Metal substitution in the metalloporphyrin linker of metal—organic framework PCN-601 for photocatalytic CO₂ reduction

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Abstract
Metalloporphyrinic metal—organic framework PCN-601 exhibits high photocatalytic performance for CO₂ reduction. The photoreduction site was speculated to be the Ni atoms in the nodes and thus the single Ni atoms in the porphyrin centers are not effectively utilized. In this study, we applied Kohn–Sham density functional theory to investigate the effect of metal (Fe, Co, or Cu) substitution in the Ni-porphyrin linker of PCN-601 on the photocatalytic CO₂ reduction. Our results show that the photocatalytic properties of Ni-porphyrin-based PCN-601, including photoexcitation, visible-light absorption, vacuum-aligned energy level, and CO₂ adsorption strength and configuration, can be further optimized by Fe substitution in the Ni-porphyrin linker. In addition, Co-porphyrin-based PCN-601 is also found to be a promising candidate for CO₂ photoreduction though its visible-light absorption is relatively weak in comparison with its Fe- and Ni-based analogs.

1. Introduction
Nowadays, fossil fuel is still the main resource to produce energy to support human activities. Nevertheless, combustion of fossil fuel leads to severe carbon dioxide (CO₂) emissions, and excessive amount of CO₂ seriously affects the balance of natural carbon cycle and brings serious environmental problems such as climate change and global warming [1]. Photocatalytic reduction of CO₂ is a promising technology to mitigate the environmental problems as well as the global energy crisis [2, 3]. However, converting CO₂ into valuable chemicals and fuels is still far from satisfactory due to the low photoconversion efficiency [4, 5].

Great efforts have been devoted to boosting the photocatalytic performance of traditional semiconductor-based photocatalysts by means of optimizing their photocatalyst structures; optimization strategies include incorporation of a co-catalyst (e.g. single metal atom, metal cluster, and photosensitizer) [6], facet or defect engineering [7, 8], and morphology regulation [9, 10]. However, precise control of the structure of a semiconductor-based photocatalyst at atomic-scale is often difficult, hampering further enhancement of photocatalytic performance [5].

In recent years, metal—organic frameworks (MOFs), a class of porous crystalline materials constructed by inorganic nodes and organic linkers [11–13], have attracted enormous attention on designing high-performance photocatalysts, owing to the impressive features (e.g. broad structural tunability, internal pore network, and high surface area) of this type of materials [14–19]. PCN-601, firstly reported by Zhou et al, is a pyrazolate-based porphyrinic MOF built from [Ni₈(OH)₄(H₂O)₂] nodes and 5,10,15,20-tetra(1H-pyrazol-4-yl)-Ni(II)-porphyrin (NiTPP⁺) linkers (see figure 1) [20]. (To highlight the metal in the porphyrin center, we will call it PCN-601(NiTPP); this type of notation will be used throughout the paper). Very recently, PCN-601(NiTPP) has been reported to be a highly effective visible-response
photocatalyst for overall CO\(_2\) reduction with water vapor at room temperature \([21]\). In terms of CO\(_2\)-to-CH\(_4\) production rate, PCN-601(NiTPP) far exceeds the analogous MOFs (PCN-222 \([22]\) and Ni\(_3\)TCPP \([23]\)) based on carboxylate porphyrin \([21]\). It is reported that excited electrons are localized on the Ni sites in the Ni-oxo nodes of this MOF \([21]\). However, it is difficult to utilize the excited electrons in 12-connected Ni-oxo nodes since in these nodes there is no open Ni sites for CO\(_2\) adsorption and only Ni-oxo nodes accompanied by one or more missing linker defects can be active for CO\(_2\) photoreduction, which therefore limits the photocatalytic performance of PCN-601(NiTPP).

It is widely known that the metal of a metalloporphyrin can significantly affect its electronic structure and chemical properties \([24–26]\). Nevertheless, the metals in the metalloporphyrin linkers of PCN-601(NiTPP) are not effectively utilized during photoreduction of CO\(_2\) due to their relatively high-lying unoccupied orbitals (this issue will be further discussed in section 3.1). Therefore, in this work, we investigate the effect of metal (i.e. Fe, Co, or Cu) substitution in the metalloporphyrin linkers of PCN-601(NiTPP) on photocatalytic CO\(_2\) reduction by using the Kohn–Sham density functional theory (DFT). We present a systematic investigation on the photocatalytic properties (e.g. photoexcitation, visible-light absorption, vacuum-aligned energy level, and CO\(_2\) adsorption strength and configuration) of PCN-601(MTPP) with M = Fe, Co, Ni, or Cu and propose a mechanism, which differs from that reported by Zhou et al \([21]\) in that the open metal sites of metalloporphyrin linkers become active sites for photoreduction. Our results show that PCN-601(FeTPP) as well as PCN-601(CoTPP) are promising candidates for visible-light-driven photocatalytic CO\(_2\) reduction.

2. Computational details

2.1. Periodic calculations

Spin-polarized DFT calculations were performed on the periodic models using the *Vienna Ab initio Simulation Package* \([27]\). The PBEsol \([28]\) exchange–correlation functional was used in structure optimizations and the HSE06 \([29]\) exchange–correlation functional was used to obtain the electronic properties. This approach is referred to as HSE06/PBEsol and has been proved to be accurate in computing the structural and electronic properties of PCN-601(NiTPP) \([21]\). The projector augmented wave method \([30]\) and a plane-wave cutoff energy of 500 eV were employed for the periodic calculations. For PBEsol-based structure optimizations and HSE06-based single-point calculations, the \(k\)-point mesh was sampled using \(2 \times 2 \times 2\) and \(1 \times 1 \times 1\) Monkhorst–Pack grids, respectively; note that \(\Gamma\) point sampling of the first Brillouin zone has been proved to be sufficient in electronic structure calculations of MOF PCN-601 \([31]\). A Hellman–Feynman force criterion of 0.02 eV Å\(^{-1}\) was used in structure optimizations.

We used the unit cells of PCN-601(MTPP) (see figure 1) with M = Fe, Co, Ni, or Cu for periodic calculations. Both atomic positions and cell shape were allowed to relax during optimization. The calculated
lattice parameters are summarized in table S1 (available online at stacks.iop.org/JPENERGY/3/034016/mmedia).

The vacuum levels of PCN-601(MTPP) were determined by a method developed by Butler et al [32]. The average of the electrostatic potential values within a spherical probe, which has a radius of 1 Å and is placed at the center of the cubic cage of the PCN-601(MTPP) framework, was used to approximate the reference potential. This method has been successfully employed in theoretical studies to obtain the absolute energy levels of orbitals (e.g. the highest occupied crystal orbital (HOCO) and the lowest unoccupied crystal orbital (LUCO)) of MOFs [14, 15, 33].

Constrained DFT (CDFT) [34, 35] was used to simulate the excited state (ES) of PCN-601(MTPP) by moving an electron in the (original) HOCO to the (original) LUCO. More specifically, CDFT calculations were performed by manually regulating the occupancies of the states of concern based on the HSE06 charge densities. We call the ES simulated by CDFT the CDFT-ES.

The adsorption energies ($E_{\text{ads}}$) of CO$_2$ on the metal atom in the porphyrin center were calculated as follows:

$$E_{\text{ads}} = E[\text{CO}_2] + E[\text{PCN-601(MTPP)}; S] - E[\text{CO}_2/\text{PCN-601(MTPP)}; S]$$

where $E[\text{CO}_2]$ is the calculated energy of an isolated CO$_2$ molecule and $E[\text{PCN-601(MTPP)}; S]$ and $E[\text{CO}_2/\text{PCN-601(MTPP)}; S]$ with $S = \text{GS}$ (ground state) or CDFT-ES are the calculated energies of PCN-601(MTPP) with GS or CDFT-ES electron configuration and CO$_2$ adsorbed PCN-601(MTPP) with GS or CDFT-ES electron configuration, respectively.

Since van der Waals interactions between gas molecules and substrate could be strong [36, 37], the D3 dispersion correction of Grimme [38] was considered in the calculations of CO$_2$ adsorption energies, namely, HSE06 + D3 was used for energy calculations on the PBEsol optimized structures.

### 2.2. Cluster calculations

We also performed cluster calculations of the isolated H$_4$MTPPP (M = Fe, Co, Ni, or Cu) linkers (see figure 2) using Gaussian 16 [39]. The isolated linkers were constructed by protonating the MTPP$^{-}$ anions cut from the optimized periodic models. The GS structures of the isolated H$_4$MTPPP linkers were optimized by relaxing the proton cappings only. The optimized GS structures were then used to perform ES calculations using time-dependent DFT (TD-DFT) with the adiabatic linear-response approximation [40], that is, we consider vertical transitions. The first 50 excited states were calculated for each isolated linker.

For the cluster calculations, we used the HSE06 exchange–correlation functional with the def2-TZVP [41] basis set for C, N, and H and the LANL2DZ [42] basis set for Fe, Co, Ni, and Cu. The absorption spectra of the isolated H$_4$MTPPP linkers were simulated by GaussView 6.0.16 [43] using a Gaussian line shape with a standard deviation of 0.40 eV.
3. Results and discussion

3.1. Ground-state electronic structures of the PCN-601(MTPP) frameworks

It is generally accepted that the ground-state electronic properties (e.g. band gap and frontier orbital composition) of a photocatalyst are valuable for evaluating the performance of that photocatalyst \[14, 15, 33\]. Therefore, we first studied the ground-state electronic structure of PCN-601(NiTPP) (i.e. the PCN-601 framework reported experimentally \[20\]). The most stable spin states of Ni(II) in the nodes and metalloporphyrin linkers of PCN-601(NiTPP) have been verified to be triplet and closed-shell singlet, respectively \[44\]; the magnetic spins of eight Ni(II) atoms in the node prefer to be arranged antiferromagnetically and the arrangement \(k\) was used for further study (see figures S1–S2 and table S2). For convenience, we will use superscripts ‘N’ and ‘L’ to represent node and linker, respectively; for example, Ni\(^N\) and Ni\(^L\) correspond to Ni in the node and Ni in the porphyrin center of the linker, respectively. The calculated density of states (DOS) of this framework shows that the HOCO is mainly contributed by the organic moiety of the metalloporphyrin linkers and the LUCO is delocalized at the Ni\(^N\) atoms and the organic moiety of the metalloporphyrin linkers (see figure 3(c)). These results are consistent with previous studies \[21, 31\] and indicate that linker (organic moiety) to Ni\(^N\) transfer of photoexcited electrons after linker (organic moiety) excitation is feasible from a thermodynamic point of view; note that the organic moiety of the linker is the (major) light-harvester of this framework and linker-to-node charge-transfer excitations are weak \[21\]. The relatively high-lying lowest unoccupied orbital of Ni\(^L\), which is located 0.13 eV above the lowest unoccupied orbital of Ni\(^N\), is probably difficult for photoexcited electrons to access. To discuss this issue, here we define the photoexcited electron transfer from the organic moiety of the metalloporphyrin linker to Ni\(^N\) as event A and the photoexcited electron transfer from the organic moiety of the metalloporphyrin linker to Ni\(^L\) as event B. Assuming that at equilibrium the distribution of transferred photoexcited electrons mainly depends on the energy difference between the two orbitals (i.e. the lowest unoccupied orbitals of Ni\(^N\) and Ni\(^L\)), the probability of the occurrence of event B relative to the probability of the occurrence of event A can be roughly estimated by the following equation:

\[
P = \frac{P(\text{event B})}{P(\text{event A})} = \frac{e^{-\frac{E_B}{kT}}}{e^{-\frac{E_A}{kT}}} = e^{\frac{E_A - E_B}{kT}}
\]

where \(E_B\) is the energy of the lowest unoccupied orbital of Ni\(^L\), \(E_A\) is the energy of the lowest unoccupied orbital of Ni\(^N\), \(k\) is the Boltzmann constant, and \(T\) is temperature.

At room temperature (298.15 K), the calculated \(P\) is 0.006, indicating that event B is substantially hindered. Experimental evidence reveals that Ni atoms are the photooxidation sites of PCN-601(NiTPP) \[21\]. Therefore, it is highly likely that most photoexcited electrons reside at Ni\(^N\) atoms and single Ni\(^L\) atoms of PCN-601(NiTPP) can hardly be utilized during photocatalysis. For photocatalytic CO\(_2\) reduction, CO\(_2\) adsorption is the first step of the reaction. In pristine PCN-601(NiTPP), Ni\(^N\) atoms are fully coordinated and

![Figure 3. Calculated total and projected density of states of (a) PCN-601(FeTPP), (b) PCN-601(CoTPP), (c) PCN-601(NiTPP), and (d) PCN-601(CuTPP). For each case, two plots with different scales are provided, and the right panel is an enlarged version of the left panel showing only a portion of the conduction band. The band gaps (i.e. HOCO–LUCO gaps) are given as well.](image-url)
only defective PCN-601(NiTPP) with missing linker defects can provide open Ni$^{2+}$ sites for CO$_2$ adsorption and reduction. Nevertheless, a high concentration of missing linker defects can destabilize the framework structure of a MOF, and effective utilization of the open metal sites of metalloporphyrin linkers can be a promising way to further boost the photocatalytic performance of PCN-601(NiTPP).

We then consider substituting the metals in the metalloporphyrin linkers of PCN-601(NiTPP) by Fe, Co, or Cu since embedding these metals with oxidation state of +2 into the porphyrin center is feasible synthetically and these metals have been reported to be potential active sites for photocatalytic CO$_2$ reduction [24–26]; the resulting MOFs are called PCN-601(FeTPP), PCN-601(CoTPP), and PCN-601(CuTPP), respectively. We found that the Ni-oxo node of these three MOFs prefers the arrangement i (see figures S1, S3–S5 and table S2). It has been reported that triplet, doublet, and doublet are the most stable spin states for Fe(II), Co(II), and Cu(II) in the porphyrin center, respectively [44, 45]. We then checked the arrangements of magnetic spins in these frameworks and found that, for PCN-601(CoTPP) and PCN-601(CuTPP), the magnetic spins tend to be arranged ferromagnetically, and for PCN-601(FeTPP), the energy of the system is only slightly affected by the arrangement of magnetic spins (see table S3), and previous studies [44, 45] suggest that Fe(II) in iron(II)-porphyrin-based MOFs prefer the ferromagnetic state. Therefore, the following discussions will focus on PCN-601(MTPP) (M = Fe, Co, or Cu) with the ferromagnetic state.

Interestingly, in comparison with PCN-601(NiTPP), the lowest unoccupied orbitals of the metals in the porphyrin centers of PCN-601(FeTPP), PCN-601(CoTPP), and PCN-601(CuTPP) are located closer to their corresponding LUCO in energy (see figure 3). In addition, for the Fe, Co, and Cu cases, the ratio of the unoccupied metal$^{1+}$ orbitals to the unoccupied Ni$^{2+}$ orbitals significantly increases in the low-energy region of conduction band (see right panels of figures 3(a)–(d)); in particular, for PCN-601(FeTPP), in the low-energy region (1.58–2.0 eV for example) of the conduction band, the unoccupied Fe$^1$ orbitals have a much higher density than the unoccupied Ni$^2$ orbitals (see right panel of figure 3(a)). These results reveal that, after substitution of metal$^{1+}$ in PCN-601(NiTPP) by Fe, Co, or Cu, photoexcited electrons in the organic moiety of the metalloporphyrin linker can be transferred to the metal$^1$ more facilely; the open metal$^1$ site with trapped photoexcited electrons can subsequently be utilized to adsorb and activate CO$_2$. It should also be noted that PCN-601(FeTPP) has the narrowest band gap (i.e. HOCO–LUCO gap) of 1.58 eV, followed by PCN-601(NiTPP) (1.73 eV), PCN-601(CuTPP) (1.93 eV), and PCN-601(CoTPP) (1.99 eV). Therefore, it can be rationally expected that the visible-light harvesting capability of PCN-601(FeTPP) is the strongest among the four MOFs. It should be noted that the discussed electronic properties of PCN-601(FeTPP) are preserved when its arrangement of magnetic spins is changed (see figure S6).

3.2. Photoexcitations in the isolated H$_4$MTPP linkers

TD-DFT calculations on the cluster model ([$\text{Ni}_4$(OH)$_4$($\text{H}_2\text{O}$)$_2$(HPz)$_{11}$]H$_3$NiTPP) of PCN-601(NiTPP) show that linker-to-node charge-transfer excitations are much weaker than the linker-localized excitations in this MOF [21], which is consistent with the common sense that metalloporphyrin linkers are the light harvesters of metalloporphyrinic MOFs [24–26]. Therefore, to further understand the photoexcitations in the PCN-601(MTPP) (M = Fe, Co, Ni, or Cu) frameworks, we then performed excited-state calculations on the corresponding isolated H$_4$MTPP species since such simplified isolated linker models are sufficient to catch the major linker-localized excitations in the MOFs. A restricted formalism was used to calculate the closed-shell singlet GS of H$_4$NiTPP, whereas an unrestricted formalism is necessary to calculate the GSs of H$_4$FeTPP (triplet), H$_4$CoTPP (doublet), and H$_4$CuTPP (doublet). For H$_4$NiTPP, the occupied orbitals are doubly occupied and the highest occupied molecular orbital and the lowest unoccupied molecular orbital (LUMO) are the frontier orbitals. For H$_4$FeTPP, H$_4$CoTPP, and H$_4$CuTPP, the unrestricted formalism gives rise to $\alpha$ (spin up) and $\beta$ (spin down) sets of singly occupied molecular orbitals (SOMOs); the highest SOMOs with $\alpha$ and $\beta$ spin states are called $\alpha$-SOMO and $\beta$-SOMO, respectively, and similarly, $\alpha$-LUMO and $\beta$-LUMO, respectively, stand for the LUMOs with $\alpha$ and $\beta$ spin states (see figure S7).

The calculated excitations of the isolated H$_4$MTPP linkers are summarized in table S4. We found that the $\alpha$-LUMO, $\alpha$-LUMO + 2, $\alpha$-LUMO + 3, $\alpha$-LUMO + 4, $\beta$-LUMO, $\beta$-LUMO + 3, $\beta$-LUMO + 4, and $\beta$-LUMO + 6 of the isolated H$_4$FeTPP linker, the $\alpha$-LUMO + 1, $\alpha$-LUMO + 2, $\alpha$-LUMO + 3, $\beta$-LUMO, $\beta$-LUMO + 2, $\beta$-LUMO + 3, and $\beta$-LUMO + 4 of the isolated H$_4$CoTPP linker, the LUMO + 2 and LUMO + 3 of the isolated H$_4$NiTPP linker, and the $\alpha$-LUMO, $\alpha$-LUMO + 5, $\beta$-LUMO, and $\beta$-LUMO + 1 of the isolated H$_4$CuTPP linker are predominantly localized on the metal in the corresponding porphyrin center (see table S5). It is encouraging to see that, in the visible region (1.7–3.2 eV), some relatively strong excitations with oscillator strengths being larger than 0.01 are associated with the mentioned orbitals of H$_4$FeTPP, H$_4$CoTPP, and H$_4$CuTPP (see table 1 and figure 4). The photoexcited electron trapped on the metal can subsequently drive the photoinduced CO$_2$ reduction. In contrast, for H$_4$NiTPP, the excitations associated with its LUMO + 2 and LUMO + 3 are quite weak (see table S5), suggesting that photoexcited electron can hardly be localized on the metal of H$_4$NiTPP, and therefore the metal may not be involved in...
Table 1. Selected excitations of the isolated \( \text{H}_4\text{FeTPP} \), \( \text{H}_4\text{CoTPP} \), and \( \text{H}_4\text{CuTPP} \) linkers.

| Excitation | Excitation energy (eV) | Oscillator strength, \( f \) | Contribution |
|------------|------------------------|----------------------------|--------------|
| \( \text{T}_0 \rightarrow \text{T}_{26} \) | 3.16 | 0.046 | \( \alpha\text{-SOMO-6} \rightarrow \alpha\text{-LUMO}, 58\% \) |
| \( \text{T}_0 \rightarrow \text{T}_{27} \) | 3.17 | 0.015 | \( \alpha\text{-SOMO-6} \rightarrow \alpha\text{-LUMO}, 24\% \), \( \beta\text{-SOMO-3} \rightarrow \beta\text{-LUMO}, 52\% \) |

\( \text{H}_4\text{CoTPP} \)

| Excitation | Excitation energy (eV) | Oscillator strength, \( f \) | Contribution |
|------------|------------------------|----------------------------|--------------|
| \( \text{D}_0 \rightarrow \text{T}_{41} \) | 3.02 | 0.090 | \( \beta\text{-SOMO-4} \rightarrow \beta\text{-LUMO}, 59\% \) |
| \( \text{D}_0 \rightarrow \text{T}_{43} \) | 3.06 | 0.027 | \( \beta\text{-SOMO-5} \rightarrow \beta\text{-LUMO}, 92\% \) |

\( \text{H}_4\text{CuTPP} \)

| Excitation | Excitation energy (eV) | Oscillator strength, \( f \) | Contribution |
|------------|------------------------|----------------------------|--------------|
| \( \text{D}_0 \rightarrow \text{T}_{48} \) | 2.77 | 0.010 | \( \beta\text{-SOMO-7} \rightarrow \beta\text{-LUMO}, 53\% \) |

\( ^{\text{a}} \) Doublet and triplet states are abbreviated as ‘D’ and ‘T’, respectively.

Figure 4. Visualization of the electronic configurations that are relevant to the selected excitations of the isolated (a) \( \text{H}_4\text{FeTPP} \), (b) \( \text{H}_4\text{CoTPP} \), and (c) \( \text{H}_4\text{CuTPP} \) linkers shown in table 1. Color scheme: C, gray; H, white; N, blue; Fe, indigo; Co, light blue; Cu, orange.

Photocatalysis. These results are consistent with the ground-state electronic-structure calculations based on periodic models.

Figure 5 shows the simulated absorption spectra of the isolated \( \text{H}_4\text{MTPP} \) linkers based on the excited-state calculations. Among the four linkers, \( \text{H}_4\text{FeTPP} \) has the lowest onset of absorption (at 1.51 eV) and the largest absorption band in the visible range, showing the most attractive light-harvesting capability, which agrees well with the periodic calculations in section 3.1.

3.3. Energy level alignment

Photocatalytic reduction of \( \text{CO}_2 \) can produce various products, including formic acid (HCOOH), carbon monoxide (CO), formaldehyde (HCHO), methanol (CH\(_3\)OH), and methane (CH\(_4\)) [6]. Previous theoretical study [15] reported that the energy levels corresponding to the reduction potentials for these reactions range from \(-4.03 \text{ eV for CO}_2/\text{CH}_4 \) to \(-3.62 \text{ eV for CO}_2/\text{HCOOH} \) (see figure 6). A photoreduction process involves consumption of photoexcited electrons by reactants (and reaction intermediates). To make this process thermodynamically feasible, the energy level of the photoexcited electron should be higher than the
energy level of that reaction. Herein, we consider the open metal\textsuperscript{L} site holding an excited electron as the photoreduction site. Therefore, the energy level of the photoexcited electron can be approximated by the energy level of the lowest unoccupied metal\textsuperscript{L} orbital. To explore the CO\textsubscript{2} photoreduction possibilities of the PCN-601(MTPP) (M = Fe, Co, Ni, or Cu) frameworks, we calculated the vacuum-aligned energies of the lowest unoccupied metal\textsuperscript{L} orbitals of these MOFs (see figure 6). We found that all of the four MOFs are potential photocatalysts for the considered reactions. However, only a few of these reactions (e.g. CO\textsubscript{2}/CH\textsubscript{4}) can be effectively driven by PCN-601(NiTPP) since the photoexcited electrons in this MOF are predominantly localized on the Ni\textsuperscript{N} sites, and in principle the energy level of LUCO (i.e. conduction band minimum) should be considered.

3.4. CO\textsubscript{2} adsorption
For photocatalytic CO\textsubscript{2} reduction, the activity is directly linked to the adsorption strength of CO\textsubscript{2} [46, 47]. However, CO\textsubscript{2} adsorption is usually weak, and enhancing the adsorption can promote the following CO\textsubscript{2} reduction process [46, 47]. Therefore, we also studied CO\textsubscript{2} adsorption on the metal\textsuperscript{L} of PCN-601(MTPP); two states (i.e. GS and CDFT-ES, see section 2.1 for details) of PCN-601(MTPP) were considered to investigate the effect of photoexcited electron on CO\textsubscript{2} adsorption. When the PCN-601(MTPP) frameworks are in their GS, the interaction between metal\textsuperscript{L} and CO\textsubscript{2} is quite weak (0.03 eV for PCN-601(NiTPP) to 0.39 eV for PCN-601(FeTPP)), and the adsorbed CO\textsubscript{2} molecules preserve their linear configuration in gas...
Figure 7. Optimized adsorption configurations of CO$_2$ on the metal of (a), (e) PCN-601(FeTPP), (b), (f) PCN-601(CoTPP), (c), (g) PCN-601(NiTPP), and (d), (h) PCN-601(CuTPP). For (a)–(d), GS electron configuration is considered, while for (e)–(h), CDFT-ES electron configuration is considered. Adsorption energies and key structural properties (i.e. O–C–O angles and metal–CO$_2$ distances) are also shown. Note that for each case only the metalloporphyrin linker and the adsorbed CO$_2$ are shown for clarity; the adsorbed CO$_2$ and the metal are represented by balls, and the organic moiety of the metalloporphyrin linker is simplified by lines. Color scheme: C of CO$_2$, purple; C of metalloporphy linker, gray; N, blue; O, red; Fe, orange; Co, light purple; Ni, light blue; Cu, brown.

phase (see figures 7(a)–(d)). Interestingly, the adsorption energies (or adsorption strengths) dramatically increase by pumping PCN-601(MTPP) into their CDFT-ES (PCN-601(FeTPP): 0.39 → 2.15 eV; PCN-601(CoTPP): 0.29 → 1.85 eV; PCN-601(NiTPP): 0.03 → 0.80 eV; PCN-601(CuTPP): 0.30 → 1.32 eV), and bent CO$_2$ adsorption configurations are observed for PCN-601(FeTPP) and PCN-601(CoTPP) (see figures 7(e)–(h)), which is probably due to the relatively high portion of photoexcited electron (which can be transferred to adsorbed CO$_2$) distributed on the metal sites in these two MOFs (see figure S8), consistent with the DOS results shown in figure 3. Not surprisingly, the increase on CO$_2$ adsorption energy is smallest for PCN-601(NiTPP) after nudging an electron from HOCO to a higher electronic state LUCO (GS → CDFT-ES), showing the power of metal substitution in the metalloporphyrin linker of PCN-601(NiTTP).

It is generally accepted that bent CO$_2$$^+$ can be easily reduced to various products of CO$_2$ photoreduction [47]. We therefore propose that for PCN-601(FeTPP) and PCN-601(CoTPP) photoreduction occurs on the open metal sites of metalloporphyrin linkers. This mechanism is different from the previously reported mechanism for PCN-601(NiTTP), in which metals in the nodes are considered as photoreduction sites [21], and shows a great advantage in utilizing metals in the porphyrin centers. Accordingly, PCN-601(FeTPP) and PCN-601(CoTPP) are predicted to be promising visible-response photocatalysts for CO$_2$ photoreduction based on their calculated photocatalytic properties (e.g. photoexcitation, visible-light absorption, vacuum-aligned energy level, and CO$_2$ adsorption strength and configuration), and the overall performance of PCN-601(FeTPP) is expected to be superior than that of PCN-601(CoTPP) according to their ground-state and excited-state properties and CO$_2$ adsorption strengths.

4. Conclusions

In this work, we first explored the ground-state electronic structures of PCN-601(NiTTP) as well as the PCN-601(MTPP) frameworks with a different metal (Fe, Co, or Cu) in the porphyrin center. We found that Fe, Co, and Cu substitution in the Ni-porphyrin linker of PCN-601(NiTTP) can effectively tune the electronic structure. The ratio of the unoccupied metal orbitals to the unoccupied Ni orbitals increases significantly in the low-energy region of the conduction band after metal substitution, suggesting that photoexcited electrons can access these orbitals more facilely after metal substitution; this was further proved by excited-state calculations on the isolated linkers. It should be noted that, among the four PCN-601(MTPP) frameworks, PCN-601(FeTPP) has the narrowest band gap of 1.58 eV, indicating that it can exhibit strong visible-light harvesting capability, which is consistent with the simulated absorption spectra of the isolated linkers.

We also explored the thermodynamic feasibilities of CO$_2$ photoreduction and showed that PCN-601(FeTPP), PCN-601(CoTPP), and PCN-601(CuTPP) are potential photocatalysts for CO$_2$
reduction. Encouragingly, when PCN-601(FeTPP) and PCN-601(CoTPP) are in their excited states (CDFT-ESs), we observed adsorption of bent CO$_2$ on the metals$^5$ with quite strong adsorption strengths, which can facilitate the subsequent CO$_2$ reduction process.

From the systematic investigation on the PCN-601(MTPP) frameworks for various properties of CO$_2$ photoreduction, we propose that PCN-601(FeTPP) and PCN-601(CoTPP) are promising candidates for CO$_2$ photoreduction, and PCN-601(FeTPP) is expected to outperform PCN-601(CoTPP). Our study also provides a theoretical guidance on improving the photocatalytic performance of metalloporphyrinic MOFs.

**Data availability statement**

All data that support the findings of this study are included within the article (and any supplementary files).

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