

Visible-Light Photoreduction of CO₂ in a Metal–Organic Framework: Boosting Electron–Hole Separation via Electron Trap States

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S Supporting Information

ABSTRACT: It is highly desirable to convert CO₂ to valuable fuels or chemicals by means of solar energy, which requires CO₂ 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 CO₂ 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 CO₂ into formate anion compared to the corresponding porphyrin ligand itself. This work provides important insights into the design of MOF-based materials for CO₂ capture and photoreduction.

Our heavy dependence on fossil fuels for energy results in excessive CO₂ 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 CO₂ is injected into underground geological formations for permanent sequestration. But catalytic transformation of the captured CO₂ into high-value chemicals and/or fuels would be more desirable than simply storing it as waste. Toward this end, chemical reduction of CO₂ 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 CO₂ photoreduction,¹ but the molecular systems are mostly limited to expensive noble metal catalysts.^{1g} TiO₂-based photocatalysts have been intensively investigated owing to their stability and availability at low cost.^{1h,2} Unfortunately, their efficiency for CO₂ photoreduction is not satisfactory, partly because of the weak CO₂ 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.^{1f}

To integrate CO₂ capture and its photocatalytic conversion using solar energy, metal–organic frameworks (MOFs),³ 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,^{4–6} especially in CO₂ capture,⁷ thanks to their high porosity and tunable interaction with CO₂ 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,⁸ thus making “MOF-based photocatalysis” possible. Some MOFs have recently been developed for photocatalytic water splitting,⁹ but reports on photocatalytic CO₂ reduction using MOFs¹⁰ or MOF-based composites¹¹ 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.^{10b,c} 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 (H₂TCPP),¹² for effective integration of CO₂ capture and CO₂ reduction under visible-light irradiation in the presence of triethanolamine (TEOA) as a sacrificial agent. The H₂TCPP ligand in PCN-222 behaves as a visible-light-harvesting unit, and the high CO₂ uptake might facilitate the enrichment of CO₂ molecules around the catalytic Zr₆ centers, thereby enhancing the photocatalytic efficiency. Furthermore, interrogations by means of ultrafast spectroscopy (together with time-resolved

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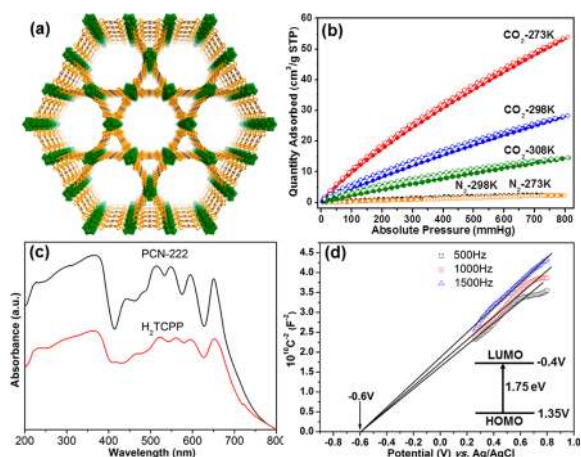


Figure 1. (a) View of the 3D network of PCN-222 featuring large channels running through the *c*-axis. (b) CO₂ and N₂ sorption isotherms of PCN-222 at different temperatures. (c) UV/vis spectra of H₂TCPP and PCN-222. (d) Mott–Schottky plots for PCN-222 in 0.2 M Na₂SO₄ aqueous solution (pH 6.8); inset is the energy diagram of the HOMO and LUMO levels of PCN-222.

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 photoreduction of captured CO₂ molecules with much higher activity than that of the H₂TCPP ligand.

Rod-shaped PCN-222, formulated as Zr₆(μ₃-OH)₈(OH)₈(TCPP)₂, was prepared according to the documented method (Supporting Information (SI), section 2, and Figure S1).¹² PCN-222 exhibits a 3D network based on Zr₆ clusters connected by H₂TCPP ligand and features ultra-large 1D channels of 3.7 nm diameter (Figures 1a and S2). Despite its high N₂ sorption at 77 K and the large BET surface area (~1728 m²/g, Figure S4), PCN-222 adsorbs little N₂ at 273 or 298 K. In contrast, it shows high CO₂ uptake of 14, 35, and 58 cm³/g at 308, 298, and 273 K at 1 atm, respectively (Figure 1b). This suggests a sound interaction between the PCN-222 framework and CO₂ molecules. The calculated heat of adsorption for CO₂ is 23.6 kJ/mol, implying that PCN-222 can be readily regenerated with low energy penalty. These features render PCN-222 a suitable material for CO₂ enrichment in a N₂-rich atmosphere.

The UV/vis spectrum of PCN-222, which well inherits the feature of the H₂TCPP ligand, shows a broad, strong absorption in the region of 200–800 nm (Figure 1c). This allows for promoting the electrons of PCN-222 to an excited state upon visible-light irradiation. To elucidate the semiconductor character of PCN-222 and its possibility for subsequent CO₂ photoreduction, Mott–Schottky measurements on PCN-222 were conducted at frequencies of 500, 1000, and 1500 Hz (Figure 1d). The positive slope of the obtained C⁻² values (vs the applied potentials) is consistent with that of the typical *n*-type semiconductors. The intersection point is independent of the frequency, and the flat band position determined from the intersection is ~−0.60 V vs Ag/AgCl (i.e., −0.40 V vs NHE). Since it is generally accepted that the bottom of the conduction band (LUMO) in *n*-type semiconductors is approximately equal to the flat-band potential,¹³ the LUMO of PCN-222 is estimated to be −0.40 V vs NHE. With the bandgap energy of PCN-222

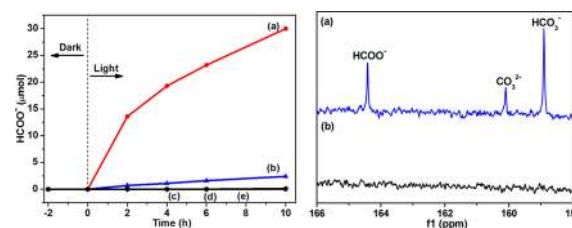


Figure 2. Left: Amount of HCOO[−] produced as a function of the time of visible-light irradiation over (a) PCN-222, (b) H₂TCPP, (c) no PCN-222, (d) no TEOA, and (e) no CO₂. The reaction with each photocatalyst (50 mg) in the MeCN/TEOA (10:1 v/v, 60 mL) solution was irradiated using a Xe lamp filtered to produce light in the range of 420–800 nm. Right: ¹³C NMR spectra for the product obtained from reaction with (a) ¹³CO₂ or (b) ¹²CO₂.

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 H₂TCPP ligand is able to act as a visible-light-harvesting unit (SI, section 4).

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^{11c,14}) 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.^{10b,c} 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[−], N₂ instead of CO₂ as a reactant was introduced into the reaction system under otherwise similar conditions. Only a trace amount (0.14 μmol) of HCOO[−] was obtained after 10 h. Furthermore, the isotopic ¹³CO₂ was employed in the photocatalytic reaction, and the product was identified by ¹³C NMR spectroscopy to confirm the origin of HCOO[−]. The ¹³C NMR spectrum clearly gave a peak at 164.8 ppm, corresponding to HCOO[−], when ¹³CO₂ was introduced,^{10b} 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^{III} ions are generated by electron transfer (SI, section 5, and Figure S14). We thus propose that, upon

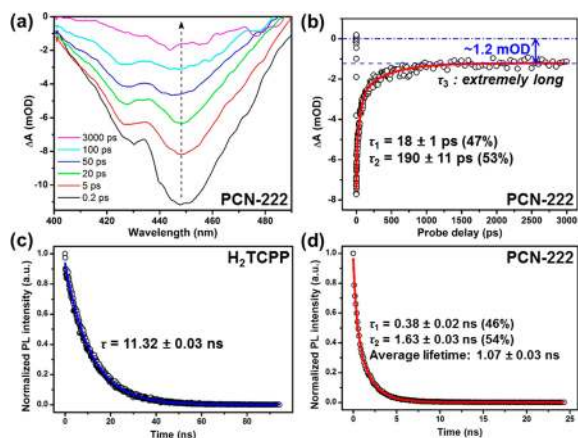


Figure 3. (a) Transient TA spectra of PCN-222 registered at different probe delays (pump at 500 nm). (b) Representative TA kinetics of PCN-222 taken at the probing wavelength of 430 nm. In (a) and (b), the TA signal is given as absorbance change (ΔA) with unit of mOD (OD is optical density). Time-resolved PL kinetics for (c) H₂TCPP and (d) PCN-222, recorded with excitation at 515 nm and emission at 712 nm.

irradiation, the H₂TCPP 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 CO₂ to HCOO⁻ in the presence of TEOA as the electron donor (SI, section 5, and Scheme S1).^{10b} During this process, TEOA might be oxidized to its aldehyde form (SI, section 6, Scheme S2 and Figure S15).

For comparison, H₂TCPP was also employed as a photocatalyst to reduce CO₂ under similar conditions. Only 2.4 μ 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 H₂TCPP ligand onto MOFs. Notably, the steady-state PL measurement (Figure S16) indicates that the transformation from H₂TCPP to PCN-222 results in pronounced PL emission quenching, implying greatly suppressed radiative electron–hole recombination in PCN-222 relative to H₂TCPP, in line with the observed higher photocatalytic activity of PCN-222 than H₂TCPP.

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.^{11b,15} 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 (ΔA) 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 ΔA recovery converges to an asymptote (dashed line in Figure 3b) with a non-zero value of ~ -1.2 mOD. Multi-exponential 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

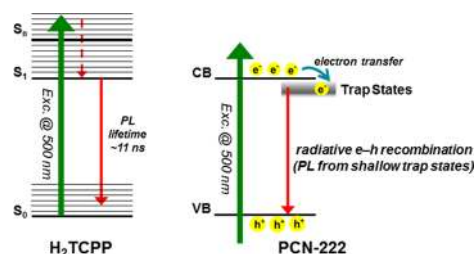


Figure 4. Mechanisms underlying the photoexcited dynamics involved in H₂TCPP (left) and PCN-222 (right). Left: S₀, S₁, and S_n denote the electronic ground state, the first electronically excited state, and a certain high-lying electronically excited state reached by the 500 nm photon, respectively. Right: VB (CB), denoting the valence (conduction) band.

should take place)¹⁵ features an extremely long lifetime (τ_3), probably a few tens to hundreds of nanoseconds or even a microsecond long.

The observed two components in the picosecond domain (τ_1 and τ_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–detraping rates) are typically in the nanosecond domain,¹⁶ we resorted to time-resolved PL spectroscopy. In Figure 3c,d, we compare the PL kinetics of H₂TCPP and PCN-222 at 712 nm emission (i.e., the maximum for the lower-lying PL band excited at 515 nm; refer to Figure S16). The PL lifetime of H₂TCPP 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 H₂TCPP (left panel), the relevant picture is quite straightforward: The 500 nm laser pulse launches an electronic transition from the ground state S₀ to a certain excited state S_n, followed by rapid intramolecular deactivation processes to the lowest-lying excited state S₁, as dictated by Kasha's rule.¹⁷ As a result, PL from S₁ to S₀ with a lifetime of ~ 11 ns was detected. On the other hand, in the semiconductor-like PCN-222 system (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)¹⁶ 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 bi-exponential component proportions, the two electron-trapping processes (47% for τ_1 and 53% for τ_2) seem to nicely coincide with the PL emissions (46% for τ_1 and 54% for τ_2), providing collateral evidence for the validity of our assignment. As compared to the S₁ state of H₂TCPP, the two trap states of PCN-222 are relatively short-lived (~ 1 ns on average for PCN-222 vs ~ 11 ns for H₂TCPP), implying relatively shallow depths. Nevertheless, the eventual recovery (to $\Delta A = 0$) featuring an extremely long lifetime τ_3 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-

ically suppressed, which reasonably explains the absence of the long-lifetime component in the time-resolved PL kinetics (refer to Figure 3d). We thus conclude that, as a direct result of the transformation from H₂TCPP to its MOF architecture (i.e., PCN-222), such a unique, deep trap state emerges and enables effective accumulation of long-lived, photogenerated electrons ready for the photocatalytic reduction of CO₂ molecules captured by PCN-222.

In summary, the photocatalytic reduction of CO₂ under visible-light irradiation has been realized, for the first time, over a photoactive porphyrin-based semiconducting MOF of PCN-222, which exhibits much better activity than the H₂TCPP ligand alone. The high CO₂ uptake capacity in the MOF might allow it to interact better with CO₂ in MeCN, thus benefiting its photocatalytic conversion. Moreover, as demonstrated by ultrafast transient absorption and photoluminescence spectroscopy, the emergence of an extremely long-lived electron trap state in PCN-222 substantially suppresses the detrimental electron–hole recombination, thereby boosting the efficiency of the CO₂ photoreduction. The current study highlights the great potential and advantages in the assembly of a photoactive molecular system, such as porphyrin, into MOFs for CO₂ photoreduction. This work not only provides a deeper understanding of the electron-transfer mechanism involved in MOFs but also should stimulate further studies toward developing more efficient visible-light-responsive MOFs for CO₂ capture and photoreduction utilizing solar energy.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b08773.

Experimental details and characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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