

## Metal–Organic Frameworks

# Auxiliary Ligand-Coordinated Nanoconfined Hydrophobic Microenvironments in Nickel(II)–Acetylide Framework for Enhanced CO<sub>2</sub> Photoreduction

Yingying Qin, Jian Lu, Chen Zhang, Linli Xu,\* and Wai-Yeung Wong\*

**Abstract:** Metal–acetylide frameworks (MAFs), featuring metal-bis(acetylide) linkages ( $-\text{C}\equiv\text{C}-\text{M}-\text{C}\equiv\text{C}-$ ), are emerging as a new class of 2D nanomaterials with promise in catalysis. Here, we report a new 2D Ni<sup>II</sup>–acetylide framework, TPA-Ni(PR<sub>3</sub>)<sub>2</sub>-GYs, that incorporates the Ni<sup>II</sup>(PR<sub>3</sub>)<sub>2</sub> moiety [R = CH<sub>3</sub> (Me), CH<sub>2</sub>CH<sub>3</sub> (Et), and CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> (Bu)] into tris(4-ethynylphenyl)amine-based graphdiyne framework (TPA-GDY). As a result, TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY exhibits an exceptional photocatalytic CO<sub>2</sub> reduction activity of 3807 μmol g<sup>-1</sup> h<sup>-1</sup> and a high selectivity of 99.4% for CO production upon visible light irradiation. Mechanistic investigations reveal a strong orbital matching effect between the *d* orbitals of Ni<sup>II</sup> and the *p* orbitals of the alkynyl C atoms in organic ligands, which not only accelerates the transfer and separation of photogenerated charge carriers but also reduces the reaction potential barrier for the formation of \*COOH intermediates. Furthermore, the high hydrophobicity of the auxiliary coordinated ligands (trialkylphosphines) to Ni center, particularly tributylphosphine, creates a nanoconfined space that enhances both the accessibility of CO<sub>2</sub> and the utilization of Ni<sup>II</sup> catalytic active sites while inhibiting hydrogen evolution. This study highlights the benefit of modulating the microenvironment around the coordinated metal center to enhance the performance of catalysts with direct metal–acetylide bonding.

## Introduction

The development of efficient and noble metal-free photocatalytic systems for the transformation of carbon dioxide (CO<sub>2</sub>) into value-added fuels has garnered significant interest as a mean to address the global energy crisis and mitigate climate issues.<sup>[1–3]</sup> However, the photocatalytic CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) typically suffers from moderate photocatalytic activity and limited selectivity. This is due to the inherent stability of the CO<sub>2</sub> molecule, stemming from its high C=O bond energy and complex multiple proton-coupled electron transfer process.<sup>[4–6]</sup> Therefore, the design and synthesis of

photocatalysts featuring robust active sites capable of efficient CO<sub>2</sub> activation and conversion is of paramount importance.

Graphdiyne, a unique allotrope of carbon, distinguishes itself from conventional *sp*<sup>2</sup> carbon materials (e.g., fullerene, carbon nanotubes (CNTs), and graphene) through its network of *sp* and *sp*<sup>2</sup> hybridized carbon atoms connected by butadiyne linkages ( $-\text{C}\equiv\text{C}-\text{C}=\text{C}-$ ). This distinctive structure endows graphdiyne with a tunable  $\pi$  system, uniformly distributed pores, and readily modifiable electronic properties.<sup>[7,8]</sup> Furthermore, the specific chemical structure of graphdiyne renders it an attractive platform for anchoring metal atoms within a well-defined coordination environment. However, their controllable preparation of graphdiyne-based catalysts remains a huge challenge due to potential structural inhomogeneities and unstable active sites. Thus, a comprehensive understanding of the catalytic mechanism on the atomic level is still lacking. Transition metal ions, serving as efficient catalytic centers, can be incorporated into graphdiyne frameworks via metal–bis(acetylide) linkages ( $-\text{C}\equiv\text{C}-\text{M}-\text{C}\equiv\text{C}-$ ), leading to the formation of a family of metal–acetylide frameworks (MAFs).<sup>[9,10]</sup> Recently, large-area Hg<sup>II</sup>–acetylide frameworks were first isolated for use in optical devices and catalysis by our group.<sup>[11–13]</sup> More relevant to this work, Ni<sup>II</sup>–, Pd<sup>II</sup>–, and Pt<sup>II</sup>–acetylide frameworks have also shown promise as efficient photocatalysts for CO<sub>2</sub>RR.<sup>[14]</sup> A key distinction between Hg<sup>II</sup>–AFs and Ni<sup>II</sup>–, Pd<sup>II</sup>–, and Pt<sup>II</sup>–AFs lies in the presence of coordinated auxiliary ligands (trialkylphosphines), which create a specific microenvironment surrounding the metal centers. Although  $-\text{C}\equiv\text{C}-\text{Hg}-\text{C}\equiv\text{C}-$  units form a linear structure,  $-\text{C}\equiv\text{C}-\text{M}(\text{PR}_3)_2-\text{C}\equiv\text{C}-$  (M = Ni<sup>II</sup>, Pd<sup>II</sup>, and Pt<sup>II</sup>) units adopt a square planar configuration

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at the metal core. The microenvironment of these metal centers can be precisely tuned through coordination with trialkylphosphine using predesigned building blocks,<sup>[9,10,15–17]</sup> offering a powerful tool to influence catalytic performance. However, the specific influence of these auxiliary coordinated ligands on the metal catalytic sites within MAFs remains largely unexplored, despite the fact that they significantly affect the catalytic performance.<sup>[14]</sup>

The surface microenvironment of a catalyst plays a critical role in dictating CO<sub>2</sub> conversion efficiency and product selectivity.<sup>[18]</sup> Photocatalytic CO<sub>2</sub> reduction typically occurs in the aqueous phase, where the limited solubility (~33 mM at 20 °C, 1 atm) and slow diffusion (~1 × 10<sup>−5</sup> cm<sup>2</sup> s<sup>−1</sup>) of CO<sub>2</sub> molecules can hinder their transport to the active sites.<sup>[19,20]</sup> Constructing a hydrophobic nanoconfined space around the active sites can increase the local CO<sub>2</sub> concentration, thereby enhancing the collision frequency of CO<sub>2</sub> with these active sites while simultaneously reducing H<sup>+</sup> concentration to suppress the competing hydrogen evolution reaction (HER).<sup>[21–23]</sup> Metal active centers can be inadvertently buried during catalyst modification or neglected due to the absence of effective catalyst design strategies, including morphology control, defect modulation, oxidation state adjustment, and hydrophobic coating.<sup>[24]</sup> To address these challenges, we designed a photocatalyst based on a 2D Ni<sup>II</sup>-AFs wherein Ni<sup>II</sup> ions are coordinated with hydrophobic trialkylphosphines to generate a nanoconfined space. We hypothesized that adjusting the length of the alkyl chains would significantly affect the photocatalytic CO<sub>2</sub>RR activity. Therefore, it is essential to investigate the confinement effects arising from the hydrophobic microenvironment of trialkylphosphines and explore their influence on the catalytic reaction processes occurring at the surface and interface within this nanoconfined space.

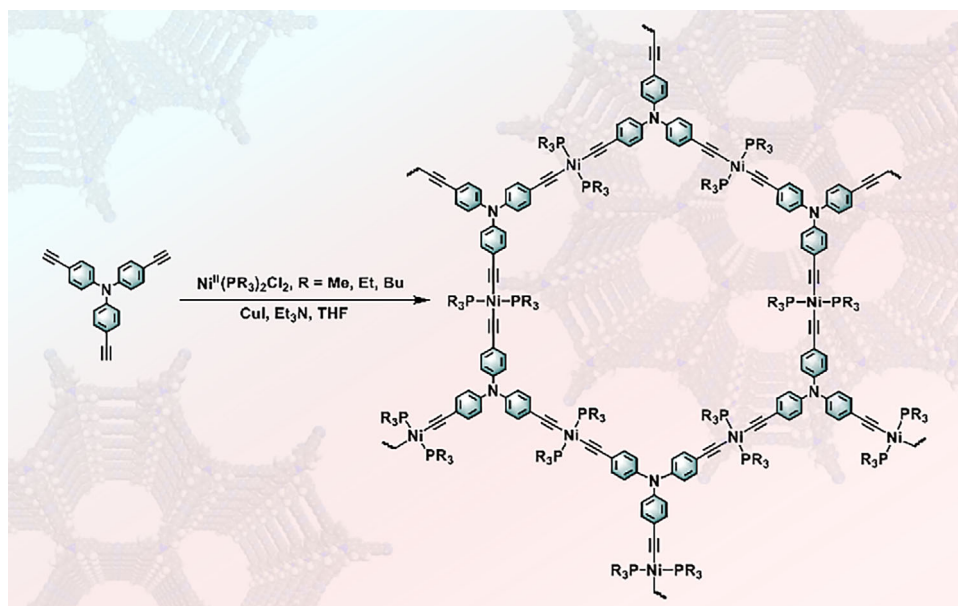
Based on these considerations, we propose a strategy to construct Ni<sup>II</sup>-AFs by modifying non-noble transition metals, fixed by bis(acetylide) bonds, with auxiliary coordinated trialkylphosphine ligands. The strong coordination between the transition metals and acetylide linkages enhances the migration barrier and binding energy of the metal atoms, preventing their migration and agglomeration while improving metal atom utilization efficiency. A synergistic effect between *d*–*p* orbital overlap between transition metal single atoms and adjacent alkynyl carbon atoms, along with  $\pi$ -conjugated moieties, accelerates the transport and separation of photogenerated charge carriers, thereby enhancing the photocatalytic CO<sub>2</sub>RR performance. Notably, the auxiliary coordinated tributylphosphine (PBu<sub>3</sub>) ligands surrounding Ni<sup>II</sup> active sites create a hydrophobic nanoconfined space that increases the collision frequency of CO<sub>2</sub> with the active centers. This work introduces a novel approach to create high photocatalytic-responsive blocks of  $\text{—C}\equiv\text{C—Ni}(\text{PR}_3)_2\text{—C}\equiv\text{C—}$  (where R = CH<sub>3</sub> (Me), CH<sub>2</sub>CH<sub>3</sub> (Et), and CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> (Bu)) capitalizing on the synergistic effect of “diacetylene sites” to anchor single-distributed transition metal atoms and their auxiliary coordinated ligands to establish a hydrophobic nanoconfined space. This approach reveals the relationship between their molecular structure and photocatalytic performance and their underlying mechanism.

## Results and Discussion

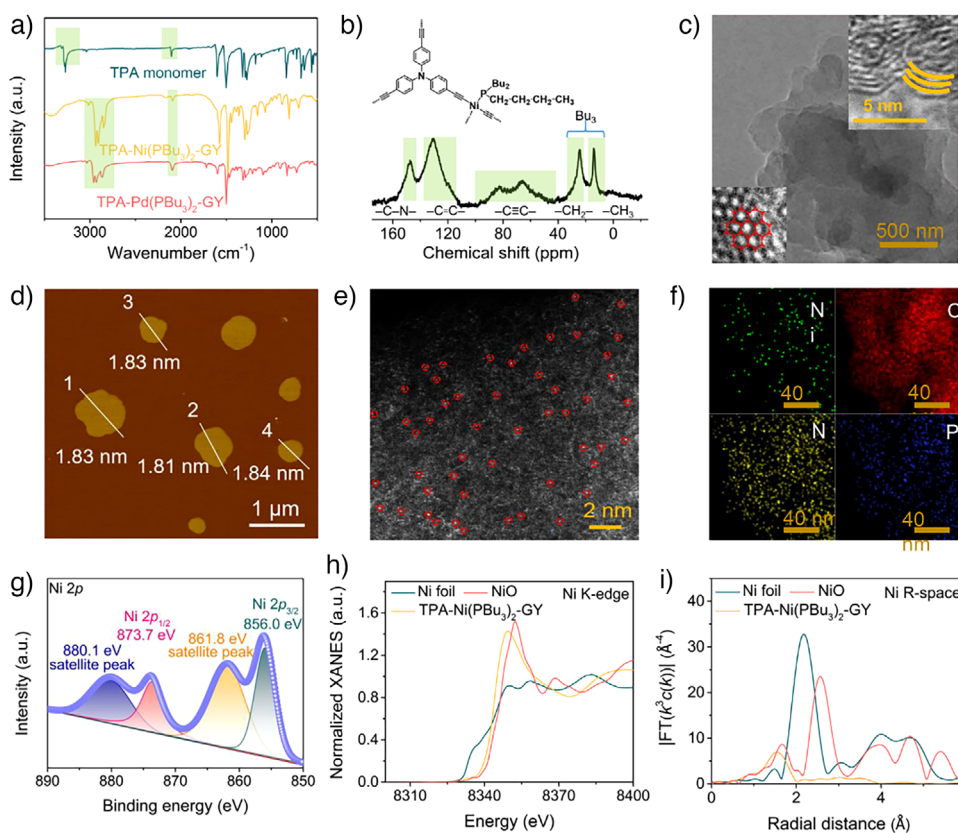
In this study, MAFs incorporating different transition metal ions (M = Ni<sup>II</sup> and Pd<sup>II</sup>) were synthesized via a base-catalyzed dehydrohalogenation reaction in tetrahydrofuran (THF) using triethylamine (TEA) and CuI as catalysts. Specifically, the organic ligand tris(4-ethynylphenyl) amine (TPA) reacted with metal complexes *trans*-Ni(PR<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (where R = Me, Et, and Bu) or *trans*-Pd(PBu<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> to form TPA-Ni(PR<sub>3</sub>)<sub>2</sub>-GYs or TPA-Pd(PBu<sub>3</sub>)<sub>2</sub>-GY (Scheme 1).

The structural characteristics and crystallinity of the TPA-M(PBu<sub>3</sub>)<sub>2</sub>-GYs were analyzed using powder X-ray diffraction (PXRD) and simulations via Materials Studio. As shown in Figure S1, TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY exhibited two broad diffraction peaks: one at 10.54°, attributed to the (111) and (021) planes, and another at 19.60°, corresponding to the  $\pi$ - $\pi$  stacking interactions between adjacent layers, associated with the (001) facet. The experimental PXRD pattern was in good agreement with the calculated pattern for an AA-stacking mode. Pawley refinements yielded unit cell parameters: *a* = *b* = 30.426 Å, *c* = 4.50 Å,  $\alpha$  =  $\beta$  = 90.0°,  $\gamma$  = 120.0°, with residuals of *R*<sub>p</sub> = 1.28% and *R*<sub>wp</sub> = 1.67%, confirming the successful synthesis of TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY. The PXRD pattern of TPA-Pd(PBu<sub>3</sub>)<sub>2</sub>-GY showed peaks at 8.49° and 19.84°, corresponding to the (020), (101), (021), and (001) planes. Theoretical simulations and Pawley refinement confirmed the same AA-stacking model for TPA-Pd(PBu<sub>3</sub>)<sub>2</sub>-GY, with unit cell parameters of *a* = *b* = 30.426 Å, *c* = 4.520 Å,  $\alpha$  =  $\beta$  = 89.999°,  $\gamma$  = 120.00° (residuals *R*<sub>p</sub> = 2.05% and *R*<sub>wp</sub> = 2.76%) (Figure S2). The chemical structures of TPA-M(PBu<sub>3</sub>)<sub>2</sub>-GYs were characterized using Fourier transform infrared (FT-IR) spectroscopy and solid-state <sup>13</sup>C and <sup>31</sup>P nuclear magnetic resonance (NMR) spectroscopy. FT-IR spectra (Figure 1a) revealed the near disappearance of the sharp  $\text{—C}\equiv\text{C—H}$  stretching vibration peaks at approximately 3265 cm<sup>−1</sup> and 2102 cm<sup>−1</sup> for the TPA ligand, alongside the emergence of new peaks at 2167 cm<sup>−1</sup>, corresponding to the  $\text{—C}\equiv\text{C—}$  stretching vibrations in the MAF. This indicates the successful formation of  $\text{—C}\equiv\text{C—M}(\text{PBu}_3)_2\text{—C}\equiv\text{C—}$  moieties. Additionally, the presence of C–H stretching vibration peaks of butyl groups (2824–2998 cm<sup>−1</sup>) in TPA-M(PBu<sub>3</sub>)<sub>2</sub>-GYs further confirms the formation of metal-acetylide networks. Solid-state <sup>13</sup>C NMR spectra showed characteristic signals for butyl groups at 14.2 ppm ( $\text{—CH}_2\text{—}$ ) and 24.6 ppm ( $\text{—CH}_3$ ), alkyne carbons ( $\text{—C}\equiv\text{C—}$ ) at 66.4 and 82.6 ppm, aromatic carbons ( $\text{—C=C—}$ ) between 100.0 and 140.0 ppm, and  $\text{—C—N—}$  at 147.2 ppm (Figures 1b and S3).<sup>[25]</sup> The peaks for  $\text{—Ni—C}\equiv\text{C}$  and  $\text{—Pd—C}\equiv\text{C}$  are challenging to detect due to the low signal sensitivity and broad range within 100–300 ppm.<sup>[26]</sup> Solid-state <sup>31</sup>P NMR spectra of TPA-M(PBu<sub>3</sub>)<sub>2</sub>-GYs exhibited primary peaks at  $\delta$  = 10 ppm, indicative of strong *p*– $\pi$  interactions between phosphorus lone pairs and adjacent diyne  $\pi$  orbitals (Figure S4),<sup>[27]</sup> confirming the successful formation of MAFs.

Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM) analyses (Figures 1c,d and S5–S9) revealed that TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY possesses a 2D layered structure with a thickness of approximately 1.8 nm and displays the Tyndall



**Scheme 1.** Schematic illustration of the synthesis process of TPA-Ni(PR<sub>3</sub>)<sub>2</sub>-GYs (R = Me, Et, and Bu).



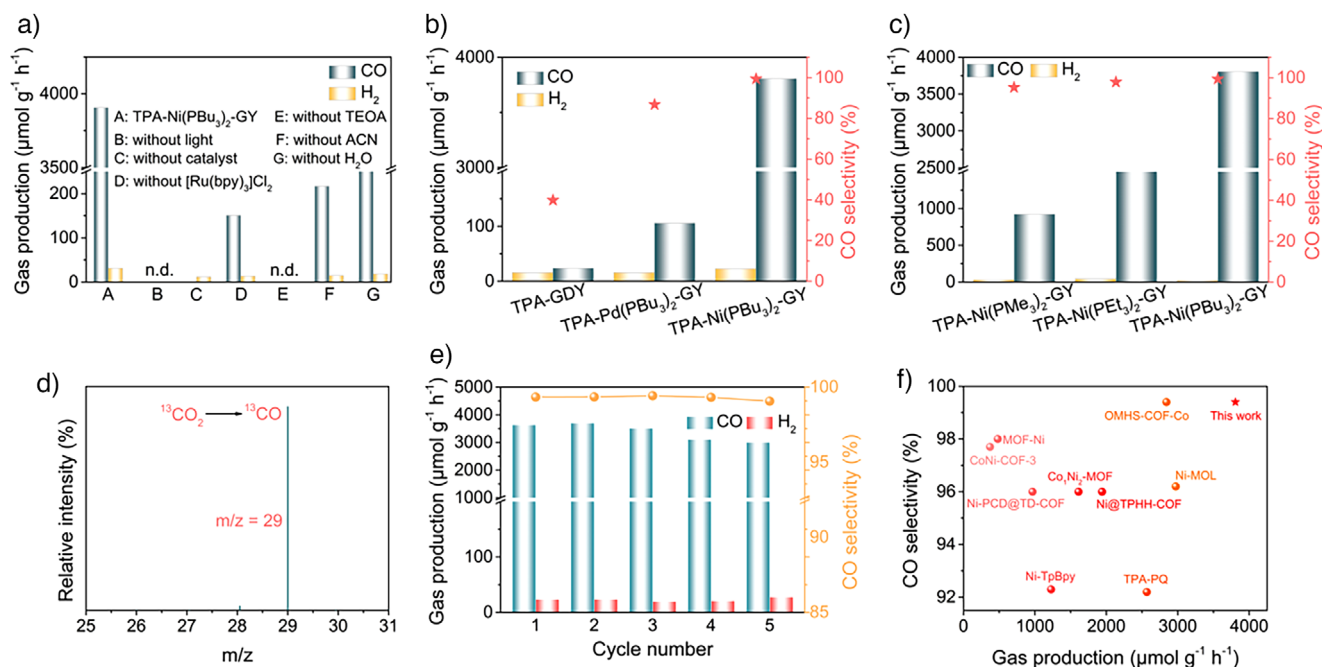
**Figure 1.** a) FT-IR spectra of TPA-M(PBu<sub>3</sub>)<sub>2</sub>-GYs (M = Ni<sup>II</sup> and Pd<sup>II</sup>). b) Solid-state <sup>13</sup>C NMR spectrum of TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY, with <sup>13</sup>C chemical shift assignments indicated on the chemical structure. c) TEM image and HRTEM images, d) AFM image, e) AC-HAADF-STEM image, and f) EDX elemental mapping of TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY. The EDX mapping show the distribution of Ni (green), P (blue), C (red), and N (yellow). g) High-resolution Ni 2p XPS spectrum of TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY. h) Ni K-edge XANES spectra of TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY, Ni foil, and NiO. i) FT EXAFS spectra at the Ni K-edge for TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY, Ni foil, and NiO.

effect in aqueous solution, suggesting colloidal behavior. High-resolution TEM (HRTEM) image showed an interlayer spacing of 4.5 Å. TPA-Pd(PBu<sub>3</sub>)<sub>2</sub>-GY also forms 2D layered nanosheets, indicating that the metal identity does not significantly alter the morphology. The aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC-HAADF-STEM) of TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY displayed many isolated bright dots marked with red circles, which were identified as atomically dispersed Ni centers (Figure 1e). Energy dispersive X-ray (EDX) mapping confirmed the homogeneous distribution of Ni, C, N, and P elements within the TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY matrix (Figure 1f). Inductively coupled plasma-mass spectrometry (ICP-MS) indicated Ni and Pd loadings of 8.31 wt% and 14.20 wt% in TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY and TPA-Pd(PBu<sub>3</sub>)<sub>2</sub>-GY, respectively (Table S1). The Brunauer–Emmett–Teller (BET) specific surface areas were 206.6 m<sup>2</sup> g<sup>−1</sup> for TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY and 110.2 m<sup>2</sup> g<sup>−1</sup> for TPA-Pd(PBu<sub>3</sub>)<sub>2</sub>-GY. The pore volume distributions were approximately 3.0 nm for both samples (Figures S10 and S11).<sup>[28]</sup> The decomposition temperatures of TPA-M(PBu<sub>3</sub>)<sub>2</sub>-GYs were below 300 °C in a N<sub>2</sub> atmosphere (Figure S12). PXRD patterns confirmed that TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY exhibited robust chemical stability in various solvents at room temperature for 24 h, with the patterns consistent with the original material (Figure S13). These properties highlight TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY as a promising candidate for photocatalytic CO<sub>2</sub>RR.

The surface chemical composition and valence states of the samples were investigated by X-ray photoelectron spectroscopy (XPS) analysis (Figures S14–S16). The high-resolution Ni 2p XPS spectra (Figure 2a) displayed a Ni 2p<sub>3/2</sub> peak at approximately 856.0 eV and a Ni 2p<sub>1/2</sub> peak at approximately 873.7 eV, consistent with divalent nickel (Ni<sup>2+</sup>). This confirms the successful integration of Ni<sup>II</sup> ions into the graphdiyne framework, with no detection of other nickel species such as NiO or metallic Ni. Additionally, satellite peaks at ~879.5 eV and ~861.5 eV indicate the presence of high-spin divalent Ni<sup>2+</sup> ions in TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY.<sup>[29]</sup> Figure 2h presents the Ni K-edge X-ray absorption near-edge structure (XANES) spectra for TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY alongside those of two references (Ni foil and NiO). The absorption edge of TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY in the XANES spectra is located at a position similar to those of Ni foil and NiO, indicating that the average oxidation state of Ni species is close to +2. The Fourier-transformed (FT) *k*<sup>3</sup>-weighted EXAFS spectra in R space reveal a primary peak at ~1.53 Å, indicative of Ni–C and Ni–P interactions, with no significant Ni–Ni, Ni–N, or Ni–O–Ni interactions at ~2.17, 1.48, and 2.57 Å, respectively, confirming the presence of single-atom Ni species (Figure 2i). By comparing TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY with other references (Figures S17–S19 and Table S2), EXAFS fitting revealed two types of coordination for Ni: Ni–C (*R*<sub>Ni–C</sub> = 1.866 ± 0.010 Å; CN = 1.9 ± 0.3) and Ni–P (*R*<sub>Ni–P</sub> = 2.054 ± 0.023 Å; CN = 2.3 ± 0.2), confirming that each Ni atom is coordinated by two C atoms and two P atoms to form a P<sub>2</sub>–Ni–C<sub>2</sub> moiety. Regarding the wavelet transforms (WT) of the Ni K-edge EXAFS (Figure S20), only one intensity maximum at approximately 4.1 Å<sup>−1</sup> was observed in TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY, attributed to the Ni–C/P

scattering contribution. These EXAFS results confirm the successful creation of the Ni<sup>II</sup>-acetylide framework, with Ni existing as isolated single atoms.

To evaluate the photocatalytic CO<sub>2</sub> reduction activity of the synthesized materials, control experiments were performed to assess the influence of individual reaction components (Figures S21–S23). As shown in Figure 2a, no carbon-containing products were detected when the photocatalyst, triethanolamine (TEOA), or light were absent or when CO<sub>2</sub> was replaced with argon (Ar). These results underscore the necessity of all these components for the TPA-M(PR<sub>3</sub>)<sub>2</sub>-GYs catalytic system to function properly. Photocatalytic tests were conducted in a mixed water/acetonitrile solution (V<sub>H<sub>2</sub>O</sub>/V<sub>CH<sub>3</sub>CN</sub> = 3:1, 4 mL) under visible light irradiation (λ > 420 nm) from a 300 W Xe-lamp, using [Ru(bpy)<sub>3</sub>]<sup>2+</sup> as the photosensitizer and TEOA (200 μL) as the sacrificial electron donor. Under these conditions, TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY achieved a remarkable CO evolution rate of 3807 μmol g<sup>−1</sup> h<sup>−1</sup> with high selectivity (99.4%) after 5 h (Figure 2b). In contrast, the metal-free TPA-GDY and TPA-Pd(PBu<sub>3</sub>)<sub>2</sub>-GY exhibited substantially lower CO evolution rates of 24 and 106 μmol g<sup>−1</sup> h<sup>−1</sup>, respectively, indicating the critical role of Ni incorporation in the enhanced activity. Importantly, the observed selectivity for CO production remained high even at reduced CO<sub>2</sub> partial pressure, demonstrating the robustness of the system. To elucidate the impact of the trialkylphosphine ligand structure on photocatalytic CO<sub>2</sub> reduction, a series of TPA-Ni(PR<sub>3</sub>)<sub>2</sub>-GYs catalysts with varying alkyl chain lengths (R = Me, Et, and Bu) were evaluated. As illustrated in Figure 2c, the photocatalytic performance exhibited a positive correlation with the length of the alkyl chain. This enhancement is likely due to the creation of a confined microenvironment by the longer alkyl chains, which promotes increased local CO<sub>2</sub> concentration and prolonged interaction between CO<sub>2</sub> molecules and the active Ni sites.<sup>[30]</sup> The absence of any detectable liquid products was confirmed by <sup>1</sup>H NMR analysis (Figures S24 and S25). The apparent quantum efficiency (AQE) of the TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY catalyst reached a maximum value of 0.8% at 450 nm (Figure S26), which aligns with the characteristic absorption spectrum of the [Ru(bpy)<sub>3</sub>]<sup>2+</sup> photosensitizer. Isotopic labelling experiments using <sup>13</sup>CO<sub>2</sub> as a feed gas unequivocally demonstrated that the CO product originated from the CO<sub>2</sub>RR, as confirmed by the detection of <sup>13</sup>CO (*m/z* = 29) via GCMS (Figure 2d). Furthermore, TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY demonstrated high durability, with no significant changes in CO production and selectivity over five cycles (Figure 2e), and its structure remained stable, as shown by XRD, FT-IR, XPS, and TEM (Figures S27–S30). A comparative analysis (Figure 2f) revealed that TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY outperforms most reported Ni-based organic photocatalysts for CO<sub>2</sub> reduction, highlighting its superior activity. The enhanced performance can be attributed to the synergistic interplay between the –C≡C–Ni(PBu<sub>3</sub>)<sub>2</sub>–C≡C– moiety and the π-conjugated graphdiyne framework, which facilitates efficient charge carrier transport and separation. Moreover, the nanoconfined hydrophobic space generated by the tributylphosphine ligands promotes a higher collision frequency between CO<sub>2</sub> molecules and the Ni catalytic



**Figure 2.** a) Control experiments demonstrating the necessity of each component for photocatalytic CO<sub>2</sub> reduction using TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY. b) CO<sub>2</sub> photoreduction activity and CO selectivity of TPA-GDY, TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY, and TPA-Pd(PBu<sub>3</sub>)<sub>2</sub>-GY under optimized conditions. c) Effect of trialkylphosphine ligand alkyl chain length (PMe<sub>3</sub>, PEt<sub>3</sub>, and PBu<sub>3</sub>) on photocatalytic CO<sub>2</sub>RR performance. d) GCMS spectrum confirming the formation of <sup>13</sup>CO (*m/z* = 29) during photocatalytic reduction of <sup>13</sup>CO<sub>2</sub> over TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY. e) Cyclic stability tests of TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY for CO<sub>2</sub> photoreduction. f) Comparison of CO<sub>2</sub> photoreduction activity of TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY with previously reported Ni-based organic photocatalysts (note: corresponding references are provided in Refs. [29 and 31–38]).

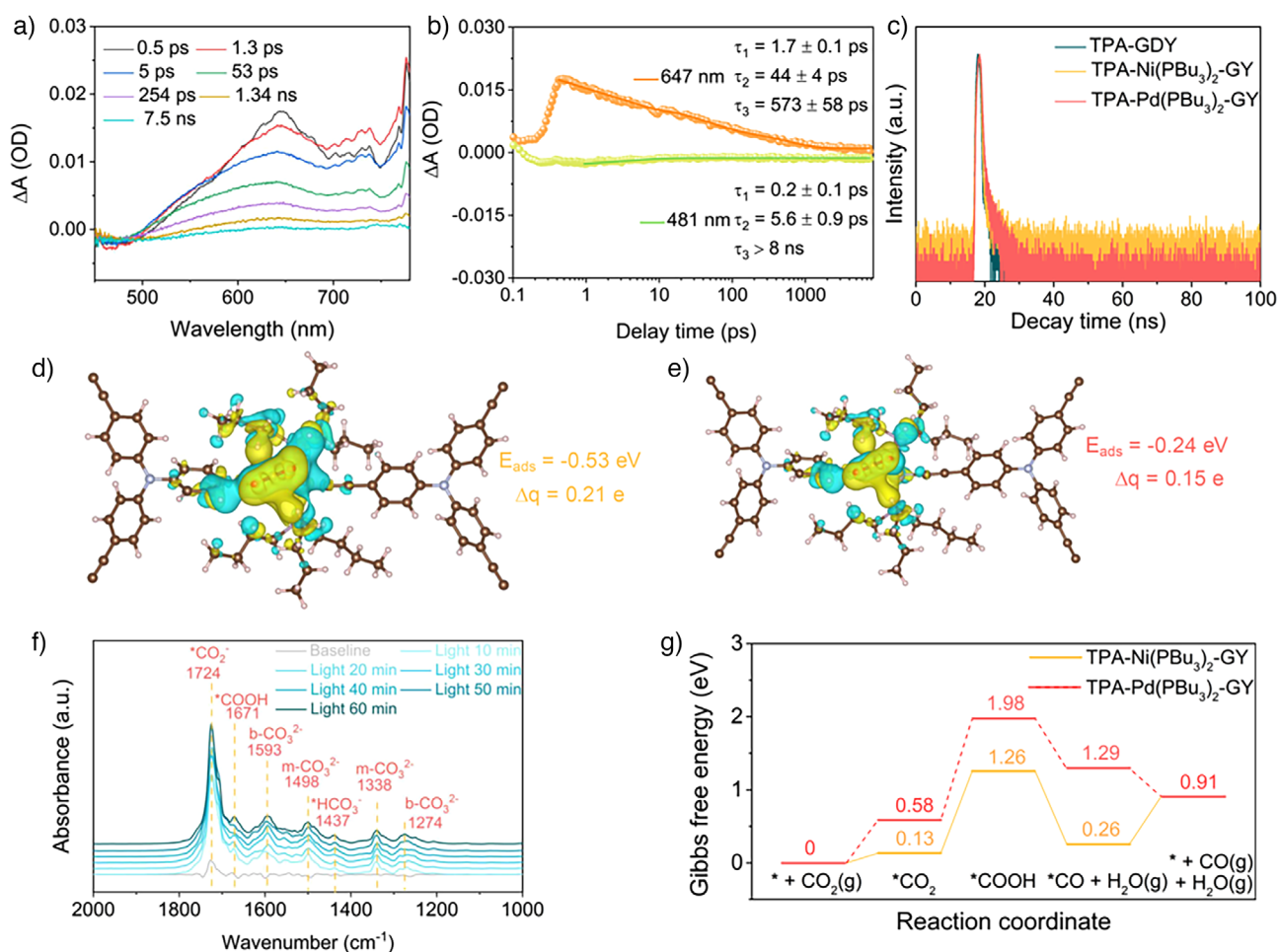
centers while simultaneously hindering proton transfer, ultimately favoring CO production and suppressing hydrogen evolution. Therefore, this catalyst design offers a promising route for addressing key challenges in photocatalytic reaction, including photocatalytic mechanisms, reaction activity, and product selectivity.

The light-harvesting properties and electronic structure of TPA-M(PBu<sub>3</sub>)<sub>2</sub>-GYs were investigated using UV–vis diffuse reflectance spectroscopy (DRS) and Mott–Schottky (MS) plots (Figure S31). Both TPA-M(PBu<sub>3</sub>)<sub>2</sub>-GYs exhibited strong absorption across a broad range of 200–800 nm, indicating their excellent visible light absorption capabilities. The optical bandgap and lowest unoccupied molecular orbital (LUMO) energy of TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY were determined to be 2.17 eV and −1.20 V (versus NHE), respectively. Combining Tauc plots and MS plots enabled the determination of the energy band structures (Figure S32). The LUMO of TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY was more positive than that of the photosensitizer [Ru(bpy)<sub>3</sub>]<sup>2+</sup> (−1.31 V versus NHE),<sup>[39]</sup> but more negative than the reduction potential of *E*<sup>o</sup> (CO<sub>2</sub>/CO) (−0.53 V versus NHE), signifying that photoexcited electrons can be readily transferred from [Ru(bpy)<sub>3</sub>]<sup>2+</sup> to TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY to drive CO<sub>2</sub>RR under visible light irradiation (Figure S33). Furthermore, TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY exhibited a stronger affinity for CO<sub>2</sub> compared to TPA-Pd(PBu<sub>3</sub>)<sub>2</sub>-GY (Figure S34), which is attributed to stronger coordination interactions between CO<sub>2</sub> and the Ni<sup>II</sup> active sites.<sup>[40]</sup>

Ultrafast femtosecond time-resolved transient absorption (fs-TA) spectroscopy was employed to probe the charge

carrier dynamics in real time (Figures 3a–c and S35). Upon excitation at 400 nm, the fs-TA spectra of TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY displayed a broad ground-state bleach (GSB) centered at around 470 nm, indicative of state-filling by photoexcited carriers. A prominent excited-state absorption (ESA) peak emerged between 500 and 780 nm, which can be attributed to singlet excited-state decay.<sup>[41]</sup> The GSB recovery kinetics were well-fitted using a three-exponential decay model, revealing a Δ*A* recovery asymptote within the 8.0 ns probe-delay limit, suggesting a prolonged carrier lifetime. The ESA dynamics at 647 nm exhibited decay constants of τ<sub>1</sub> = 1.7 ± 0.1 ps, τ<sub>2</sub> = 44 ± 4 ps, and τ<sub>3</sub> = 573 ± 58 ps. In contrast, the transient spectrum of TPA-Pd(PBu<sub>3</sub>)<sub>2</sub>-GY was dominated by GSB near 590 nm, associated with charge transfer transitions, with a long bleaching signal lifetime exceeding 8.0 ns (Figure S36). Photoelectric measurements further support these observations. The fluorescence lifetimes of TPA-GDY, TPA-Pd(PBu<sub>3</sub>)<sub>2</sub>-GY, and TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY were measured to be 0.95, 1.06, and 1.17 ns, respectively (Figure 3c and Table S4). TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY displayed the strongest photocurrent response and the smallest semicircle diameter in the electrochemical impedance spectroscopy (EIS) results (Figure S37), indicating effective suppression of charge carrier recombination and superior intramolecular charge transfer capability.<sup>[42,43]</sup>

To further investigate the CO<sub>2</sub> affinity and electron distribution in TPA-M(PBu<sub>3</sub>)<sub>2</sub>-GYs, density functional theory (DFT) calculations and CO<sub>2</sub> absorption experiments were performed. The calculations revealed that CO<sub>2</sub> adsorption on

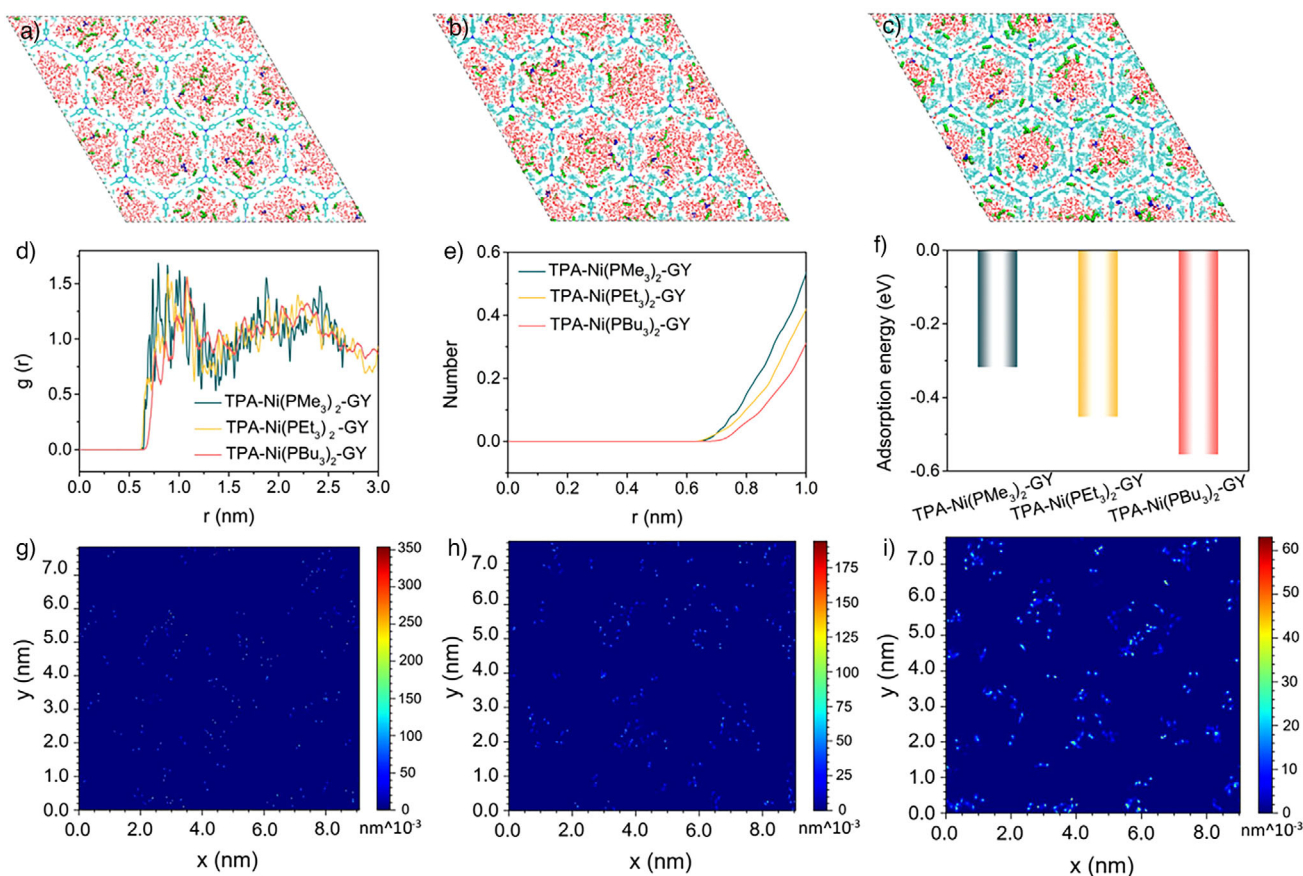


**Figure 3.** a) TA spectra of TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY following excitation at 400 nm, with varying time delays. b) fs-TA kinetics of TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY, with solid lines representing multiexponential fits to the TA data. c) Time-resolved fluorescence decay spectra of TPA-GDY, TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY, and TPA-Pd(PBu<sub>3</sub>)<sub>2</sub>-GY. Charge density difference isosurfaces (level 0.0001 e Bohr<sup>-3</sup>) for CO<sub>2</sub> adsorbed on d) TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY and e) TPA-Pd(PBu<sub>3</sub>)<sub>2</sub>-GY, with yellow and cyan colors indicating electron accumulation and depletion, respectively. f) In situ DRIFTS spectra monitoring surface intermediates during CO<sub>2</sub> reduction over TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY under visible light irradiation. g) Calculated free energy diagram for CO<sub>2</sub>RR on TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY.

TPA-M(PBu<sub>3</sub>)<sub>2</sub>-GYs is thermodynamically favorable. TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY exhibited a more negative adsorption energy (−0.53 eV) compared to TPA-Pd(PBu<sub>3</sub>)<sub>2</sub>-GY (−0.24 eV), indicating stronger host–guest interactions with CO<sub>2</sub>. Charge density difference analysis revealed that CO<sub>2</sub> gains 0.21 electron from TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY and 0.15 electron from TPA-Pd(PBu<sub>3</sub>)<sub>2</sub>-GY (Figure 3d–e), confirming that Ni<sup>II</sup> ions enhance both the binding strength and polarization of \*CO<sub>2</sub>, thereby facilitating CO<sub>2</sub> adsorption and activation.<sup>[44]</sup> In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was used to dynamically monitor adsorbed CO<sub>2</sub> and CO<sub>2</sub>-derived species on TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY during photocatalysis (Figure 3g). The adsorption peaks at approximately 1338 cm<sup>-1</sup> and 1498 cm<sup>-1</sup> can be assigned to monodentate carbonate (*m*-CO<sub>3</sub><sup>2-</sup>), whereas peaks near 1274 cm<sup>-1</sup> and 1593 cm<sup>-1</sup> are attributed to bidentate carbonate (*b*-CO<sub>3</sub><sup>2-</sup>).<sup>[45,46]</sup> The peak observed at 1437 cm<sup>-1</sup> is assigned to bicarbonate (\*HCO<sub>3</sub><sup>-</sup>) stretching vibrations.<sup>[47]</sup> The adsorption peak at 1671 cm<sup>-1</sup> suggests the formation of carboxylic acid (\*COOH), a key intermediate in CO<sub>2</sub>

photoreduction.<sup>[25]</sup> The emergence of \*CO<sub>2</sub> at 1724 cm<sup>-1</sup> with prolonged irradiation suggested CO<sub>2</sub> activation via CO<sub>2</sub> + e<sup>-</sup> → \*CO<sub>2</sub> (Figure 3g).<sup>[48,49]</sup> Increasing peak intensities for the intermediates and products with extended irradiation confirmed the photocatalytic CO<sub>2</sub> reduction products with a consecutive reaction pathway. The calculated Gibbs free energies for CO<sub>2</sub> to CO conversion on metal active sites within TPA-M(PBu<sub>3</sub>)<sub>2</sub>-GYs (Figures 3h and S38–S40) revealed that the rate-determining step (RDS) is the formation of \*COOH during photocatalytic CO<sub>2</sub>RR via \*CO<sub>2</sub> + H<sup>+</sup> + e<sup>-</sup> → \*COOH.<sup>[50,51]</sup> TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY exhibits a reduced energy barrier for \*COOH formation (1.13 eV) compared to TPA-Pd(PBu<sub>3</sub>)<sub>2</sub>-GY (1.40 eV), which is attributed to the strong interactions between —C≡C—Ni<sup>II</sup>—C≡C— and \*COOH, thereby reducing the activation energy for CO<sub>2</sub> activation and ultimately enhancing the overall photocatalytic CO<sub>2</sub> reduction performance.

To investigate the impact of the hydrophobic microenvironment on the photocatalytic CO<sub>2</sub> reduction performance of TPA-M(PR<sub>3</sub>)<sub>2</sub>-GYs, we performed water contact angle



**Figure 4.** Density distribution of  $\text{CO}_2$  and  $\text{H}^+$  calculated from MD simulations, along with the corresponding final snapshot for (a) TPA-Ni(PMe<sub>3</sub>)<sub>2</sub>-GY, (b) TPA-Ni(PEt<sub>3</sub>)<sub>2</sub>-GY, and (c) TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY. (d) Radial distribution functions (RDF,  $g(r)$ ) for the trialkylphosphines (PMe<sub>3</sub>, PEt<sub>3</sub>, and PBu<sub>3</sub>) as a function of the distance from the Ni<sup>II</sup> catalytic centers to the H atoms of water ( $H_w$ ). (e) Statistical distribution of  $\text{H}^+$  ions in the vicinity of the Ni<sup>II</sup> catalytic centers for three types of branched chains in the trialkylphosphines (PMe<sub>3</sub>, PEt<sub>3</sub>, and PBu<sub>3</sub>). (f) Calculated  $\text{CO}_2$  adsorption energies on TPA-Ni(PR<sub>3</sub>)<sub>2</sub>-GYs as a function of the alkyl chain length in the trialkylphosphines. (g–i) 2D planar distribution probability maps for the  $\text{CO}_2$  density around the Ni–PBu<sub>3</sub> moiety.

measurements and in situ DRIFTS analysis of the adsorption behaviors toward  $\text{H}_2\text{O}$  and  $\text{CO}_2$  on TPA-M(PR<sub>3</sub>)<sub>2</sub>-GYs. The results indicate that as the alkyl chain length increases, both the hydrophobicity and  $\text{CO}_2$  adsorption capacity of the samples are enhanced, as evidenced by Figures S41 and S42. Molecular dynamics (MD) simulations demonstrated that increasing the length of trialkylphosphines (PMe<sub>3</sub>, PEt<sub>3</sub>, PBu<sub>3</sub>) surrounding the Ni<sup>II</sup> catalytic centers in TPA-Ni(PR<sub>3</sub>)<sub>2</sub>-GYs reduced  $\text{H}^+$  ion concentration and increased  $\text{CO}_2$  concentration near these centers (Figures 4a–c and S43). This suggests that longer alkyl chains improve  $\text{CO}_2$  capture and reduction while inhibiting HER, consistent with the observed photocatalytic performance. Radial distribution function (RDF,  $g(r)$ ) analysis revealed that longer alkyl chains decrease the RDF peak intensity and shift the peak to larger distances (Figure 4d–e), indicating that PBu<sub>3</sub> exhibits stronger hydrophobic properties compared to PMe<sub>3</sub> and PEt<sub>3</sub>. Consequently, the distance between Ni<sup>II</sup> in the Ni–PBu<sub>3</sub> moiety and the nearest water molecules was maximized, leading to a reduction in hydrogen proton density around Ni<sup>II</sup>.<sup>[22]</sup> Under the influence of nanoconfinement, the adsorp-

tion energy of Ni<sup>II</sup> for  $\text{CO}_2$  increased with the length of the alkyl chain (Figure 4f), and the electron transfer number after  $\text{CO}_2$  adsorption also increased (Figure S44), further corroborating that modifying the alkyl chain length effectively regulates the microenvironment of the metal catalytic centers. As evident from Figure 4g–i, the distribution of  $\text{CO}_2$  around the Ni–PBu<sub>3</sub> moiety became progressively more concentrated. Furthermore, the interaction between TPA-Ni(PR<sub>3</sub>)<sub>2</sub>-GYs and  $\text{CO}_2$  molecules can be intuitively visualized using the independent gradient model based on Hirshfeld partition (IGMH) model (Figure S45). This study reveals both weak and strong attractive interactions between TPA-Ni(PR<sub>3</sub>)<sub>2</sub>-GYs and  $\text{CO}_2$  molecules. Notably, the TPA-Ni(PBu<sub>3</sub>)<sub>2</sub>-GY model exhibits a larger isosurface area in cyan and green colors, suggesting a higher binding affinity for  $\text{CO}_2$  molecules compared to TPA-Ni(PMe<sub>3</sub>)<sub>2</sub>-GY and TPA-Ni(PEt<sub>3</sub>)<sub>2</sub>-GY. Therefore, the confinement effect produced by the hydrophobic microenvironment constructed by alkyl chains enhances the concentration of reactants and active intermediates in the catalytic reaction system, thereby improving the photocatalytic  $\text{CO}_2$  performance.

## Conclusion

In summary, this study introduces a novel class of 2D metal-organic hybrid photocatalysts based on MAFs, enabling the precise integration of transition metal ions into an extended  $\pi$ -conjugated system through the unique metal-bis(acetylide) linkages. Hydrophobic trialkylphosphine chains were strategically employed to create a nanoconfined environment around the catalytic sites. The synergistic  $d$ - $p$  orbital overlap between  $\text{Ni}^{\text{II}}$  and adjacent alkynyl carbon atoms, coupled with the highly  $\pi$ -conjugated moieties, facilitates efficient charge carrier transfer and optimizes the adsorption energy of intermediates and reactants, thus enhancing photocatalytic  $\text{CO}_2$  reduction performance. The hydrophobic confined space created by tributylphosphine increases the collision frequency of  $\text{CO}_2$  with the active centers while simultaneously reducing proton transfer. Consequently, TPA-Ni( $\text{PBu}_3$ )<sub>2</sub>-GY exhibited superior  $\text{CO}_2$  photoreduction activity ( $3807 \mu\text{mol g}^{-1} \text{h}^{-1}$ ) and  $\text{CO}$  selectivity (99.4%) under visible light irradiation, exceeding those of TPA-Pd( $\text{PBu}_3$ )<sub>2</sub>-GY ( $106 \mu\text{mol g}^{-1} \text{h}^{-1}$ ) and TPA-GDY ( $24 \mu\text{mol g}^{-1} \text{h}^{-1}$ ) by factors of 35.9 and 158.6, respectively. This work provides a unique framework for the rational design of efficient  $\text{CO}_2$  reduction photocatalysts and underscores the potential of graphdiyne as a versatile building block in future catalyst design for sustainable energy conversion.

## Supporting Information

The authors have cited additional references within the Supporting Information.<sup>[23,31–38,52–73]</sup>

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## Conflict of Interests

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

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