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Multielectron transportation of polyoxometalate-grafted metalloporphyrin coordination frameworks for selective CO₂-to-CH₄ photoconversion

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Abstract

Photocatalytic CO₂ reduction into energy carriers is of utmost importance due to the rising concentrations of carbon dioxide and the depleting energy resource. However, the highly selective generation of desirable hydrocarbon fuel, such as methane (CH₄), from CO₂ remains extremely challenging. Herein, we present two stable polyoxometalate-grafted metalloporphyrin coordination frameworks (POMCFs), which are constructed with reductive Zn-ε-Keggin clusters and photosensitive TCPP linkers, exhibiting high selectivity (> 96%) for CH₄ formation in photocatalytic CO₂ reduction system. To our knowledge, the high CH₄ selectivity of POMCFs has surpassed all of the reported coordination framework-based heterogeneous photocatalysts for CO₂-to-CH₄ conversion. Significantly, the introduction of Zn-ε-Keggin cluster with strong reducing ability is the important origin for POMCFs to obtain high photocatalytic selectivity for CH₄ formation, considering that eight Mo⁵⁺ atoms can theoretically donate eight electrons to fulfill the multi-electrons reduction process of CO₂ to CH₄ transformation.

Keywords: reductive polyoxometalate, coordination frameworks, CO₂ photoreduction, high selectivity, methane.
Introduction

Excessive CO₂ discharge derived from the continuous burning of fossil fuels has caused global warming and environmental issues [1-2]. Artificial conversion of excess CO₂ into serviceable energy product is an important pathway to achieve sustainable development [3-6]. Solar-driven photocatalytic reduction of CO₂ to carbon-neutral fuels (CO, CH₄) and/or value-added chemicals (HCOOH, CH₃OH) affords a feasible strategy for the aforesaid conversion [7-11]. The implementation of this reaction can mitigate the greenhouse effect and energy crisis simultaneously. However, the structural activation process of CO₂ molecule is particularly difficult because of its intrinsically chemical inertness and high C=O bond cleavage enthalpy [12]. In order to circumvent the highly negative equilibrium potential (versus NHE) for thermodynamically unfavourable CO₂⁻ intermediate, proton-assisted multiple electron reductive products including chemicals and/or hydrocarbon are commonly obtained so as to lower the activation energy of photocatalytic CO₂ conversion [10]. Even so, the formation of high-order proton and electron transferring products still needs to surmount considerable kinetic barrier, and the competitive H₂ evolution further increase the difficulty for getting the aiming product selectively [13-14]. For instance, the photosynthesis of CH₄, one kind of most desirable and valuable hydrocarbon fuel in photoreaction system, has been a grand challenge [15], since the accomplishment of eight-electron transport process requires the photocatalyst to offer both strong reducing capability and sufficient electrons theoretically.

At present, the reported photocatalysts for CH₄ formation mainly fall into two categories: i) heterogeneous nanoscale semiconductors [16-18], which exhibit relatively low activity and selectivity for CH₄ despite of suitable band gaps and well recyclability; ii) homogeneous molecular metal complexes, with identifiable active centres, very few of which show high activity and selectivity of CH₄ [19]. Although their crystallography essence is propitious to the clarification of photocatalytic mechanism [20-26], the structural dissolubility makes them hard to separate from reductive products. In view of the practical application, constructing heterogeneous photocatalyst with well-defined structure for selective CH₄ generation maybe a good chance. Recently, a handful of moderated or high-valence metal or metal cluster-based coordination frameworks (MCFs) have been investigated in the field of CO₂ photoconversion [27-37], but the majority of reductive products primarily focus on
two electron-transferred CO/HCOOH. Only individual porphyrin-based MCF family (MOF-525) presents a low selectivity for CH₄ generation [28], which is probably related to insufficient redox and electron-donating abilities of catalytically active units. In addition, the structural collapsibility of ordinary MCFs in aqueous phase enables the photocatalytic reaction to occur exclusively in organic medium [29-30] that no doubt exerts adverse effects on the environment.

Based on the aforementioned considerations, we conceived that polyoxometalate (POM)-based coordination frameworks (POMCFs), with well-known structural stability and favorable catalytic performance [38-39], are probably more beneficial to execute photocatalytic reduction of CO₂ due to the synergistic effect originated from the integration of POM and MCF [40-43]. In particular, the Zn-ε-Keggin cluster of PMo₁₂ “electron sponges” family [44-45], including eight Mo^V atoms, can behave as a strong reductive component and contribute eight electrons theoretically. In addition, the Zn-ε-Keggin, a tetrahedral node, is formed by four-trapped Zn(II) locating in ε-Keggin (PMo₁₂). Compared with most anionic POMs, the ε-Keggin modified with metal Zn becomes a cationic cluster, which is favorable for coordination with organic ligands. Consequently, if the reductive POM cluster and porphyrin derivative can be employed to fabricate POMCF, having both the visible-light harvesting and photo-excited electron migration, that would be a good strategy towards selectively photoreducing CO₂ to multielectron reductive products.

Herein we report two structural analogous porphyrin-based POMCFs, [PMo⁸Mo⁴V₄O₃₅(OH)₅Zn₄]₂[Zn-TCPP][2H₂O]-xGuest (NNU-13, H₂TCPP = tetrakis[4-carboxyphenyl]-porphyrin) and [PMo⁸Mo⁴V₄O₃₅(OH)₅Zn₄]₂[Zn-TCPP][2H₂O]-yGuest (NNU-14), constructed with {ε-PMo⁸Mo⁴O₄₀Zn₄} (Zn-ε-Keggin [45], PMo₁₂ capped with four Zn^{II} ions) nodes and porphyrin derivative (H₂TCPP) bridging ligands. Both of them show expected architectural stability and preeminent performance on photocatalytic reduction of CO₂. The whole photocatalytic reaction was performed in aqueous solution, without any participation of photosensitizer and precious metal co-catalyst. It is worth noting that the strong reducing ability of Zn-ε-Keggin entity, combined with remarkable optical and electrical properties of TCPP linker, successfully endows these compounds superior photocatalytic selectivity for CH₄ production. To our knowledge, the high CH₄ selectivity of 96.6% for NNU-13 have surpassed all of the reported
heterogeneous coordination framework-based photocatalysts [46], while NNU-14 displays a slightly low CH\textsubscript{4} selectivity of 96.2% by reason of subtle structural deformation.

**Results and Discussion**

Crystalline NNU-13 and NNU-14, prepared through similar hydrothermal synthesis protocols (Supplementary Fig. 1), show nearly identical host framework constructed from Zn-\(\varepsilon\)-Keggin nodes and 4-connected TCPP linkers. Single-crystal X-ray diffraction analysis demonstrated that these two compounds crystallize in the orthorhombic \(Fmmm\) (NNU-13) and monoclinic \(C2/m\) (NNU-14) space groups (Supplementary Table 1) respectively. We have been working on the polyoxometalate-grafted photosensitive / electrosensitive ligands, such as NNU-13 and Co-PMOF [47]. Compared to the synthesis method of NNU-13, the pH value of the solution was different and TPT was additionally added when NNU-14 was synthesized. The TPT acts as a templating agent in the synthesis of NNU-14. In each Zn-\(\varepsilon\)-Keggin cluster, two Zn1 sites along \(b\) axis coordinate with two different TCPP ligands, while the remaining two Zn2 sites along \(a\) axis oppositely bridges with two adjacent Zn-\(\varepsilon\)-Keggin motifs, under the symmetry operation of \(2_1\) screw axis, forming a wavy POM chain in the end (Fig. 1a and 1b). In comparison, octahedral Zn3 atom is captured by the “pocket” of TCPP center with two axial coordinated H\textsubscript{2}O molecules. Four carboxyl groups of each TCPP ligand concurrently are linked to four Zn1 atoms from different Zn-\(\varepsilon\)-Keggin clusters of four POM chains (Fig. 1c). Subsequently, a three-dimensional network is established by connecting Zn-TCPP linkers with Zn1 sites of the POM chain alternately (Supplementary Fig. 2-3), leading to an approximate dihedral angle of 105.6° between POM chain and Zn3-TCPP metalloligand along crystallographic \(a\) axis (Fig. 1d). Ultimately, NNU-13 shows a two-fold interpenetrated mog topological structure (Supplementary Fig. 4a) as a result of multiple existing symmetry elements (rotation and screw axes together with mirror and glide planes). Likewise, NNU-14 also has the same mog topology (Supplementary Fig. 4b), but its comparatively low spatial symmetry gives rise to approximate dihedral angles of 113.3° and 97.7° between POM chain and Zn-TCPP linker along crystallographic \(a\) axis (Fig. 1d). Notably, this structural distortion leads to the divergence on lattice parameters (Supplementary Fig. 5) and the shortest Zn-Zn
distances (between the active Zn center in TCPP pocket and the nearest Zn atom on Zn-ε-Keggin cluster) of 10.7 (NNU-13) and 10.1 Å (NNU-14), respectively (Fig. 1e and Supplementary Table 2b).

The phase purity and chemical stability of NNU-13 and NNU-14 compounds were confirmed by powder X-ray diffraction (PXRD) patterns (Supplementary Fig. 6). The two POMCF samples were separately immersed into aqueous solutions with various pH values from 5 to 12 for at least 12 hours. Noticeably, PXRD patterns of all treated crystals remain intact, indicating there was no phase transition or structural collapse occurred, even under the condition of conventionally artificial photosynthesis reaction system (Supplementary Fig. 6) [48]. The two POMCFs are relatively stable mainly due to the high temperature hydrothermal synthesis and small pore sizes.

There are many other strategies that can be used for the synthesis of stable Zn-MOF such as the introduction of hydrophobic methyl groups [49]. NNU-13 can adsorb CO2 with the maximum uptake of 34.1 cm3 / g at 298 K, while NNU-14 can adsorb CO2 with the maximum uptake of 14.3 cm3 / g at 298 K (Supplementary Fig. 7). Both NNU-13 and NNU-14 have the ability to capture CO2, which is conducive to CO2 photoreduction. Besides, in order to validate the visible-light enrichment capability, the corresponding diffuse reflectance UV/vis spectra were characterized. Both the compound NNU-13 and NNU-14 exhibit broad adsorption covering the whole UV-vis region, as well as a red shift of the Soret band, along with a slight increase in the band intensity (Supplementary Fig. 8a). Moreover, the decreased number of adsorption peaks at Q band compared with free H2TCPP ligand, associated with increased molecular symmetry for metalloporphyrin, indicates the occurrence of charge transfer between zinc ion and TCPP ligand. Based on these results, the band gaps are ca. 1.59 (NNU-13) and 1.64 eV (NNU-14), slightly higher than H2TCPP ligand of 1.53 eV (Supplementary Fig. 8b), unveiling the potential for these POMCFs being as semiconducting photocatalysts. To elucidate the semiconductor character of title compounds and their possibilities for subsequently photocatalytic conversion of CO2, Mott–Schottky measurements were performed at different frequencies (Supplementary Fig. 8c and d). From the C−2 values vs applied potentials function relationship, the positive slopes of curves are consistent with that of the typical n-type semiconductors, and the flat band potentials determined from the intersection point are approximately −1.18 V vs. Ag/AgCl (NNU-13) and −1.30 V vs. Ag/AgCl.
(NNU-14). Since the bottom of the conduction band (LUMO) in n-type semiconductors is commonly close to the flat-band potential [50], the LUMO of NNU-13 and NNU-14 can be estimated to be −0.98 V (vs. NHE) and −1.10 V (vs. NHE), respectively (Supplementary Fig. 8c and d). In view of such negative potentials for LUMO in POMCFs, CO2 molecule theoretically can be converted into CO (−0.53 V vs. NHE) and CH4 (−0.24 V vs. NHE) upon visible-light irradiation. The CV curves of NNU-13 and NNU-14 were carried out in the reaction solution and four pairs of redox peaks appeared in the potential range from -0.6 V to 0.5 V vs. Ag/AgCl, attributing to the four single electron transfer of POM secondary building block in alkaline solution (Supplementary Fig. 9).

The visible light-driven CO2 reduction of NNU-13 and NNU-14 were conducted under pure CO2 atmosphere in aqueous solution with triethanolamine (TEOA) as a sacrificial agent, in the absence of any photosensitizer and precious metal co-catalysts. Gaseous CH4 and CO are the main reactive products detected by gas chromatography, and no competitive H2 evolution was observed in the whole photoreaction process (Fig. 2 and Supplementary Fig. 10 and 11). Such low photocatalytic H2 production activities of NNU-13 and NNU-14 can be further supported by replacing CO2 with N2 (Supplementary Table 3). After 6 hours, only 0.055 (NNU-13) and 0.035 (NNU-14) μmol H2 were detected under identical reaction conditions, without any CO generated. As indicated by Fig. 2a and b, the output of CH4 increases steadily with a prolonged time of light irradiation, while the CO yield has a negligible growth. With the reaction going on, the amount of CH4 for NNU-13 reaches to maximum 3.52 μmol (i.e., 704 μmol g−1) after 6 h, whereas NNU-14 performs a CH4 generation of 1.56 μmol (i.e., 312 μmol g−1) after 7 h. By contrast, the CO amounts determined after reaction peaked at 4.2 μmol g−1 h−1 (NNU-13) and 1.2 μmol g−1 h−1 (NNU-14). Moreover, both of NNU-13 and NNU-14 exhibit high selectivity (CH4 over CO) of 96.6% and 96.2% (Fig. 2c), due to the similar connection strategy between POM and TCPP. It is worth noting that both selectivity and activity of CH4 for these POMCFs are the highest among the reported heterogeneous coordination framework-based photocatalysts applied in photocatalytic reduction of CO2 (Supplementary Table 4) [28, 34]. There are no Co and Fe in NNU-13 and NNU-14, which reveals that the generation of CH4 eliminates the interference of Fe and Co (Supplementary Table 5). The relevant parameters of this
photo-reduction system, including TONs, TOFs and $\Phi$ $\text{CH}_4$, are summarized in Supplementary Table 6. The overall $\text{CH}_4$-TON of NNU-13 was estimated to be 3.56, which is higher than that of NNU-14 (1.57), suggesting that both of these complexes are indeed catalytic for $\text{CO}_2$-to-$\text{CH}_4$ conversion. The apparent quantum yield of these optimized POMCFs-promoted $\text{CO}_2$ photo-reduction systems were estimated to be 0.04% (NNU-13) and 0.02% (NNU-14) at monochromatic irradiation of $\lambda = 550$ nm. Obviously, compound NNU-13 has higher photocatalytic $\text{CO}_2$ reduction activity than NNU-14, as demonstrated by evidently distinguishing transient photocurrent responses and electrochemical impedance spectra (Supplementary Fig. 12 and 13). Although both of them display obvious photocurrent responses to visible light irradiation, NNU-13 has much higher photocurrent than that of NNU-14, which means a better separation efficiency of the photo-induced electron-hole pairs for NNU-13. At the same time, the semicircle size of the Nyquist plot for NNU-13 is much smaller, reflecting an acceleration of interfacial charge transfer process, in accordance with above photocurrent response results. These differences in the charge separation and the kinetics of charge transfer can be attributed to the structural distortion on dihedral angles between POM chain and Zn-TCPP linker in NNU-13 and NNU-14.

Additionally, a series of reference experiments were conducted in the absence of POMCF catalysts, $\text{CO}_2$ or light illumination, no detectable products were observed in the reaction system (Supplementary Table 3). Moreover, the influence of different POMCF qualities on the activity of photoconversion $\text{CO}_2$ reaction was also investigated [31], for which the high selectivity of $\text{CH}_4$ over CO was still be retained (Supplementary Fig. 14). The photocatalytic stability of these POMCFs was evaluated using recycling tests. From the time course plots of $\text{CH}_4$ evolution, the photocatalysts maintain excellent activities even after three cycles (Supplementary Fig. 15). The slight decay in the $\text{CH}_4$ evolution rate in each successive run probably attributed to the mass loss in the recovery process of used samples. There has no noticeable alteration on the IR and PXRD patterns performed before and after three cycles of photocatalytic reaction that confirmed the structural robustness of NNU-13 and NNU-14 (Supplementary Fig. 16 and 17). Moreover, the filtrate reaction was further executed to confirm the heterogeneous nature of these POMCFs. Once the catalysts were removed from the reaction system after several hours’ photocatalytic reduction,
the production of CH₄ and CO stopped, that clearly preclude the influence of potential intermediate or decomposed active component on the product generation (Supplementary Fig. 18). From these results, both of NNU-13 and NNU-14 possess high durability toward the CO₂ photocatalytic reduction under visible-light irradiation. After photocatalytic reaction, trace amounts of formic acid were produced in aqueous solution as detected by ion chromatograph. An isotopic experiment that using $^{13}$CO₂ as substrate was performed under identical photocatalytic reaction conditions to validate the carbon source of the generated gases [18, 33, 51], and the products were analyzed by gas chromatography and mass spectra. As shown in Fig. 2d and Supplementary Fig. 19-20, the peaks at m/z = 17/16/15/14 and m/z = 29 were assigned to fragments of $^{13}$CH₄ and $^{13}$CO, respectively, providing a solid proof that these POMCFs are indeed active and capable of selectively converting CO₂ to CH₄ under visible-light irradiation. In addition, taking NNU-13 for example, the experiment under CO atmosphere was carried out. And the result verifies that CO is an intermediate for further CH₄ generation (Supplementary Fig. 21).

To disclose the origin and difference of photocatalytic performances of NNU-13 and NNU-14, the roles of structural components including POM subunit (Zn-$\varepsilon$-Keggin) and TCPP organic linker were considered. On the one hand, it is well known that all the previously reported TCPP-based MOF photocatalysts in photocatalytic CO₂ reduction system, involving mono/multi-metal active center either in moderate or high valence state, tend to produce high CO over CH₄ selectivity and activity, such as MOF-525 family and Zr-MOFs [28, 34]. Although high-valent metal clusters could serve as multi-electron acceptor in some cases, its poor reducing ability makes it hard to contribute enough electrons to satisfy the eight-electron process of CH₄. Therefore, based on the reported porphyrin-MOFs for CO₂ photoreduction, two-electron transferred CO as frequently predominant gaseous product probably related to the reduction intensity of active center. To confirm the photocatalytic activity of NNU-13 on the production of CH₄, a series of control experiments were carried out, which involve Zn-$\varepsilon$-Keggin (Supplementary Fig. 22 and 23), Zn-TCPP, and the mixture of Zn-$\varepsilon$-Keggin and Zn-TCPP as independent photocatalysts (Supplementary Table 7). It is obvious that both of Zn-$\varepsilon$-keggin cluster and Zn-TCPP linker produced CO (370 μmol g⁻¹ and 16 μmol g⁻¹, respectively), while the mixtures of Zn-$\varepsilon$-Keggin (POM) and Zn-TCPP (sensitizer) produced CO and CH₄ with lower
yield and selectivity for CH₄. By contrast, NNU-13 assembled with POM and porphyrin showed a higher yield and selectivity for CH₄. Moreover, the generated CO from Zn-ε-Keggin was mainly used for CH₄ formation. Therefore, the integration of photosensitive TCPP with reductive Zn-ε-Keggin within NNU-13 and NNU-14 played an indispensable role in obtaining high CH₄ selectivity. On the other hand, in order to eliminate the potential impact of TCPP linker on high CH₄ selectivity and activity of NNU-13 and NNU-14, similar Zn-ε-Keggin-based POMCF (NNU-12) (Supplementary Fig. 24 and 25) [52], with H₂BCPT instead of TCPP as bridging ligand and light-harvesting unit, was synthesized to execute comparable CO₂ photocatalytic reaction. We found that NNU-12 still maintained a high CH₄ over CO selectivity of 81.3% (Supplementary Table 8), which again corroborated the significance of POM component with strong reducing ability and electron transferring ability (i.e., redox ability). Because of the eight Mo⁵⁺ atoms in reductive Zn-ε-Keggin cluster, it can theoretically easily offer eight electrons to complete the eight-electron reduction process from CO₂ to CH₄. Of course, the relatively poor photocatalytic activity of CH₄ in NNU-12 also indicated the important roles of excellent visible-light harvesting and electron transport capabilities of TCPP linker. In particular for NNU-13 and NNU-14, whose high photocatalytic properties are primarily realized by the synergistic incorporation of advantages of Zn-ε-Keggin node and TCPP linker. In other words, the photo-generated electrons transferred from TCPP linker flowing to POM cluster are indispensable to the efficient photocatalytic CO₂ reduction. Additionally, the relative location and distance between the active center in TCPP pocket and Zn-ε-Keggin cluster (Fig. 1e) result in different levels of competition on CO₂ molecule absorbed, as well as different amounts of active sites in the crystal cells (Supplementary Fig. 5) of NNU-13 and NNU-14, both of which are probably responsible for discrepant photocatalytic activities for these POMCFs.

To obtain a deeper understanding on photo-excited charge carrier separation mechanism in these porphyrin-based POMCFs catalytic systems, the theoretical calculation was carried out based on density functional theory (DFT). The total density of states (TDOS), partial density of states (PDOS) and band structures were shown in Supplementary Fig. 26-27 and 3a-c, and the Fermi levels were taken as the energy zero. From the TDOS, we could see that the alpha-DOS is different from the beta-DOS which suggested the MCF was with a single electron and a magnetic
property (Supplementary Fig. 26). From the PDOS, we could see that the tops of valence band (VB) were composed of the states of all elements, which means top of valence band was distribution by both POMs and TCPP. The bottom of conduction band (CB) was composed of the O 2p states, Zn 3d states and Mo 4d states. We could see that the Zn 3d states which composed the bottom of CB are those in POMs. It suggested that the bottom of CB was distributed substantially by POMs. This composition of DOS suggested that both POMs and TCPP could act as electron donor while only POMs act as electron acceptor. In this case, once the light irradiates the MCF, the electrons in VB are exited. Despite the charge transfer in POMs, the electrons in TCPP will be excited and transferred to POMs, which matches our experimental prediction very well. In order to show the distribution clearly, the partial charge density maps of VB and CB were shown in Fig. 3d and 3e. The partial charge density maps were intuitional figures involving the predominant distribution and transferring direction of CB and VB electrons. According to the partial charge density maps, we could see that the VB was distributed by TCPP while the CB was distributed by POMs. Despite the charge transfer in POMs, TCPP may act as electron donor and POMs may act as electron acceptor, which matched well with our analysis of DOS. Based on above calculations, the mechanism could be explained as follows: the light irradiates on the MCF and the electrons in VB are firstly excited. Subsequently, the electrons in VB (TCPP) transfer to CB (POMs), which can be further utilized for the activation and reduction of absorbed CO₂.

In the light of the combination of the experimental results and theoretical calculations, a mechanism with respect to the superior photocatalytic CO₂ reduction performances of TCPP-based POMCFs and possible photo-generated electrons transport pathway in the system was proposed (Fig. 4). For most of the porphyrin-based MCFs, the catalytic active sites generally situated at the metal-modified porphyrin center and/or relatively high-valent metal/metal cluster nodes [28, 34]. The porphyrin segments absorb the photos to generate electrons and allow the procreant electron transfer to central metal ions/cluster, leading to the formation of CO as the primary gas product. However, for the TCPP-based POMCFs with strong reducing ability (NNU-13 and NNU-14), the predominant product is CH₄. As the calculations revealed, the electrons of the tops of valence band (VB) were mainly concentrated on TCPP ligands (Fig. 3d). The TCPP linkers absorb the light
and move the photo-generated electrons on VB toward the reductive Zn-ε-Keggin fragments. Zn-ε-Keggin and Zn-TCPP have been used as catalysts to perform CO₂ photoreduction reactions, respectively, and the results are listed in Supplementary Table 7. Obviously, these results illustrate that the synergistic effect between Zn-ε-Keggin and Zn-TCPP in NNU-13 can further reduce the produced CO to CH₄, and CO is indeed the intermediate for CO₂-to-CH₄ conversion. Ultimately, the enrichment of electrons on the reductive Zn-ε-Keggin fragments (based on the eight MoV atoms) probably makes it preferable to provide enough electrons to CO₂, allowing the further combination with the protons from the water to produce eight-electron transferred CH₄. In the meantime, trace amount of two-electron transferred CO are still more likely to be generated on the Zn-TCPP sites relying on the LMCT effect. Therefore, CH₄ was the predominant reduced product with high selectivity in gas production of the TCPP-based POMCF catalytic system. Of course, the MoVI ions also received the generated electrons and then deliver them, but with lower activity than MoV atoms. TEOA as sacrificial reagent consumed electron holes of the valence band. The protons mainly come from the water due to it as the reaction solvent. An additional verification experiment that using NNU-13 and acetonitrile (aprotic solvent including a little water) as photocatalyst and reagent was performed to prove this consideration, only generating very small amount of CO (ca. 10 μmol g⁻¹).

Conclusion

In summary, the heterogeneous photocatalytic reduction of CO₂ to CH₄ in the aqueous phase is realized for the first time over POM-containing MCFs, NNU-13 and NNU-14, fabricated with reductive Zn-ε-Keggin cluster and visible-light responsive TCPP linker. Theoretical calculations revealed that the photo-generated carriers of VB and CB are mostly distributed on TCPP group and Zn-ε-Keggin cluster, respectively. Consequently, the photo-excited electrons more easily flow to POM port by efficient intercoupling between reductive Zn-ε-Keggin unit and TCPP linker. Therefore, these POMC Fs exhibit high photocatalytic CH₄ selectivity (> 96%) and activity that have far surpassed all of the reported MCF-based photocatalysts. Noted that the introduction of POM building blocks with potent reducing ability not only
endows NNU-13 and NNU-14 with favorable structural rigidity, but also it indeed facilitates the photocatalytic selectivity of CH₄ by theoretically delivering adequate electrons to accomplish the eight-electron reduction of the CO₂ molecule. We expect such a feasible approach, assembling strong reducing component into visible-light sensitized photocatalyst architecture, can ignite research enthusiasm towards the construction of efficient POMCFs photocatalysts for highly selective reduction of CO₂ to CH₄ or other high-valued hydrocarbons.

Methods


Na₂MoO₄·2H₂O (310 mg, 1.28 mmol), H₃PO₃ (10 mg, 0.125 mmol), zinc chloride (68 mg, 0.50 mmol), tetrabutylammonium hydroxide (TBAOH) 10 wt % solution in water (250 μL) and H₂O (3.5 mL) were charged in a Pyrex vial and stirred for 10 min. Then, the pH value of the mixture was adjusted to 5.0 by 2 mol/L HCl. Subsequently, meso-tetra(4-carboxyphenyl)porphine (H₂TCPP) (118.23 mg, 0.15 mmol), Mo powder 99.99% (25 mg, 0.26 mmol) and 250 μL dimethylacetamide were added into the mixture and stirred for 15 min. The mixture was sealed in a 15 mL Teflon-lined stainless steel container and then heated at 180 °C for 72 h. After cooling to room temperature at 15 °C·h⁻¹, dark-violet block crystals of NNU-13 were collected (yield 76% based on H₂TCPP).

Synthesis of NNU-14.

Na₂MoO₄·2H₂O (618 mg, 2.55 mmol), H₃PO₃ (20 mg, 0.25 mmol), zinc chloride (136 mg, 1.00 mmol), tetrabutylammonium hydroxide (TBAOH) 10 wt % solution in water (500 μL) and H₂O (7 mL) were charged in a Pyrex vial and stirred for 10 min. Then, the pH value of the mixture was adjusted to 2.0 by 2 mol/L HCl. Subsequently, tris-(4-pyridyl)triazine (TPT) (46.85 mg, 0.15 mmol), Meso-Tetra(4-carboxyphenyl)porphine (H₂TCPP) (118.23 mg, 0.15 mmol), Mo powder 99.99% (25 mg, 0.26 mmol) and 500 μL dimethylacetamide were added into the mixture and stirred for 15 min. The mixture was sealed in a 15 mL Teflon-lined
stainless steel container and then heated at 180 °C for 72 h. After cooling to room temperature at 15 °C·h⁻¹, dark-violet cuboid crystals of NNU-14 were obtained (yield 64% based on H₂TCPP).

**Single-Crystal X-ray Crystallography.**

Single-crystal XRD data of NNU-13 and NNU-14 have been measured on a Bruker APEXII CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 296K. These two structures were solved by direct method and SHELXT program, and refined on Olex² software by SHELXL program. Multi-scan technique was used to Absorption corrections. The TBA⁺ cations could not be detected in the structure, and some other guest molecules are disordered. Thus, the data were further corrected with SQUEEZE on PLATON software to eliminate some guest molecules and then check the space group of these two crystals. The detailed crystallographic information and selected bond lengths were listed in Supplementary Table 1 and Table 2a.

**Photochemical measurements.**

The photocatalytic CO₂ reduction experiments were probed on evaluation system (CEL-SPH2N, CEaulight, China) in a 100 mL quartz container, and the two round openings of the container were sealed with rubber mats. A xenon arc lamp (CEL-HXF300/CEL-HXUV300, 200 mW / cm²) with a UV-cutoff filter (420-800 nm) was utilized as irradiation source. The as-prepared photocatalyst (5 mg) was evacuated in mixed solutions (30 ml) with AR TEOA (2 ml) and deionized water (28 ml), and pre-degassed with CO₂ (99.999%) for 30 min to remove air before irradiation. The pH values were determined to be 10.5, 10.5 and 7.3 in the absence of the catalyst with TEOA, after suspension of the catalyst, and after sparging with CO₂ (30 min). The sealed reaction system (CO₂ pressure of 1 atm) was positioned about 10 cm away from visible light source, and kept stirring constantly to ensure the photocatalyst particles in suspension. The reactor was connected with a circulating cooling water system to maintain the solutions temperature at around 20°C. Gaseous product was measured by gas chromatography (GC-7900, CEaulight, China, column type: TDX-1) equipped with a flame ionization detector (FID) and a thermal
conductivity (TCD). The isotope-labeled experiments were recorded by gas chromatography-mass spectrometry (GC-MS, 7890A and 5875C, Agilent). GC-MS column (19091P-Q04PT), gas (He as carrier), flow rate (1.4 mL/min, 5.2027 psi) oven ramping parameters (injector temperature: 250 °C, column temperature is constant temperatures: 30 °C).

Photoelectrochemical studies.

5 mg crystal samples was grinded and dispersed in 1 mL mixed solution of ethanol and water under sonication for 1 hour. Then, 10 μL above turbid liquid was daubed on indium-tin oxide (ITO) glass with fixed a circular area (diameter is 6 cm) and the electrode was dried about 24 h in desiccator. The electrochemical experiments were performed on an electrochemical workstation (CHI 660e) in a standard three-electrode system. The Mott–Schottky tests were performed in 0.2 M Na₂SO₄ solution, using catalyst/ITO electrode as the working electrode, Ag/AgCl electrode as the reference electrode and Pt plate as the counter electrode at different frequencies of 500 Hz, 1000 Hz and 1500 Hz. The photocurrent tests were carried out in tris-HCl electrolyte (0.1 M) at a bias of 0.0 V using Xe lamp as light source. Electrochemical impedance spectroscopy (EIS) measurement was carried out on the electrochemical workstation (Bio-Logic, VSP) by applying an AC voltage with 10 mV amplitude in a frequency range from 1000 kHz to 100 mHz.

Supplementary data

Supplementary data are available at NSR online.

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**Author contributions**
Y.-Q.L. conceived and designed the project. Q.H., J.L. and L.Z. performed the experiments, Q.H., F.L., L.-Z.D. and H.-C.Z. collected and analysed the data. Q.W. and W.G. performed the DFT calculations. Q.H., J.L. and Y-Q.L. co-wrote the paper. Y.-H.X. and L.-K.Y. assisted with the experiments and characterizations. All authors discussed the results and commented on the manuscript.

**References**


**Figure Captions**

**Figure 1.** Ball-and-stick view of NNU-13 and NNU-14 crystal structures. (a) four Zn atoms tetrahedron-capped Zn-ε-Keggin cluster; (b) a wavy POM chain was formed by Zn-ε-Keggin units, under the symmetry operation of 21 screw axis; (c) four carboxyl groups of every Zn-TCPP ligand concurrently contact with four different Zn-ε-Keggin clusters from four POM chains; the dihedral angles between POM chain and Zn-TCPP metalloligand in (d) NNU-13 and NNU-14 (coordinated H2O molecules have been eliminated for clarity); the shortest Zn-Zn3 distances in (e) NNU-13 and NNU-14. Color code: Mo, green; Zn, purple; O, red; N, blue; P, yellow and C, grey. Hydrogen atoms have been eliminated for clarity.
**Figure 2.** Performance for photoreduction CO₂ into CH₄. Amounts of CH₄ and CO produced as a function of the visible illumination time over (a) NNU-13 and (b) NNU-14; (c) total product yield and selectivity of gas products in photoreduction of CO₂; (d) the Mass spectra of ¹³CH₄ recorded under a ¹³CO₂ atmosphere, and about the detail spectra of comparative experiments are shown in Supplementary information. The photoreduction of CO₂ reaction occurred in the H₂O/TEOA (14:1 V/V, 30 ml) solution with photocatalyst (5 mg), and illuminated via a Xe arc lamp with a UV-cutoff filter (420-800 nm).
**Figure 3.** Partial density of states (PDOS). (a) Mo and total Zn atoms, (b) C, O and N atoms, (c) Mo atoms, Zn atoms in POMs and Zn atoms in TCPP. Partial charge density maps of (d) Valence band and (e) conduction band above the Fermi level for NNU-13.

**Figure 4.** Proposed mechanism for photocatalytic CO$_2$ reduction over POMCFs under visible-light irradiation.