer the visible light energy into electron energy, which transferred to the catalyst with the help of electron donor (TEA). Under the irradiation of visible light, the ground state ZnTPP firstly turned into excited state (S_1). This could be proved by the UV-vis and fluorescence spectrum of ZnTPP (Fig 3). And the long enough excited-state life time of ZnTPP (τ=2 ns[18]) could allow the complex turn into a lower-energy but long-lived T_1 state (τ=1.5 ms).[19] Thus $[ZnTPP]^-$ could be quenched more easily by TEA. $[ZnTPP]^-$ then transferred electrons to the catalyst and turns into the ground state to fulfill the reaction. (as shown in Scheme 1)

The catalytic mechanism of *fac*-[Mn(phen)(CO)$_3$Br] could be summarized in two processes which were illustrated in Scheme 1. For both processes, in the solvent, the Mn compound was firstly combined with the solvent molecular to replace Br and got electrons from [$ZnTPP^-$] at the same time. This part of the reaction was proved by the cyclic voltammograms of *fac*-[Mn(phen)$(CO)_3$Br]. According to Fig 1, it has been declared that there are three reduction peaks in the *fac*-[Mn(phen)$(CO)_3$Br] cyclic voltammogram under CO_2 condition, -1.2 V, -1.5 V and -1.75 V vs. SCE. In a certain electrochemical reaction, *fac*-[Mn(phen)$(CO)_3$Br] firstly lost the Br^- ion and then reacted with MeCN, the solvent molecule. And then a Mn-Mn dimer, [Mn(phen)$(CO)_3]_2$ was formed. This process could be confirmed by the reduction peak at -1.5 V vs. SCE in the cyclic voltammetry of *fac*-[Mn(phen)$(CO)_3$Br]. The similar observation was reported and attributed to the formation of Mn-Mn dimer. [9] The dimer quickly received electrons from one-electron reduced [$ZnTPP^-$] and then transformed to [Mn(phen)$(CO)_3]^-$. According to the comparison of the cyclic voltammetry, the peak current achieved a 1.88 times enhancement under CO_2 compared with that in N_2 atmosphere. It indicated that there were reactions between the manganese compound and CO_2. The existence of the metal dimer in the catalytic system was also confirmed by other reports.[4d,9,14] And for this dimer, there was only one reaction path, in which it reacted with protons to form a [Mn(phen)$(CO)_3$H] structure. Following that step, the acetonitrile molecules were then attached to the metal part (manganese) of the catalyst, which also leaded to the addition of CO_2 to replace the solvent molecule.

H_2O, one kind of the weak Brønsted acid, also plays an important role to help with the catalytic reaction in this process. As shown in many other metal carbonyl catalysts, water was a necessary reagent to acquire the catalytic activity.[20] In a manganese catalyst case, the addition of a weak Brønsted acid made the stabilization of the manganese-carbon dioxide intermediate through a protonation, which also promoted the break of one of the C-O bonds of CO_2 to form CO.[21] In Scheme 1, the proton from H_2O was attached to the oxygen atom, which was linked with the carbonyl in the molecule, to form a [Mn(phen)$(CO)_3$(COOH)]$^+$ structure (one of the C=C double bond in the CO_2 molecule already broken up in the previous step). A similar process was reported by Shakeri and his co-workers in the research of the photoreduction of CO_2 with Re(I) complex.[22] In the reported research, the [C=O] fraction falls out to produce CO after the shedding of the [–O–H] fraction after receiving electrons in the homogeneous system.

The formic acid formation could be attributed to the reaction between TEA and [Mn(phen)$(CO)_3]^-$ which has no linkage with Br atom as well as the acetonitrile molecule. The concentration of TEA reached 0.1M in the homogeneous system, which was far more than that of ZnTPP (0.05 mM). Thus although TEA was added as the electron donor and sacrificial reagent to quench the excited ZnTPP, its concentration was high enough for the its reaction with [Mn(phen)$(CO)_3]^-$ species even the reaction rate is slow. The electrons transferred from TEA in aid of the bonding between [Mn(phen)$(CO)_3]^-$ and protons.[6] Then the CO_2 molecules attached with the manganese species to form a hybrid with a structure of [Mn(phen)$(CO)_3$(COOH)]. Because this species was neutral, it was not likely to react in the similar way as Process I. Finally, another proton combined with [Mn(phen)$(CO)_3$(COOH)] to fulfill the CO_2 conversion and release formic acid.

Reusability

The reusability of the photocatalyst is also one of the most important factors for application. In order to confirm the reusability of the photocatalyst system, Group 3 in Table 1 was chosen as the target to study the reusability of the photocatalyst system. The catalyst solutions were irradiated for one hour and sampled for the products determination. Then the solutions were refreshed with CO_2 in dark condition. Four cycles of experiment data were compared.

It could be seen from Fig 7 that after 1 hour of photoreduction, TON_{CO} and TON_{HCOOH} were detected as 53 and 11. And after four runs, TON_{CO} and TON_{HCOOH} were 41 and 7, respectively. Although the amount of the products decreased slightly, the catalyst system kept the high product selection and yield for the CO_2 conversion.

Conclusion

Abundant manganese phenanthroline complex was combined with the zinc porphyrin to perform the efficient CO_2 conversion under the visible light irradiation. The zinc porphyrin was acted as photosensitizer to absorb the visible photon and induce the formation of reduced manganese complex in the presence of electron donor. The ratio of manganese and zinc complexes in the solution affected the efficiency of CO_2 reduction. The TON of CO formation was 64 when the ratio of Mn/Zn was 2:1. The liquid product formic acid was achieved with TON of 16 under the same conditions. In addition, the zinc porphyrin photosensitizer prevented the hydrogen formation from protons in this system.

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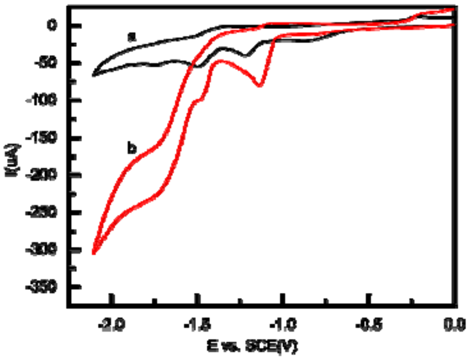


Fig 1 Cyclic voltammogram of *fac*-[Mn(phen)(CO)$_3$Br] in MeCN/H$_2$O(v/v=20:1) bubbled by nitrogen (a) and saturated with CO$_2$ (b)

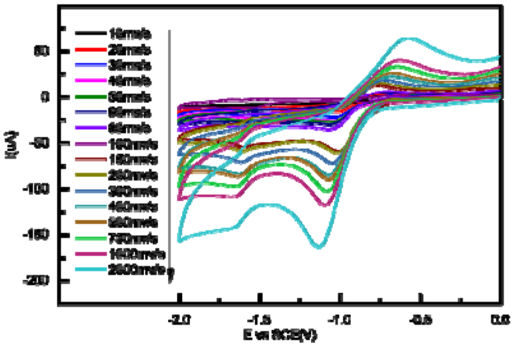


Fig 2 Cyclic Voltammetry of the ZnTPP under the condition of different current from 10mV/s to 2000mV/s

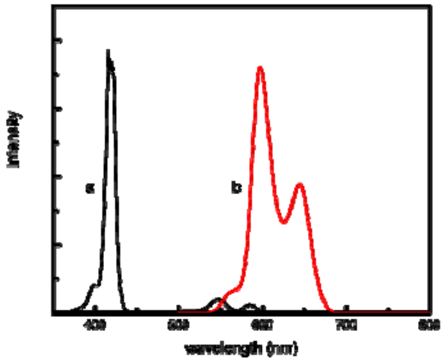


Fig 3 UV-vis (a) and fluorescence (b) spectrum of ZnTPP

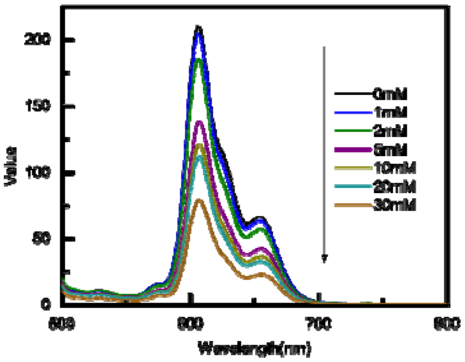


Fig 4 Fluorescence quenching data of ZnTPP with the concentration of TEA from 0 mM to 30 mM

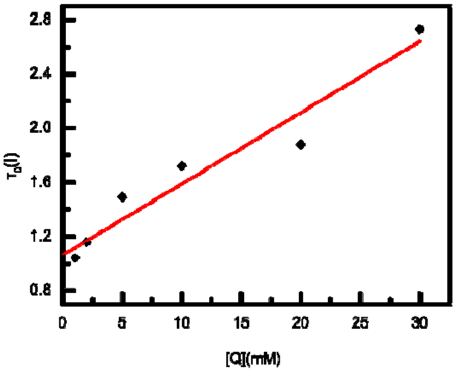


Fig 5 The linear plot of the ZnTPP fluorescence ratio versus TEA concentration according to the Stern−Volmer equation

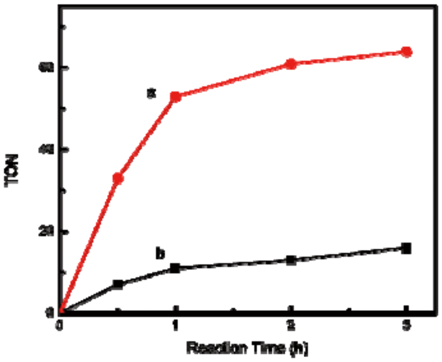


Fig 6 The formation of CO (a) and formic acid (b) during the whole photoreaction of Group 3.

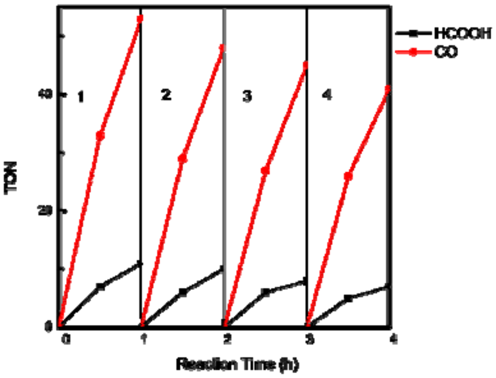
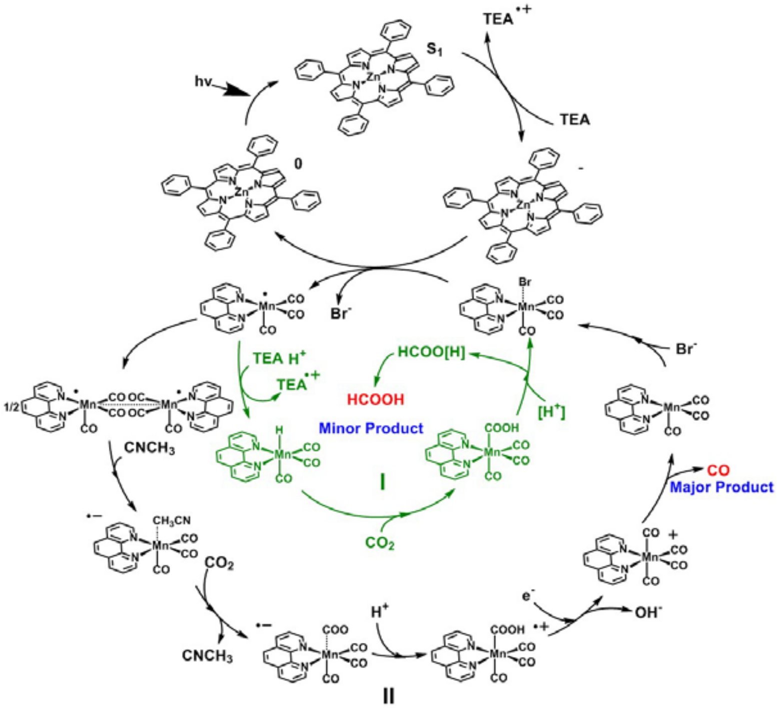


Fig 7 Reusability of the photocatalyst system under the solar irradiation.



Scheme 1 Proposed Reaction Mechanism

Table 1 Photocatalytic reactions

Group Number	***fac*-[Mn(phen)(CO)$_3$Br]/ZnTPP**[a]	**TON**[b]	
		CO	HCOOH
1	4:1	119	19
2	3:1	97	18
3	2:1	64	16
4	1:1	12	10
5	1:2	8	6
6	Only *fac*-[Mn(phen)(CO)$_3$Br][c]	2	1
7	Only ZnTPP[d]	0	0

Irradiation with 500w xenon lamp conducted on a solution containing a Mn complex (0.5 mM), ZnTPP in a certain concentration, TEA (0.1 M) in a MeCN-Water (v/v=20:1) solution under a CO_2 atmosphere. The reaction time in this experiment was set to be 180 minutes.

[a] In this photoreaction, the concentration of *fac*-[Mn(phen)(CO)$_3$Br] and ZnTPP were set as the following part: 1. *fac*-[Mn(phen)(CO)$_3$Br] 2mM, ZnTPP 0.5mM; 2. *fac*-[Mn(phen)(CO)$_3$Br] 1.5mM, ZnTPP 0.5mM; 3. *fac*-[Mn(phen)(CO)$_3$Br] 0.5mM, ZnTPP 0.25mM; 4. *fac*-[Mn(phen)(CO)$_3$Br] 0.5mM, ZnTPP 0.5mM; 5. *fac*-[Mn(phen)(CO)$_3$Br] 0.5mM, ZnTPP 1mM.

[b] According to the existing formula, TON = n(product)/n(catalyst).

[c] In this group, only Mn(phen)(CO)$_3$Br was added into the system, with the concentration of 0.5mM.

[d] In this group, only ZnTPP was added into the system, with the concentration of 0.5mM.