Visible-Light-Driven Methane Conversion with Oxygen Enabled by Atomically Precise Nickel Catalyst

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It remains an extreme challenge to activate thermodynamically unfavorable, chemically inert methane molecules under mild conditions. Herein, we report a molecular-like nickel-thiolate hexameric cluster [Ni6(PET)12; PET = SC2H4Ph] catalyst that resembles a double crown, comprising of a hexagonal Ni6 kernel encapsulated by an exterior shell of 12 thiolates capable of efficient conversion of methane plus O2 to methanol and formic acid under visible light irradiation. Exclusive photocatalysis by Ni6(PET)12 is related to its suitable molecular orbital gap, energy alignment, and the unique atomic-packing structure able to harvest solar energy to activate O2 with the subsequent accomplishment of H-atom abstraction from sluggish methane. This work is a major step toward promising practical applications of atomically precise metal catalysts in arduous bond cleavages and construction of low-carbon alkanes, with the potential to further facilitate fossil energy conversions.

Keywords: CH4, O2, atomic level, nanocluster, chemicals

Introduction

The chemical utilization of methane as the principal component of natural gas is essential in the chemical industry.1 Currently, the strategy for achieving methane transformation into other chemicals is typically by indirect routes. An example is methanol synthesis from methane involving steam methane reforming (SMR) into syngas (a mixture of CO and H2) and the subsequent methanol synthesis.2,3 Indirect processes entail harsh conditions such as considerably high temperatures that tend to be costly. Thus, the development of alternative
pathways for the direct conversion of methane into high-value fine chemicals is highly desirable, but this task is exceptionally challenging primarily because methane has an extremely stable molecular structure, low electron and proton affinity, low polarizability, and high C-H bond energy; overall, its direct conversion is thermodynamically unfavorable.-inspired by enzymatic catalysis, metal-exchanged zeolites have been reported to mimic the structural arrangement of active sites in the methane monooxygenase enzymes that can oxidize methane to methanol at ambient temperatures, but so far exhibit no highly desirable ability in the methane conversion.

Atomically precise metal nanoclusters composed of an exact number of metal atoms protected by a specific number of ligands have recently drawn significant research attention. Such metal nanoclusters provide a unique opportunity to bridge the structural gap between atoms and nanoparticles, where the exact relationship of structure and properties can be established. Studies have confirmed that ultrasmall metal nanoclusters show excitonic nature with discrete electron energy gaps, different from the plasmonic behavior of large-size metal nanoparticles with collective electron energy levels.

The distinct difference in the electronic structures between nanoclusters and nanoparticles could cause the divergence of the photocatalysis origin. Recently, we questioned whether metal nanocluster catalysts might directly catalyze the chemically inert methane with molecular oxygen toward high-value products using solar energy. We recognized that excitonic metal nanoclusters would hold promise being used as photocatalysts to solve this problem that cannot be accessed by plasmonic metal nanoparticles. If successful, it might provide the first general example of the photocatalytic reaction of methane with molecular oxygen driven by metal catalysts.

In this work, we report that a light-harvesting metal nanocluster, nickel-thiolate hexameric cluster \([\text{Ni}_6(\text{PET})_{12}]\), has extraordinary ability to activate methane and oxygen under visible light irradiation and subsequently control the conversion of methane and \(O_2\) along the reaction paths toward liquid chemicals (methanol and formic acid) with 100% selectivity. We achieved the fundamental insights into the photocatalytic reaction mechanism of methane oxidation over the \(\text{Ni}_6(\text{PET})_{12}\) catalyst with combined experimental and computational efforts.

**Experimental Methods**

**Synthesis of \(\text{Ni}_6(\text{PET})_{12}\) nanoclusters**

Precisely 0.30 mmol NiCl\(_2\)-6H\(_2\)O was added to 15 mL tetrahydrofuran, followed by the addition of 0.35 mmol tetraoctylammonium bromide (TOAB) solution. The solution mixture was stirred for 1 h at 0 °C. Then 1.5 mmol 2-phenylethanol (PET) was added to the flask. After ~1 h, 2.2 mmol NaBH\(_4\) freshly dissolved in ultrapure water (6 mL) was added to the reaction flask. The reaction was allowed to proceed under constant stirring for 3 h and then continued overnight. The solution was dried by a rotary evaporation technique, and the crude products, including \(\text{Ni}_6(\text{PET})_{12}\), \(\text{Ni}_5(\text{PET})_{10}\), and \(\text{Ni}_4(\text{PET})_8\), were washed with ethanol three to five times. The three nanoclusters can be separated by thin-layer chromatography (TLC).

**Synthesis of the supported cluster catalysts**

The supported nanocluster catalysts were obtained by stirring a solution of the nanoclusters in CH\(_2\)Cl\(_2\) with a calculated amount of oxide supports for 24 h. Then the samples were dried by flowing nitrogen.

**Photocatalytic oxidation of methane**

The photocatalytic reaction of methane oxidation was carried out in a 100 mL reactor (CEL-HPR100T+; Ceaulight, Beijing, China) irradiated by a 300 W xenon lamp (CEL-HXF300; Ceaulight). A 400 nm UV cut filter was installed to block the UV wavelength range irradiation. The light intensity was ~377 mW/cm\(^2\) measured at the upper position of reaction solution with a calibrated wavelength of 550 nm (Model 1918-R Power Meter; Newport, Irvine, California, United States of America). The reaction was performed under ambient temperature. A magnetic stirrer was used to facilitate the mass transfer between the reactants and catalysts. Before the catalytic tests, the supported \(\text{Ni}_6(\text{PET})_{12}\) catalysts were treated with a mixture of gas (5% H\(_2\) and 95% N\(_2\)) at 150 °C for 1 h. In a typical catalysis test, 50 mg catalyst was dispersed in 5 mL of ultrapure water, followed by flushing the reactor with a mixed gas containing 2 MPa methane and 1 MPa oxygen. The reaction was performed under visible light irradiation for a certain time with a stirring speed of 700 rpm. After 2 h, the gas product was analyzed using a gas chromatograph packed with TDX-01 carbon molecular sieve column and a thermal conductivity detector; the liquid products were analyzed using a gas chromatograph packed with TDX-01 carbon molecular sieve column and a thermal conductivity detector.

**Characterizations**

Absorption spectra were recorded on a UV–vis spectrophotometer using Shimadzu UV-1800 (Shimadzu Corporation, Kyoto, Japan). Diffuse reflectance UV–vis spectra were recorded on a UV–vis spectrophotometer using Shimadzu UV-3600. The loading weight of Ni was determined by the inductively coupled plasma-atomic
Emission spectroscopy (ICP-AES; Optima 5300DV). Electron paramagnetic resonance (EPR) was recorded at room temperature with X-band Bruker EMX (Bruker, Karlsruhe, Germany) operating at 9.85 GHz field modulation and 20 mW microwave power. Also, the aqueous products were analyzed by $^1$H NMR (Bruker ARX-400) using D$_2$O as a solvent. The photoelectrochemical measurement was performed on a CHI660E electrochemical analyzer workstation (CH Instruments, Inc., Shanghai, China) in a standard three-electrode system using a platinum foil as a counter electrode, a glassy carbon as the working electrode, and a saturated Ag/AgCl as a reference electrode. A 300 W Xe lamp was used as the light source on the measurement. The measurement was carried out at room temperature in 1.0 mol/L Na$_2$SO$_4$, applying a 0.2 V bias voltage.

**Computational details**

The Ni$_6$(PET)$_{12}$ catalyst was modeled at the density functional theory (DFT) level using a simplified Ni$_6$(SCH$_3$)$_{12}$ model. This is a reasonable simplification as the thiol (SR) ligands as the methane oxidation reaction occurs on the side surface of the Ni$_6$(SR)$_{12}$ double-crown ring that is not substantially affected sterically by the SR ligands. The relevant species along the methane photooxidation pathway catalyzed by Ni$_6$(SR)$_{12}$ were optimized at the DFT level with the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional and the correlation-consistent basis set, Aug-cc-pVDZ(PP), based on pseudopotentials. Vibrational frequencies were calculated for the fully optimized structures to obtain the zero-point energy, thermal, and entropy corrections. The ground states of the fresh Ni$_6$(SR)$_{12}$ were predicted to be singlet, and up to triplet states were examined for all of the active species, considering the involvement of O$_2$ (triplet). The electronic structures for the optimized catalytic species were also analyzed at the PBE/Aug-cc-pVDZ(-pp) level since we found that the hybrid DFT functional significantly overestimated the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap for Ni$_6$(SR)$_{12}$. The UV–vis spectra for the reaction intermediate complexes for the methane oxidation reactions over Ni$_6$(SR)$_{12}$ were predicted at the PBE/Aug-cc-pVDZ(-pp) level. The optimization, frequency, and electronic structure calculations were performed using the Gaussian 09 software package.

The photocatalytic activities of Ni$_6$(SR)$_{12}$ with different adsorbates (the adsorption was optimized at the PBE
level) at different incident frequencies were predicted using the real-time time-dependent DFT (RT-TDDFT).38 The RT-TDDFT calculation was carried out using the NWChem 6.8 (Environmental Molecular Sciences Laboratory) EMSL at the Pacific Northwest National Laboratory (PNNL) in Washington State.39

Results and Discussion

Atomically precise Ni₆(PET)₁₂ nanocluster possesses a double-crown core, as shown in Figure 1a, where six nickel atoms are arranged approximately in a hexagonal ring with six sulfur atoms forming Ni-S-Ni bridges above the ring plane and another six sulfur atoms forming bridges below the ring plane.40,41 The strong quantum dot behaviors of Ni₆(PET)₁₂ are manifested in the optical property (Figure 1b). The prominent band at 338 nm (3.67 eV) could be assigned to the excitations from Ni-S bonding orbitals to Ni-S* antibonding orbitals of Ni₆(PET)₁₂, based on the calculated molecular orbital energy levels, as well as the atomic contributions in the molecular orbitals at DFT level (Figure 1c). Another prominent band at 409 nm (3.03 eV) and broadband at 556 nm (2.23 eV) were assigned to the excitations from the Ni 3d lone pairs to Ni-S* antibonding orbitals, respectively. Therefore, it is recognized that the Ni₆(PET)₁₂ nanocluster might be able to harvest solar energy in the visible range.

Next, we sought to explore the photocatalytic properties of the Ni₆(PET)₁₂ nanocluster for methane oxidation with O₂ under visible light illumination. Intriguingly, regardless of the type of support used (SiO₂, ZrO₂, Al₂O₃, or TiO₂), methanol and formic acid could be obtained on the Ni₆(PET)₁₂ catalysts with ∼0.2 mol methane conversion per hour (Figure 2a). No byproduct-like CO₂ was produced in the catalyst systems. Instead, it is an attractive result since CO₂ cannot be eliminated in the high-temperature oxidation reactions of methane, particularly in oxidative coupling.42 It is worth noting that the different oxide supports had little activity for methane oxidation under identical conditions. The photocatalytic performances of loaded Ni₆(PET)₁₂ were comparable with wide-gap semiconductors such as ZrO₂ and moderate-gap semiconductors such as TiO₂, suggesting that the hot-electron injection from Ni₆(PET)₁₂ to the
conduction band of the semiconductor was not required for methane oxidation, and the reaction likely occurred on the Ni₆(PET)₁₂ cluster. Considering that Ni₆(PET)₁₂ itself contained carbon sources, comparison experiments were conducted. When either CH₄ or O₂ was introduced into the Ni₆(PET)₁₂ system, no product was detected, suggesting that the products indeed evolved from methane conversion. More interestingly, the activity of Ni₆(PET)₁₂ was barely boosted when the light source was switched from visible light to full-spectrum illumination (Figure 2b), implying that the photocatalytic reaction is driven solely by visible light; thus, has promising practical applications for methane conversion using solar energy. Moreover, the Ni₆(PET)₁₂ catalyst exhibited excellent photocatalytic stability and showed no deactivation during multiple light-on and light-off cycles (Figure 2c). Notably, we were pleased to observe that with other double-crown-like Ni nanoclusters (Supporting Information Figure S2), Ni₄(PET)₈ and Ni₅(PET)₁₀, the desired products, methanol, and formic acid were also obtained under identical conditions (Figure 2d), which revealed the intrinsic quality of Ni₆(SR)₂₀ (n = 4, 5, and 6) of the visible-light-induced methane oxidation.

We initiated mechanistic studies to unveil the photocatalytic origin of Ni₆(PET)₁₂ for the methane and O₂ conversion reaction. The diffuse reflectance optical spectra of the supported Ni₆(PET)₁₂ catalysts retained characteristic optical absorption of the Ni₆(PET)₁₂ nanocluster (Figure 3a), supporting the notion that the atomic structure of the loaded Ni₆(PET)₁₂ was not changed. Transient photocurrent responses of the catalysts under different conditions were carried out. Compared with pure ZrO₂, the photocurrent of Ni₆(PET)₁₂/ZrO₂ was drastically enhanced (Figure 3b), showing that the Ni₆(PET)₁₂ clusters could serve as trapping sites for the photoexcited electrons. Compared with the case under air flow, the photocurrent of the Ni₆(SR)₁₂ catalyst was quenched under pure O₂ atmosphere (Figure 3c), likely due to more photogenerated electrons consumed by more adsorbed O₂ molecules onto Ni₆(PET)₁₂, hinting that Ni₆(PET)₁₂ might activate O₂ under light irradiation. When the flowing gas was switched from pure O₂ to CH₄, as shown in Figure 3c, the photocurrent of the Ni₆(PET)₁₂ catalyst was quenched further under the CH₄ atmosphere, suggesting that Ni₆(PET)₁₂ preferred to activate O₂, followed by CH₄. To deepen our understanding of the reaction network of the methane oxidation, the potential active oxygen species were determined by EPR spectroscopy in which the trapping agent disodium 4,5-dihydroxy-1,3-benzenedisulfonate (Tiron) detected superoxide species (Figure 3d), revealing that superoxide

Figure 3 | (a) The diffuse reflectance optical spectra of the supported Ni₆(PET)₁₂ catalysts. (b) Photocurrent responses of Ni₆(PET)₁₂/ZrO₂ and ZrO₂ under different atmospheres. (c) Photocurrent responses of Ni₆(PET)₁₂/ZrO₂ under different atmospheres. (d) EPR profiles obtained from the methane oxidation catalyzed by the Ni₆(PET)₁₂ catalyst without light (0 min) and with light for 10 min.
was the active oxygen species in the visible-light-excited reaction process of methane and O$_2$ over Ni$_6$(PET)$_{12}$. RT-TDDFT calculations were carried out to understand the photocatalysis of Ni$_6$(SR)$_{12}$ on the activation of O$_2$ and CH$_4$ during the methane oxidation reaction. We considered two comparative systems, *OO + CH$_4$ and O$_2$ + CH$_4$, for the RT-TDDFT calculations (Figure 4). *OO denotes Ni$_6$(SR)$_{12}$ in the complex, and *OO denotes Ni$_6$(SR)$_{12}$(O$_2$) triplet with O$_2$ adsorbed on a Ni. Both *OO + CH$_4$ and O$_2$ + CH$_4$ have triplet ground states. In both systems, CH$_4$ was placed near O$_2$ with an H–O distance being 1.5 Å, an O–O–H angle being 109°, and a C–H–O angle being 180°. Notably, this is merely one configuration of CH$_4$ colliding with O$_2$ among an infinite number of possible configurations; it is considered because such an orientation might favor the charge transfer between C–H and O$_2$. First, we examined the photocatalytic activity of *OO + CH$_4$ system using RT-TDDFT calculations (Figure 4a), during which the system was excited by a Gaussian pulse for over 25 fs. The center of the Gaussian pulse was placed at $t = 9.5$ fs so that the pulse only leads to negligible electric fields at $t = 0$ and 19 fs. Three distinct center frequencies ($v_C$, the frequency at the Gaussian center in the momentum space) of the Gaussian pulse were chosen to represent quasi-monochromatic light sources, for which the center energies ($E_C = h_v$) were 0.80, 1.25, and 3.00 eV, respectively. All the quasi-monochromatic pulses have the same full width at half maximum (FWHM) of 1 eV in the momentum space and the same maximum electric field of 50 mV/nm.

The RT-TDDFT calculations showed that all three Gaussian pulses cause oscillation of the dipole moment and total charge density of the molecular system at $t = 0$. Δ$t$ indicates the oscillation period, and $h_v$ is the energy associated with oscillation frequency.

**Figure 4** | (a and b) Evolution of the dipole moment for *OO + CH$_4$ and O$_2$ + CH$_4$ with an intermolecular O–H distance of 1.5 Å in response to a Gaussian pulse at the RT-TDDFT level. The Gaussian pulse has energy ($E_C$) of 3.00 eV at the Gaussian center and FWHM of 1 eV in the momentum space. (c) Adsorption spectra obtained by the Fourier transform of the dipole moment evolution after the Gaussian pulse fully disperses ($t > 19$ fs). (d–f) Oscillation of total charge density relative to the original total charge density of the molecular system at $t = 0$: (d) *OO + CH$_4$ under a Gaussian pulse with $E_C = 1.25$ eV; (e) *OO + CH$_4$ under a Gaussian pulse with $E_C = 3.00$ eV; (f) O$_2$ + CH$_4$ under a Gaussian pulse with $E_C = 3.00$ eV. The purple and blue shades indicate gain and loss of electron density with respect to the charge density of the molecular system at $t = 0$. Δ$t$ indicates the oscillation period, and $h_v$ is the energy associated with oscillation frequency.
dipole oscillation with the largest amplitudes, implying that the photoenergy was facilely absorbed by the catalyst. The absorption spectra for *OO + CH4 under the three pulses were predicted based on the Fourier transformation of the time evolution of the dipole moment for t > 19 fs (Figure 4c). For a pulse with EC = 0.8 eV, a major absorption peak at 1.3 eV was found; for a pulse with EC = 1.25 eV, major peaks at 1.3 and 1.7 eV were found; and for a pulse with EC = 3.00 eV, strong bands at 2.7 and 3.4 eV were observed. These peaks corresponded to the excitation energies of *OO and CH4. Figures 4d and 4e illustrate the oscillation of the total charge density, which was taken after the incident pulse had faded away. The oscillation shown in Figure 4d has a period of 3.1 fs, which corresponded to a 1.3 eV excitation (h/Δt) with charge density being transferred from HOMO-1 or HOMO-2 of Ni6(SR)12 (Supporting Information Figure S4) to the πg singly occupied molecular orbital (SOMO) of O2. The oscillation shown in Figure 4e with a period of 1.5 fs corresponds to a 2.7 eV excitation. Frontier molecular orbital analysis revealed that this oscillation motion was most likely related to the charge transfer from the HOMO of Ni6(SR)12 to the πg SOMO + 1 of O2. Charge transfer from Ni6(SR)12 to O2 was found at both 1.3 and 2.7 eV absorptions, which led us to infer that O2 could be converted to O2* in the ground state (1.3 eV) or excited state (2.7 eV) under visible light. Besides, the excited O2* has a singly occupied πg orbit, which might facilitate CH4 activation due to its facile interaction with the 1s orbital of H of incoming CH4. Therefore, blue visible or UV incident light could be conducive to CH4 oxidation over Ni6(SR)12.

Next, RT-TDDFT calculations were performed for the O2 + CH4 system using the EC = 3.00 eV incident pulse (Figure 4b). The postincidence dipole oscillation was weak for O2 + CH4, even under a pulse with EC = 3.00 eV and FWHM = 1.00 eV. Meanwhile, only negligible peaks with energy >4 eV are found in the absorption spectrum (Figure 4c). These suggest that the CH4 reaction with O2 is photoinactive without the catalyst. We obtained a charge-density oscillation with a period of 0.8 fs and estimated energy of 5.2 eV (Figure 4f), which corresponded to the oscillation of electron density between the two SOMOs of O2. This oscillation did not change the electronic structure of O2 substantially, and thus, O2 remained inert in the reaction with CH4.

Based on the RT-TDDFT results, we proposed that the activation of CH4 could be facilitated by a photoinduced charge transfer and excitation, and constructed possible reaction pathways for the CH4 oxidation over Ni6(SR)12 toward the formation of CH3OH and HCOOH, as shown in Figures 5a and 5b. The reaction enthalpies (ΔH) and Gibbs free energies (ΔG) at 298 K are predicted at the PBE/Aug-cc-pVDZ level. For the formation of CH3OH, Ni6(SR)12 first adsorbs O2 at the Ni atomic site, to form a triplet Ni6(SR)12O2 complex, denoted as *OO (* indicates the Ni6(SR)12 catalyst hereafter). The adsorption of O2 is exothermic by ΔH = −3.1 kcal/mol but endergonic by ΔG = 6.1 kcal/mol due to the entropy correction. As discussed above, under visible or UV-vis radiation, the charge can be transferred from Ni6(SR)12 to O2, and hence OO transiently possesses excessive electron in the excited state. This could lead to *OO reaction with CH4 to form *OOH and •CH3 via C-H bond cleavage and O-H bond formation with ΔG = 43.8 kcal/mol (1.9 eV). The *OOH will recombine spontaneously with •CH3 with ΔG = −42.9 kcal/mol to form singlet *CH3OOH in the ground state. CH3OOH might dissociate into CH3O• and •OH via O-O cleavage. However, the dissociation has a ΔG = 36.1 kcal/mol, and thus, requires a photoenergy. It has been reported that the photolysis of gas-phase CH3OOH requires a UV-vis radiation with energy >5 eV. Therefore, for photolysis to occur, Ni6(SR)12 needs to play an active role. The RT-TDDFT calculations showed that charge transfer from Ni6(SR)12 to CH3OOH did not occur at ground-state *CH3OOH singlet under the Gaussian pulse with EC = 3.00 eV (Supporting Information Figure S5). Instead, it occurred with an incident energy of 2.7 eV for the *CH3OOH triplet, which is 20.6 kcal/mol higher in free energy at 298 K (Supporting Information Figure S6). This implies that further reaction requires a ground-state *CH3OOH to be excited with a minimal photon energy of 0.9 eV, viable under visible irradiation. Additionally, the energy split between the two SOMOs of the *CH3OOH triplet is only 0.4 eV; hence the singlet-to-triplet excitation is presumably, kinetically facile. Accordingly, the resultant •OCH3 doublet from the photolysis of *CH3OOH could react with CH4 to form the CH3OH product and a CH3• with ΔG = 15.4 kcal/mol, also photocatalytic over Ni6(SR)12, as shown by the RT-TDDFT prediction (Supporting Information Figure S7). CH3• can recombine with •OH (resulting from photolysis of *CH3OOH) to form another CH3OH. Therefore, the reaction equation can be written as 2CH4 + O2 → 2CH3OH, involving two photocatalytic steps.

The CH3OH product from CH4 oxidation could be further oxidized (Figure 5b). First, H of CH3OH is subtracted from the photoexcited *OO, which yields *OOH and •CH3OH. Then *OOH and •CH3OH recombine to form •HOCH2OOH. The photolysis of gas-phase HOCH2OOH in the troposphere requires radiation energy >4.28 eV, but this process might be promoted by Ni6(SR)12, according to the RT-TDDFT results (Supporting Information Figure S8). The ground-state singlet of *HOCH2OOH is found to be photoinactive, and yet the triplet exhibits a weak photoinduced charge transfer under incident radiation of 3.31 eV in energy (Supporting Information Figures S8 and S9), compared with that of *CH3OOH triplet from Ni6(SR)12 to the peroxide O between C and Ni. The singlet-to-triplet excitation of *HOCH2OOH only
requires minimal photon energy of 15.7 kcal/mol or 0.7 eV, and the energy split of the SOMOs of *HOCH2OOH triplet is only 0.4 eV, which suggests that such excitation is most likely viable under visible irradiation. Hence, the photolysis of *HOCH2OOH will produce *OCH2OH and •OH. A charge can be facilely transferred from Ni6(SR)12 to the O of OCH2OH bonded to Ni in *OCH2OH under 2.85 eV radiation energy, according to the RT-TDDFT prediction (Supporting Information Figure S10). Since the CH4:O2 ratio is low for the oxidation reaction beyond CH3OH, the CH4 concentration is likely not to be high enough to enable the reaction of *CH3OOH with CH4. Instead, •OH from the previous reaction step will react with *OCH2OH to subtract an H from the CH2 moiety of OCH2OH. This yields the HCOOH product and H2O.

Experimentally, switching from visible light to full-spectrum illumination resulted in no appreciable change in the catalytic efficiency using the Ni6 catalyst, but there was an increase in its selectivity toward formic acid (Figure 2). We have provided the following tentative explanation based on the DFT results. According to the proposed reaction pathways, the formation of CH3OH is mainly limited by the photodissociation of the *CH3OOH triplet intermediate with a barrier of 2.7 eV, whereas the formation of HCOOH is limited by the photodissociation of the *HOCH2OOH triplet intermediate with a higher barrier of 3.3 eV. To reach maximal efficiency of the conversion, visible irradiation may suffice for the formation of CH3OH, while an UV A (with slightly higher energy than blue light) induced reaction might be desirable for the formation of HCOOH. We also noticed that CH3OH is the precursor for the HCOOH reaction, so the total yield is governed mostly by the formation of CH3OH. Therefore, switching from visible light to a full-spectrum illumination will significantly promote further conversion of CH3OH into HCOOH without changing the overall catalytic efficiency.

The experimental results also showed that the Ni4(PET)8 and Ni5(PET)10 clusters exhibited lower catalytic efficiencies than Ni6(PET)12 under the same reaction conditions. The proposed reaction pathways for methane plus O2 reaction over the Ni6(SR)12 catalyst toward the synthesis of (a) CH3OH and (b) HCOOH. The reaction Gibbs free energies and enthalpies at 298 K predicted at the PBE/Aug-cc-pVDZ level are shown in red and black texts.

Figure 5 | Proposed reaction pathways for methane plus O2 reaction over the Ni6(SR)12 catalyst toward the synthesis of (a) CH3OH and (b) HCOOH. The reaction Gibbs free energies and enthalpies at 298 K predicted at the PBE/Aug-cc-pVDZ level are shown in red and black texts.
conditions (Figure 2). The proposed reaction mechanism suggests that the electron transfer from the thiolated Ni cluster to the O-containing adsorbate is critical for photocatalytic activity. Therefore, the efficiency of the Ni₆(PET)₉, Ni₆(PET)₁₀, and Ni₆(PET)₁₂ catalysts might be associated with the alignments of the cluster’s SOMO and the O-acceptor orbital in forming the rate-limiting species CH₃OOOH⁺. The DFT calculations revealed that the SOMO-acceptor gaps for CH₃OOOH⁺ over Ni₆(PET)₉, Ni₆(PET)₁₀, and Ni₆(PET)₁₂ were 2.0, 2.2, and 1.7 eV, respectively (Supporting Information Figure S11), implying that Ni₆(PET)₁₂ possess the most catalytic efficiency, which was in good agreement with the experimental results. The smaller SOMO-acceptor gap of CH₃OOOH⁺ over Ni₆(PET)₁₂ might be attributable to the interaction between the more diffuse Ni-S antibonding orbital and the O-acceptor orbital, as the increased number of Ni (PET) repeating unit led to more delocalized Ni-S orbitals, indicated by the band broadening in the predicted partial density of states (PDOS).

Overall, we proposed similar photocatalytic reaction mechanisms for the reactions leading to the formation of the CH₃OH and HCOOH products due to the consistent role of Ni₆(SR)₁₂. RT-TDDFT calculations showed that Ni₆(SR)₁₂ was capable of activating the doublet and triplet O-containing species bonded to Ni via the Ni–O bond. The doublet species included *OOH, *OCH₃, and *OCH₂OH, and the triplet species included the ground-state *OO, the excited-state *CH₃OOH, and *HOCH₂OH. The PDOS were predicted for the relevant O-containing species over Ni₆(SR)₁₂ (Supporting Information Figure S12). It was found that the O bonded to Ni in the doublet and triplet complexes could introduce acceptor states [unoccupied molecular orbitals below or near the LUMO of Ni₆(SR)₁₂] in the electronic structure (Supporting Information Figure S13). This was understood as the Ni-adsorbed O in the doublet and triplet species contained a half-occupied O 2p orbital that coupled with the empty d orbital of Ni to form a low-lying occupied state. For *OO, *OOH, *OCH₃, and *OCH₂OH, the HOMO-acceptor gaps (or SOMO-acceptor gaps for doublet and triplet) were found to be smaller than the HOMO-LUMO gap for pure Ni₆(SR)₁₂ (1.44 eV at PBE/Aug-cc-pVDZ level); here, HOMO and LUMO referred to the corresponding molecular orbitals belonging to the Ni₆(SR)₁₂ catalyst rather than the whole complex. For the CH₃OOH⁺ and HOCH₂OH (singlets and triplets), the lowest energy acceptor states were found above the LUMO level of Ni₆(SR)₁₂. For singlets, the HOMO-acceptor gaps were found to be ~2.5 eV due to the split of Ni₆(SR)₁₂ "valence band" edge and the less negative HOMO energies. The small HOMO-acceptor gaps for the doublet and triplet intermediates allowed for the charge transfer from the Ni₆(SR)₁₂ to the adsorbate and promoted O site reactions, including photolysis and H-subtraction. Ni₆(SR)₁₂ is expected to be a general photocatalyst for reactions of O-containing species with occupied O 2p orbitals, such as reactions of O₂ and peroxides. There are several reasons for that: (1) the suitable molecular orbital gap and energy alignment of Ni₆(SR)₁₂ are conducive to forming acceptor states that are photoactive in visible light range; (2) the local planar square NiS₄ structure around the Ni active site determines that Ni has an empty d orbital perpendicular to the NiS₄ plane, which makes Ni–O bonding possible; and (3) both the high “valence bands” and the lowest “conduction bands” of Ni₆(SR)₁₂ are dominated by the d orbital of Ni, so photoexcitation from visible and near-UV radiations is expected to be dominated by Ni d–d transitions, accounting for the photocatalytic stability of Ni₆(SR)₁₂.

Conclusion
We synthesized the Ni₆(PET)₁₂ catalyst and demonstrated both experimentally and theoretically that it is capable of harvesting solar energy to convert methane and oxygen to methanol and formic acid in the visible light range, for which the reactivity could be correlated with the double-crown configuration and unique electronic structure of the catalyst. The atomically precise metal nature of the catalyst offers fundamental insights into methane conversion over heterogeneous catalysts. Thus, this will enable control of the catalytic activity and selectivity toward synthesizing high-value products efficiently. We anticipate that our studies will find application in using atomically precise metals in various challenging bond cleavages and construction of alkanes. Further, using the photon energy of visible light undoubtedly facilitates fossil energy conversions under mild conditions.

Supporting Information
Supporting Information is available.

Conflict of Interest
There is no conflict of interest to report.

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References
1. Labinger, J. A.; Bercaw, J. E. Understanding and Exploiting C–H Bond Activation. Nature 2002, 417, 507–514.
2. Gesser, H. D.; Hunter, N. R.; Prakash, C. B. The Direct Conversion of Methane to Methanol by Controlled Oxidation. *Chem. Rev.* **1985**, *85*, 235–244.

3. Caballero, A.; Pérez, P. J. Methane as Raw Material in Synthetic Chemistry: The Final Frontier. *Chem. Soc. Rev.* **2013**, *42*, 8809-8820.

4. Spivey, J. J.; Hutchings, G. Catalytic Aromatization of Methane. *Chem. Soc. Rev.* **2014**, *43*, 792–803.

5. Lang, S. M.; Bernhardt, T. M.; Barnett, R. N.; Landman, U. Methane Activation and Catalytic Ethylene Formation on Free Au\textsuperscript{II}. *Angew. Chem. Int. Ed.* **2010**, *49*, 980–983.

6. Banerjee, R.; Proshlyakov, Y.; Lipscomb, J. D.; Proshlyakov, D. A.; Structure of the Key Species in the Enzymatic Oxidation of Methane to Methanol. *Nature* **2015**, *518*, 431–434.

7. Grundner, S.; Markovits, M. A. C.; Li, G.; Tromp, M.; Pikdo, E. A.; Hensen, E. J. M.; Jentys, A.; Sanchez-Sanchez, M.; Lercher, J. A. Single-Site Trinuclear Copper Oxygen Clusters in Mordenite for Selective Conversion of Methane to Methanol. *Nat. Commun.* **2015**, *6*, 7546.

8. Snyder, B. E. R.; Vanelderen, P.; Bols, M. L.; Hallaert, S. D.; Böttger, L. H.; Ungur, L.; Pierloot, K.; Schoonheydt, R. A.; Sels, B. F.; Solomon, E. I. The Active Site of Low-Temperature Methane Hydroxylation in Iron-Containing Zeolites. *Nature* **2016**, *536*, 317–321.

9. Sushkevich, V. L.; Palagin, D.; Nanocchiari, M.; van Bokhoven, J. A. Selective Anaerobic Oxidation of Methane Enables Direct Synthesis of Methanol. *Science* **2017**, *356*, 523–527.

10. Hammond, C.; Forde, M. M.; Rahim, M. H. A.; Thetford, A.; He, Q.; Jenkins, R. L.; Dimitratos, N.; Lopez-Sanchez, J. A.; Dummer, N. F.; Murphy, D. M.; Carley, A. F.; Taylor, S. H.; Willock, D. J.; Stangland, E. E.; Kang, J.; Hagen, H.; Kiely, C. J.; Hutchings, G. J. Direct Catalytic Conversion of Methane to Methanol in an Aqueous Medium by Using Copper-Promoted Fe-ZSM-5. *Angew. Chem. Int. Ed.* **2012**, *52*, 5219–5223.

11. Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.; Bushnell, D. A.; Kornberg, R. D. Structure of a Thiol Monolayer-Protected Gold Nanoparticle at 1.1 Å Resolution. *Science* **2007**, *318*, 430–433.

12. Azubel, M.; Kojistov, J.; Malola, S.; Bushnell, D.; Hura, G. L.; Koh, A. L.; Tsunoyama, H.; Tsukuda, T.; Pettersson, M.; Häkkinen, H.; Kornberg, R. D. Electron Microscopy of Gold Nanoparticles at Atomic Resolution. *Science* **2014**, *345*, 909–912.

13. Zeng, C.; Chen, Y.; Kirschbaum, K.; Lambright, K. J.; Jin, R. Emergence of Hierarchical Structural Complexities in Nanoparticles and Their Assembly. *Science* **2016**, *354*, 1580–1584.

14. Narouz, M. R.; Osten, K.; Unsworth, P. J.; Man, R. W. Y.; Salorinne, K.; Takano, S.; Tomihara, K.; Kaappa, S.; Malola, S.; Dinh, C.; Padmos, J. D.; Ayoo, K.; Garrett, P. J.; Nambo, M.; Horton, J. H.; Sargent, E. H.; Häkkinen, H.; Tsukuda, T.; Crudden, C. M. N-Heterocyclic Carbene-Functionalyzed Mag- nic-Number Gold Nanoclusters. *Nat. Chem.* **2019**, *11*, 419–425.

15. Yuan, S.; Xu, C.; Li, J.; Wang, Q. A Ligand-Protected Golden Fullerene: The Dipyrrolidylamido Au\textsubscript{133}\textsuperscript{3+} Nanocluster. *Angew. Chem. Int. Ed.* **2019**, *131*, 5967–5970.
Oxygen by Photoexcited Au$_{25}$(SR)$_{18}$ Clusters. Chem. Mater. 2014, 26, 2777–2788.
31. Liu, C.; Ren, X.; Lin, F.; Fu, X.; Lin, X.; Li, T.; Sun, K.; Huang, J. Structure of the Au$_{23-x}$Ag$_x$(S-Adm)$_{15}$ Nanocluster and Its Application for Photocatalytic Degradation of Organic Pollutants. Angew. Chem. Int. Ed. 2019, 137, 11457–11461.

32. Becke, A. D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. J. Chem. Phys. 1993, 98, 5648–5652.
33. Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. Phys. Rev. Lett. 1996, 77, 3865–3868.
34. Kendall, R. A.; Dunning, T. H.; Harrison, R. J. Electron Affinities of the First-Row Atoms Revisited-Systematic Basis-Sets and Wave-Functions. J. Chem. Phys. 1992, 96, 6796–6806.
35. Peterson, K. A. Systematically Convergent Basis Sets with Relativistic Pseudopotentials. I. Correlation Consistent Basis Sets for the Post-d Group 13-15 Elements. J. Chem. Phys. 2003, 119, 11099–11112.
36. Peterson, K. A.; Figgen, D.; Goll, E.; Stoll, H.; Dolg, M. Systematically Convergent Basis Sets with Relativistic Pseudopotentials. II. Small-Core Pseudopotentials and Correlation Consistent Basis Sets for the Post-d Group 16–18 Elements. J. Chem. Phys. 2003, 119, 11113–11123.
37. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision B.01; Gaussian, Inc.: Wallingford, CT, 2009.

38. Lopata, K.; Govind, N. Modeling Fast Electron Dynamics with Real-Time Time-Dependent Density Functional Theory: Application to Small Molecules and Chromophores. J. Chem. Theory Comput. 2011, 7, 1344–1355.
39. Valiev, M.; Bylaska, E. J.; Govind, N.; Kowalski, K.; Straatsma, T. P.; van Dam, H. J. J.; Wang, D.; Nieplocha, J.; Apra, E.; Windus, T. L.; de Jong, W. A. NWChem: A Comprehensive and Scalable Open-Source Solution for Large Scale Molecular Simulations. Comput. Phys. Commun. 2010, 181, 1477–1489.
40. Kagalwala, H. N.; Gottlieb, E.; Li, G.; Li, T.; Jin, R.; Bernhard, S. Photocatalytic Hydrogen Generation System Using a Nickel-Thiolate Hexameric Cluster. Inorg. Chem. 2013, 52, 9094–9101.
41. Cheng, X.; Chai, X.; Hu, W.; Li, S.; Zhu, Y. The On-and-Off Dynamics of Thiophene on a Nickel Cluster Enables Efficient Hydrodesulfurization and Excellent Stability at High Temperatures. Nanoscale 2019, 17, 4369–4375.
42. Song, J.; Sun, Y.; Ba, R.; Huang, S.; Zhao, Y.; Zhang, J.; Sun, Y.; Zhu, Y. Monodisperse Sr–La$_2$O$_3$ Hybrid Nanofibers for Oxidative Coupling of Methane to Synthesize C$_2$ Hydrocarbons. Nanoscale 2015, 7, 2260–2264.
43. Vaghjiani, G. L.; Ravishankara, A. R. Kinetics and Mechanism of OH Reaction with CH$_3$OOH. J. Phys. Chem. 1989, 93, 1948–1959.
44. Bauerle, S.; Moortgat, G. K. Absorption Cross-Sections of HOCH$_2$OOH Vapor Between 205 and 360 nm at 298 K. Chem. Phys. Lett. 1999, 309, 43–48.