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Supporting Information

ABSTRACT: It is highly desirable to convert CO$_2$ to valuable fuels or chemicals by means of solar energy, which requires CO$_2$ enrichment around photocatalysts from the atmosphere. Here we demonstrate that a porphyrin-involved metal–organic framework (MOF), PCN-222, can selectively capture and further photoreduce CO$_2$ with high efficiency under visible-light irradiation. Mechanistic information gleaned from ultrafast transient absorption spectroscopy (combined with time-resolved photoluminescence spectroscopy) has elucidated the relationship between the photocatalytic activity and the electron–hole separation efficiency. The presence of a deep electron trap state in PCN-222 effectively inhibits the detrimental, radiative electron–hole recombination. As a direct result, PCN-222 significantly enhances photocatalytic conversion of CO$_2$ into formate anion compared to the corresponding porphyrin ligand itself. This work provides important insights into the design of MOF-based materials for CO$_2$ capture and photoreduction.

Our heavy dependence on fossil fuels for energy results in excessive CO$_2$ emissions and global warming. Tremendous efforts have been made to address this challenge. Currently, carbon capture and sequestration/separation from post-combustion effluents is an accepted working approach. The captured CO$_2$ is injected into underground geological formations for permanent sequestration. But catalytic transformation of the captured CO$_2$ into high-value chemicals and/or fuels would be more desirable than simply storing it as waste. Toward this end, chemical reduction of CO$_2$ with solar energy is one of the most promising solutions. In the past decades, diverse semiconductors, metal-incorporated zeolites, and metal complexes have been exploited for CO$_2$ photoreduction, but the molecular systems are mostly limited to expensive noble metal catalysts. TiO$_2$-based photocatalysts have been intensively investigated owing to their stability and availability at low cost. Unfortunately, their efficiency for CO$_2$ photoreduction is not satisfactory, partly because of the weak CO$_2$ adsorption on the catalyst surface. In addition, most of the reported photocatalysts are active only in the ultraviolet (UV) region. Given that UV light accounts for only ∼4% while visible light contributes ∼43% of solar energy, it is rather imperative to develop visible-light-responsive photocatalysts.

To integrate CO$_2$ capture and its photocatalytic conversion using solar energy, metal–organic frameworks (MOFs), a relatively new class of porous materials, could be a judicious choice. MOFs have been extensively studied over the past two decades and demonstrated to possess promising applications in many fields, especially in CO$_2$ capture, thanks to their high porosity and tunable interaction with CO$_2$ molecules. In addition, previous studies have revealed that metal clusters in MOFs can behave as inorganic semiconductor quantum entities, and the organic linkers could serve as antenna to activate these metal clusters upon photoexcitation, thus making ‘MOF-based photocatalysis’ possible. Some MOFs have recently been developed for photocatalytic water splitting, but reports on photocatalytic CO$_2$ reduction using MOFs or MOF-based composites are still very rare. Meanwhile, the catalytic mechanism remains largely unclear. Given the versatile and tailorable characters of MOF structures, the utilization of solar energy by MOFs, especially in the visible region, could be feasible by judiciously selecting metal ions and organic linkers. However, the current modulation of light absorption over MOFs is limited to a narrow range by tethering the ligand with one or two additional amine groups. To efficiently harvest visible light, it is desired to develop MOFs with absorption covering the visible region as widely as possible.

With all these in mind, we have employed a very stable mesoporous zirconium–porphyrin MOF, PCN-222 (also called MOF-545 or MMPF-6), based on tetrakis(4-carboxyphenyl)porphyrin (H$_2$TCPP), for effective integration of CO$_2$ capture and CO$_2$ reduction under visible-light irradiation in the presence of triethanolamine (TEOA) as a sacrificial agent. The H$_2$TCPP ligand in PCN-222 behaves as a visible-light-harvesting unit, and the high CO$_2$ uptake might facilitate the enrichment of CO$_2$ molecules around the catalytic Zr$_6$ centers, thereby enhancing the photocatalytic efficiency. Furthermore, interrogations by means of ultrafast spectroscopy (together with time-resolved

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photoluminescence (PL) spectroscopy), for the first time on a MOF photocatalyst, have allowed us to unveil the underlying mechanism. We have found that the emergence of a type of deep electron trap state in PCN-222 enables effective suppression of the detrimental electron-hole recombination. Hence, PCN-222 is capable of supplying long-lifetime electrons for the photocatalytic reduction of captured CO2 molecules with much higher activity than that of the H2TCP ligand.

Red-shaped PCN-222, formulated as Zr6(µ3-OH)4(µ-OH)x(TCP₂)2, was prepared according to the documented method (Supporting Information (SI), section 2, and Figure S1). PCN-222 exhibits a 3D network based on Zr₆ clusters connected by H₂TCP ligand and features ultra-large 1D channels of 3.7 nm diameter (Figures 1a and S2). Despite its high N₂ sorption at 77 K (∼1728 m²/g, Figure S4), PCN-222 adsors little N₂ at 273 or 298 K. In contrast, it shows K and the large BET surface area (1728 m²/g, Figure S4), inset is the energy diagram of the HOMO and LUMO levels of PCN-222.

Figure 1. (a) View of the 3D network of PCN-222 featuring large channels running through the c-axis. (b) CO₂ and N₂ sorption isotherms of PCN-222 at different temperatures. (c) UV/vis spectra of H₂TCP and PCN-222. (d) Mott–Schottky plots for PCN-222 in 0.2 M Na₂SO₄ aqueous solution (pH 6.8); inset is the energy diagram of the HOMO and LUMO levels of PCN-222.

Photocatalytic reduction of CO₂ over PCN-222 was conducted with TEOA in CH₃CN as solvent (due to its good solubility for CO₂ and possible cation-solvating property, beneficial for electron transfer to CO₂), under visible-light irradiation (Figure 2, left). Remarkably, PCN-222 exhibits significant photocatalytic activity for CO₂ reduction. The HCOO⁻ anion was continuously produced, the amount increasing to 30 μmol in 10 h, much higher than the values observed over UiO-66-NH₂ and MIL-125-NH₂ under similar conditions. No other products can be detected in the gas and liquid phases (Figures S8 and S9), suggesting that the catalyst is highly selective toward the conversion. Examining the stability of PCN-222, recycling experiments demonstrate that no noticeable change in the yield rate of HCOO⁻ occurs during the three reaction runs (Figure S10). The powder X-ray diffraction profile further manifests that the structure of PCN-222 is retained after reaction (Figure S11). No HCOO⁻ was detected in the absence of either PCN-222 or TEOA, demonstrating their critical roles in the reaction. Moreover, no HCOO⁻ was generated when the reaction was carried out in the dark, demonstrating a truly photocatalytic behavior (Figure 2, left). To verify the origin of HCOO⁻, when 13CO₂ was introduced, while that signal was not detected with 12CO₂ only (Figure 2, right, and Figures S12 and S13). The results unambiguously demonstrate that the produced HCOO⁻ anion indeed comes from CO₂. It is safe to conclude that PCN-222 is very active and capable of selectively converting CO₂ to HCOO⁻ under visible-light irradiation. To unveil the mechanism behind the CO₂ photoreduction over PCN-222, electron spin resonance studies were conducted and revealed that Zr(VI) ions are generated by electron transfer (SI, section 5, and Figure S14). We thus propose that, upon estimated to be 1.75 eV from the Tauc plot (Figure S5), its valence band (HOMO) is then calculated to be 1.35 V vs NHE (Figure 1d). Given the more negative potential of LUMO in PCN-222 than the reduction potential of CO₂ to formate (−0.28 V vs NHE), it is theoretically feasible for the photocatalytic reduction of CO₂ to generate formate over PCN-222. The Mott–Schottky plot and UV/vis spectrum suggest that the H₂TCP ligand is able to act as a visible-light-harvesting unit (SI, section 4).

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irradiation, the H$_2$TCPP in PCN-222 behaves as an antenna to absorb visible light to its excited state, which then transfers electrons to the Zr oxo clusters for reduction of CO$_2$ to HCOO$^-$ in the presence of TEOA as the electron donor (SI, section 5, and Scheme S1). During this process, TEOA might be oxidized to its aldehyde form (SI, section 6, Scheme S2 and Figure S15).

For comparison, H$_2$TCPP was also employed as a photocatalyst to reduce CO$_2$ under similar conditions. Only 2.4 $\mu$mol of HCOO$^-$ was produced after 10 h (Figure 2, left, and Table S1), confirming that the photocatalytic activity can be greatly enhanced by assembling the H$_2$TCPP ligand onto MOFs. Notably, the steady-state PL measurements (Figure S16) indicate that the transformation from H$_2$TCPP to PCN-222 results in pronounced PL emission quenching, implying greatly suppressed radiative electron–hole recombination in PCN-222 relative to H$_2$TCPP, in line with the observed higher photocatalytic activity of PCN-222 than H$_2$TCPP.

To gain a deeper understanding of the efficacy of photoexcited charge separation in PCN-222, we resorted to ultrafast transient absorption (TA) spectroscopy, a robust tool for tracking in real time the charge carrier dynamics in nanosystems. In our TA measurements, a femtosecond visible pump/white-light continuum (WLC) probe scheme was adopted (see SI for details of the pump/probe experiments). The center wavelength of the pump pulses was chosen at 500 nm (i.e., 2.48 eV), which can effectively photoinduce an interband transition in the semiconductor-like PCN-222 system. Figure 3a shows the transient TA spectra recorded at probe delays from 0.2 to 3000 ps, all of which manifest as negative absorbance changes ($\Delta A$) due to ground-state bleaching, noting that the WLC probe (400–490 nm) is blue-shifted relative to the 500 nm pump. As the WLC probe yields essentially the same TA kinetics in this spectral region, we show in Figure 3b a typical spectrum taken at 430 nm. Within the probe-delay limit of our pump/probe spectrometer (∼3 ns), the $\Delta A$ recovery converges to an asymptote (dashed line in Figure 3b) with a non-zero value of $\sim$1.2 mOD. Multiexponential fitting to this asymptotic recovery gives rise to two characteristic time constants, $\tau_1 = 18 \pm 1$ ps (47%) and $\tau_2 = 190 \pm 11$ ps (53%). Notably, the nearly perfect parallelism between the asymptote and the $\Delta A = 0$ line (dashed-dotted line in Figure 3b) suggests that the eventual recovery to $\Delta A = 0$ (a process that should take place) features an extremely long lifetime ($\tau_2$), probably a few tens to hundreds of nanoseconds or even a microsecond long.

The observed two components in the picosecond domain ($\tau_1$ and $\tau_2$) may reflect the electron dynamics associated with the electron trap states that are energetically located within the bandgap of PCN-222. Considering that the lifetimes of such trap states (characterizing the electron-detrapping rates) are typically in the nanosecond domain, we resorted to time-resolved PL spectroscopy. In Figure 3c,d, we compare the PL kinetics of H$_2$TCPP and PCN-222 at 712 nm emission (i.e., the maximum of the lower-lying PL band excited at 515 nm; refer to Figure S16). The PL lifetime of H$_2$TCPP is determined to be 11.32 ± 0.03 ns. Interestingly, similarly to the TA case, two lifetimes with sizable components were also observed for the PL of PCN-222: $\tau_1 = 0.38 \pm 0.02$ ns (46%) and $\tau_2 = 1.63 \pm 0.03$ ns (54%), or 1.07 ± 0.03 ns on average.

By combining the above TA and PL observations, we illustrate the pertinent mechanisms underlying the photoexcited dynamics involved in the two systems (Figure 4). For the molecular system of H$_2$TCPP (left panel), the relevant picture is quite straightforward: The 500 nm laser pulse launches an electronic transition from the ground state $S_0$ to a certain excited state $S_1$ followed by rapid intramolecular deactivation processes to the lowest-lying excited state $S_2$, as dictated by Kasha’s rule. As a result, the pertinent mechanisms underlying the photoexcited dynamics of the two systems (right panel), the existence of two distinct lifetimes for the PL emissions monitored at ∼712 nm (i.e., 1.74 eV, slightly below the 1.75 eV bandgap) suggests that the radiative electron–hole recombination could originate from two trap states (acting as PL emission centers) that are located in very close proximity to the conduction band bottom. These two near-band-edge trap states receive and accumulate the photogenerated electrons transferred from the conduction band bottom in a bi-exponential relaxation manner, reflecting their different trap depths. In terms of the biexponential component proportions, the two electron-trapping processes (47% for $\tau_1$ and 53% for $\tau_2$) seem to nicely coincide with the PL emissions (46% for $\tau_1$ and 54% for $\tau_2$), providing collateral evidence for the validity of our assignment. As compared to the $S_1$ state of H$_2$TCPP, the two trap states of PCN-222 are relatively short-lived (∼1 ns on average for PCN-222 vs ∼11 ns for H$_2$TCPP), implying relatively shallow depths. Nevertheless, the eventual recovery (to $\Delta A = 0$) featuring an extremely long lifetime $\tau_2$ most likely correlates to a third trap state having a rather deep depth. The detrapping of electrons from this deep trap state turns out to be so slow that its corresponding radiative electron–hole recombination is dramat-
visible-light irradiation has been realized, for the electron state in PCN-222 substantially suppresses the detrimental copy, the emergence of an extremely long-lived electron trap photocatalytic conversion. Moreover, as demonstrated by the molecular system, such as porphyrin, into MOFs for CO2 photoreduction. The current study highlights the great potential and advantages in the assembly of a photoactive molecular system, such as porphyrin, into MOFs but also should stimulate further studies toward developing more efficient visible-light-responsive MOFs for CO2 capture and photoreduction utilizing solar energy.

**REFERENCES**


