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Selective Catalytic Conversion of Acetylene to Ethylene Powered by Water and Visible Light

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Abstract: The production of polymer-grade ethylene requires the purification of ethylene feed from acetylene contaminant. Accomplishing this task by state-of-the-art thermal hydrogenation requires high temperature, external feed of H₂ gas, and noble metal catalysts, and is not only expensive and energy-intensive but also prone to overhydrogenate to ethane. We report a photocatalytic system to reduce acetylene to ethylene with >99% selectivity for ethylene under both non-competitive (no ethylene co-feed) and competitive (ethylene co-feed) conditions, and near 100% conversion under the latter industrially relevant condition. Our system uses a molecular catalyst based on earth-abundant cobalt operating under ambient conditions and sensitized by either [Ru(bpy)₃]²⁺ or an inexpensive organic semiconductor (mpg-CN) under visible light. These features and the use of water as a proton source offer substantial advantages over current hydrogenation technologies with respect to selectivity and sustainability.

Results and discussion

The energy footprint associated with commodity separation and purification accounts for 10-15% of the world's energy consumption and the demand for commodities could triple by 2050 ¹. A prime example is the commodity chemical ethylene (C₂H₄), an intermediate in the production of ~50-60% of all plastics ². Ethylene is obtained by steam cracking, and typically contains ~1 vol.% acetylene (C₂H₂) contaminant. Acetylene is poisonous to downstream polymerization catalysts and therefore is usually removed by catalytic thermal hydrogenation (Fig. 1A) with a precious metal (Pd)-based catalyst ³. This process has ample room for improvement in terms of price (*e.g.*, ~10,000\$ per kg Pd ⁴) and selectivity (85% for >90% conversion at 200 °C ⁵ where the side product is ethane). Over-hydrogenation to ethane is an inherent limitation of precious metal catalysts that achieve high conversion using H₂ as the hydrogen source ^{3,5,6}. Traditional thermal hydrogenation also has disadvantages with respect to safety and sustainability: it is an energy-intensive (high-pressure, high-temperature) thermochemical reaction in an H₂ atmosphere, where the H₂ is usually needed in excess and this excess must be separated to avoid possible thermal runaway processes ³. Physisorption-based acetylene purification (Fig. 1B) is energy-efficient ^{7,8}, but wastes the separated acetylene rather than converting it to valuable ethylene.

Ideally, we would transition from energy-intensive thermochemical routes for ethylene purification to sustainably driven, selective electrochemical and/or photochemical semi-hydrogenation of acetylene impurity. A scheme that does not require an H₂ feed would mitigate greenhouse-gas emission since steam methane reforming, which co-produces 75.0 kg CO₂ per MJ of H₂, accounts for three quarters of all H₂ global production ⁹. Recently, the mild conditions of electrochemical transformations have been exploited to achieve near 100% conversion of acetylene in the presence of excess of ethylene (0.5 vol.% C₂H₂, 20 vol.% C₂H₄, Ar balance) with

21% energy efficiency, and ethylene selectivity of 90.1% with 0.08% residual hydrogen¹⁰. Direct photochemical hydrogenation could be at least as impactful as electrochemical approaches given that it has the potential to use abundant, sustainable solar irradiation, rather than the electrical grid, as its energy input^{11–15}. With respect to light-powered hydrogenation, a photothermal system achieved 99% conversion in the presence of excess of ethylene and H₂ gas (1 vol.% C₂H₂, 20 vol.% C₂H₄, 20 vol.% H₂, Ar balance) but with a selectivity of only 93.5%¹⁶. A photocatalytic system achieved 97% selectivity but with a pure acetylene feed (5 vol.%, He balance) and H₂ gas, and had a lower saturated acetylene hydrogenation yield (~5%) than the analogous thermal reaction (~18%)¹⁷. Both of these systems have the disadvantage of requiring the precious metal Pd as the catalyst and an external feed of flammable H₂.

Here, we achieve >99% selective, visible light-powered, catalytic conversion of acetylene to ethylene with no Pd and no H₂ gas, and at room temperature. Water is the proton source and an earth-abundant metal (cobalt), in the form of a cobalt porphyrin molecule, [*meso*-tetra(4-sulfonatophenyl)porphyrinato}cobalt(III)] (CoTPPS), is the catalyst (Fig. 1C). The catalyst is photosensitized by tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate ([Ru(bpy)₃]²⁺) ($E_p = -1.33$ V vs. SCE)¹⁸ or, without sacrificing selectivity, by precious metal-free mesoporous graphitic carbon nitride (mpg-CN) ($E_{1/2} = -1.50$ V vs. SCE)^{19,20}; both sensitizers have the ability to absorb visible light and subsequently transfer an electron from their excited states to produce the Co(I) active species ($E_{1/2} [\text{Co}^{\text{II}}/\text{Co}^{\text{I}}] = -0.91$ V vs. SCE)¹⁸ (Fig. 2A).

There is much precedent for chemical^{21,22} and photo-reductions of cobalt compounds to catalytically active Co(I) states^{23–25} to access a diverse set of catalytic reductions. Our choice of catalyst is bio-inspired. Co(I) complexes of vitamin B12 or porphyrin act as non-protein models for nitrogenase in the reduction of non-physiological nitrogen- (*e.g.* nitrous oxide) and carbon-

based (*e.g.* alkyne) substrates ^{21,22,26}. Reduction of Co(III) porphyrin or Co(II) phthalocyanines by sodium borohydride enables conversion of acetylene to ethylene, but with significant ethane and hydrogen side products ^{21,22}. Light-driven strategies for catalytic acetylene to ethylene conversion have however not been reported.

Our three-component catalytic reaction mixture contains 1 μM CoTPPS catalyst, 50 μM $[\text{Ru}(\text{bpy})_3]^{2+}$ sensitizer, and 0.1 M sodium ascorbate (NaAsc) sacrificial reductant under C_2H_2 in an aqueous bicarbonate buffer (pH 8.4, in order to disfavor competitive proton reduction, *vide infra*). In a typical run, we illuminated 2.0 mL of this mixture (aq) under 1 atm C_2H_2 (≥ 99.5 vol.%) using a 450 nm light-emitting diode (LED, $140 \text{ mW}\cdot\text{cm}^{-2}$); the supplementary materials contain details of the photocatalytic setup. Illumination for 24 h produced C_2H_4 with selectivity for ethylene over ethane ($S_{\text{C}_2\text{H}_4}$) $>99\%$ (no detectable C_2H_6) and TON = 1,967, which confirms the catalytic nature of the reaction (Fig. 2B, inset and Supplementary Fig. 1). No other gases (*e.g.*, H_2) were detected (Supplementary Table 1). Upon increasing $[\text{Ru}(\text{bpy})_3]^{2+}$ by a factor of five to 250 μM , the TON (C_2H_4) increased by $\sim 35\%$ with $S_{\text{C}_2\text{H}_4} >99\%$ after 6 h of illumination; further increase of $[\text{Ru}(\text{bpy})_3]^{2+}$ did not increase the amount of produced C_2H_4 (Supplementary Fig. 2). The concentration of C_2H_4 produced increased with the concentration of catalyst but saturated at $[\text{CoTPPS}] \sim 25 \mu\text{M}$ (Supplementary Fig. 3), probably because of parasitic light absorption by CoTPPS (Supplementary Fig. 4). No C_2H_4 is produced in the absence of sensitizer, catalyst, sacrificial donor, light or C_2H_2 feedstock (Fig. 2B). When we perform the photoreduction reaction with cobalt nanoparticles (as opposed to CoTPPS), the TON decreases dramatically, and when we add mercury to the CoTPPS system, the TON is not meaningfully affected (Supplementary Table 1). These control experiments unequivocally prove that this reaction is primarily homogeneous and photocatalytic, powered by $[\text{Ru}(\text{bpy})_3]^{2+}$ -sensitized CoTPPS.

Ethylene production saturates after 24 h (Fig. 2B, inset) due to degradation of both $[\text{Ru}(\text{bpy})_3]^{2+}$ and CoTPPS, probably by the oxidized sacrificial reductant, dehydroascorbic acid, which also inhibits catalysis when added directly to the reaction mixture (Supplementary Fig. 5, Supplementary Table 1).

The photocatalytic activity of our acetylene reduction system is tolerant to presence of various gases, including O_2 , CO_2 , and CO (Supplementary Figs. 6-8), the latter two of which are typically present as impurities²⁷. CO adsorbs to the active sites of conventional hydrogenation catalysts and acts as an inhibitor; tolerance to these adventitious adsorbates highlights our system's potential advantages over traditional catalysts in an industrial setting.

We can replace the $[\text{Ru}(\text{bpy})_3]^{2+}$ photosensitizer with the organic semiconductor mpg-CN, which is a broadband absorber and can be prepared at only a few dollars per kg from readily available starting material^{19,20}. A system containing 10 μM CoTPPS, 2.5 mg mpg-CN and 0.05 M NaAsc + 0.2 M TEOA under C_2H_2 (≥ 99.5 vol.%) in water (pH 10.6) produced C_2H_4 with TON = 87, $S_{\text{C}_2\text{H}_4} > 99\%$ after 12 h of illumination with a 450 nm LED, and TON = 49, $S_{\text{C}_2\text{H}_4} > 99\%$ after 12 h of illumination with white light irradiation ($140 \text{ mW}\cdot\text{cm}^{-2}$, 1.4 suns at AM 1.5 G) (Fig. 2C, Supplementary Table 1).

A major advantage of the CoTPPS system with respect to sustainability is that it does not require an external feed of H_2 , so we investigated the source of protons/hydrogens further. Our three-component system did not evolve any detectable H_2 (Supplementary Table 1), so it is extremely unlikely that *in situ* production of H_2 is a source of hydrogen here. When we conducted experiments in H_2O and using C_2H_2 (5 vol.%, He balance) as feedstock, gas chromatography/mass spectrometry (GC-MS) analysis identified C_2H_4 ($m/z = 28$) as the reaction product (Fig. 3D green). When the photoreduction was instead performed in D_2O solvent, we observed C_2D_4 ($m/z = 32$)

(Fig. 3D purple), produced by exchange between the feedstock C_2H_2 and D_2O , which we pre-equilibrated before illumination^{28,29}; the supplementary materials contain details of sample preparation and GC-MS experiments. These two experiments prove unambiguously that not only is acetylene the precursor for the observed C_2H_4 , but also the protons added to make the C_2H_4 reduction product originate from the water solvent.

Based on our experimental results and the literature^{18,21,36,22,23,30–35}, we diagram a probable mechanism for the visible-light-driven reduction of C_2H_2 to C_2H_4 in Fig. 3A. The shift of the CoTPPS Soret band from 426 nm to 412 nm upon addition of NaAsc indicates that the starting $[Co^{III}P(H_2O)_2]$ species is reduced spontaneously to $[Co^{II}P(H_2O)]$ by NaAsc (Fig. 3B and Supplementary Fig. 9)¹⁸. Following light absorption by $[Ru(bpy)_3]^{2+}$, the emission of the excited state $[Ru(bpy)_3]^{2+*}$ photosensitizer (PS*) is quenched by hole transfer to NaAsc to form $[Ru(bpy)_2(bpy^{\cdot-})]^+$ (PS⁻), followed by electron transfer from PS⁻ ($E_p = -1.42$ V vs Ag/AgCl) to $[Co^{II}P(H_2O)_2]$ ($E_{1/2} = -0.87$ V vs. Ag/AgCl) to form the low valent $[Co^I P]^-$ species¹⁸ (Supplementary Figs. 10 and 11). We determined the order of charge transfer reactions by measuring the bimolecular rate constants for quenching of the photoluminescence of PS* by Stern-Volmer analysis (Fig. 3C and the supplementary information). These data show that photoinduced hole transfer to NaAsc is a factor of 1,000 faster than photoinduced electron transfer to CoTPPS. The nucleophilic attack by Co(I) species on one of the carbon atoms of the electrophilic C_2H_2 , via a π complex, is followed by a rapid addition of a proton from water^{23,30,31}. In the final segments of the photocatalytic cycle (Fig. 3A), a second protonation of the Co–C bond by water yields C_2H_4 and $[Co^{II}P(H_2O)_2]$ and re-starts the cycle.

We confirmed that the Co(I) species is the active site to which C_2H_2 binds by adding $NaBH_4$, which is known to reduce the Co(III) of the CoTPPS to Co(I), to a CoTPPS solution without

photosensitizer or light ^{21,22}. We convert acetylene to ethylene under these conditions, although H₂ is the major product ^{21,22} (Supplementary Table 1).

We rule out a mechanism in which [Co^IP]⁻ reacts with water to yield the cobalt hydride intermediate [Co^{III}-H], which then coordinates C₂H₂ and releases C₂H₄ after a second protonation step ^{23,32,33,37} because our three-component system did not evolve any detectable H₂, even when the sample was purged with Ar instead of C₂H₂ (Supplementary Table 1). Based on a previous report of H₂ evolution using a CoTPPS catalyst at pH <8 in a phosphate buffer ³⁵, we believe we disfavor formation of [Co^{III}-H] due to the pH of our bicarbonate system (8.4, whereas the acid-base equilibrium constant between Co(I) and Co(III)-H is pK_a = 7.7). We also rule out the presence of radical intermediates because C₂H₄ formation is not affected by adding the radical trap TEMPO to the reaction mixture (Supplementary Table 1) ^{32-34,36}.

We specified further the geometry of the interaction between C₂H₂ and the CoTPPS catalyst by analyzing the stereoselectivity of the reduction reaction through gas-phase IR spectroscopy of the C₂H₂D₂ (*m/z* = 30) product (Fig. 3D blue) obtained when we performed the photoreduction in D₂O solvent and using C₂H₂ (5 vol.%, He balance) as feedstock; the supplementary materials contain details of the sample preparation and the GC-MS experiments. The reaction of C₂H₂ in D₂O ^{28,29} could lead to *cis*-, *trans*- or *asymmetric*-ethylene-*d*₂. The IR spectrum of the gaseous product had an intense absorption peak at 842 cm⁻¹ assigned to the non-planar vibration ω_7 of *cis*-C₂H₂D₂ ³⁸, Fig. 3E. Other minor peaks are attributable to ω_8 C₂HD₃ (919 cm⁻¹) from the partially H/D exchanged acetylene substrate ³⁸, and to two other isomers of ethylene (*asymmetric*-C₂H₂D₂ and *trans*-C₂H₂D₂ at 943 and 987 cm⁻¹, respectively) ³⁸ (Fig. 3E). This result shows that the proton additions from water occur predominantly in a *syn*-manner (on one side of the triple bond of the

substrate), which is consistent with the formation of a *cis*-alkene product from the cobalt(I)-catalyzed reduction of propylene in alkaline media³⁰ and consistent with our proposed mechanism.

We suspect that the high selectivity of our three-component photocatalytic system originates in the better ability of the nucleophilic Co(I) species of the CoTPPS catalyst to coordinate highly electrophilic alkynes than less electrophilic alkenes^{23,31,39,40}.

Importantly for potential industrial application of this process, our [Ru(bpy)₃]²⁺-sensitized CoTPPS system selectively photoreduces acetylene even in the presence of excess of ethylene (1 vol.% C₂H₂, 30 vol.% C₂H₄, He balance). This ethylene/acetylene mixture is a typical industrial ethylene feed and requires a highly selective catalyst to eliminate ethane production. Our system achieved near 100% conversion of C₂H₂ from this mixture with >99% selectivity for ethylene (no detectable C₂H₆) after 18 h of illumination (Fig. 4 and Supplementary Fig. 12).

Our photocatalytic system is not limited to conversion of acetylene. Illumination of the three-component system ([Ru(bpy)₃]²⁺, CoTPPS, NaAsc) under 1 atm propyne (C₃H₄, ≥99 vol.%) produced propylene (C₃H₆) with >99% selectivity over propane (C₃H₈) (Supplementary Fig. 13). This result demonstrates the suitability of this system for the isolation of a pure industrial propylene stream from propyne⁴¹, a task not accomplished by steam cracking but necessary for the production of polymer-grade propylene, which together with ethylene accounts for ~80% of global plastic demand².

Finally, CoTPPS can be replaced with a tetracarboxyphenyl cobalt porphyrin (CoTPPC) (Supplementary Table 1), which can be anchored to an electrode to exploit this catalytic cycle in a photoelectrochemical cell⁴².

Until photosynthetic cascade reactions are developed enough to produce ethylene from CO₂ feedstock, we need to produce this important commodity chemical with the lowest energy footprint

possible. Our selective photocatalytic strategy is a major step toward that goal. Our system reduces acetylene into ethylene with several advantages over the present hydrogenation technology, including (i) operation with near 100% conversion in an ethylene-rich gas feed and >99% selectivity under both non-competitive (no ethylene co-feed) and competitive (ethylene co-feed) conditions, the latter being industrially relevant; (ii) operation at room temperature using light and water in place of high temperature and an external H₂ feed, and (iii) use of earth-abundant cobalt in the catalyst, which works not only in combination with the benchmark photosensitizer [Ru(bpy)₃]²⁺, but also with inexpensive and organic mpg-CN. The photoreduction strategy is sustainable, robust, and selective enough to complement, if not eventually replace, thermal hydrogenation to create polymer-grade ethylene.

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Data availability

All data needed to evaluate the conclusions in this manuscript are available within this article and its Supplementary Information.

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Author contributions

FA (Weiss Laboratory), LÐ (Stupp Laboratory) and EAW conceived the project, contributed to the experimental design, and wrote the manuscript. EAW directed the research. FA and LÐ designed and performed most of the experiments and analyzed the results. FA, LÐ and NS carried out the gas chromatography experiments. LÐ synthesized the porphyrin catalyst and the carbon nitride. EAW and SIS secured the funding. All the authors contributed to manuscript preparation.

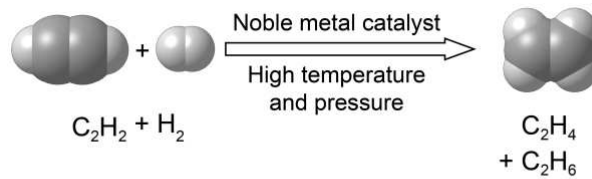
Competing interests

The authors FA, LD, EAW, SIS are co-inventors on a provisional patent application entitled “Selective Photocatalytic Reduction of Acetylene to Ethylene in Water and at Room Temperature” related to this work.

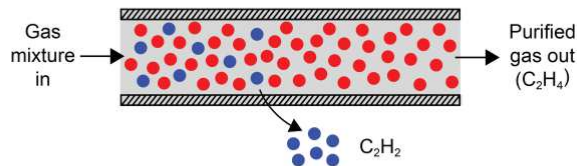
Additional information

Correspondence and requests for materials should be addressed to EAW

A Catalytic hydrogenation of acetylene (present technology)



B Sorbent separation of acetylene



C Photoreduction of acetylene (this work)

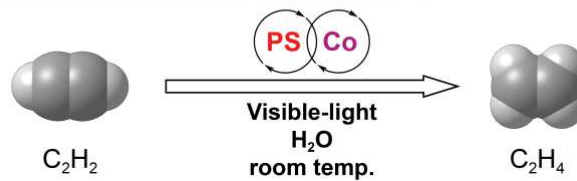


Fig. 1. Strategies for producing pure C_2H_4 from C_2H_2 . (A) The state-of-the-art process for purifying ethylene to polymer-grade: semi-hydrogenation of impurity acetylene using noble-metal catalysts at high temperature. (B) Capture and separation of acetylene from acetylene/ethylene mixtures using porous materials. (C) This work: >99% selective photoreduction of acetylene to ethylene powered by visible light and water at room temperature.

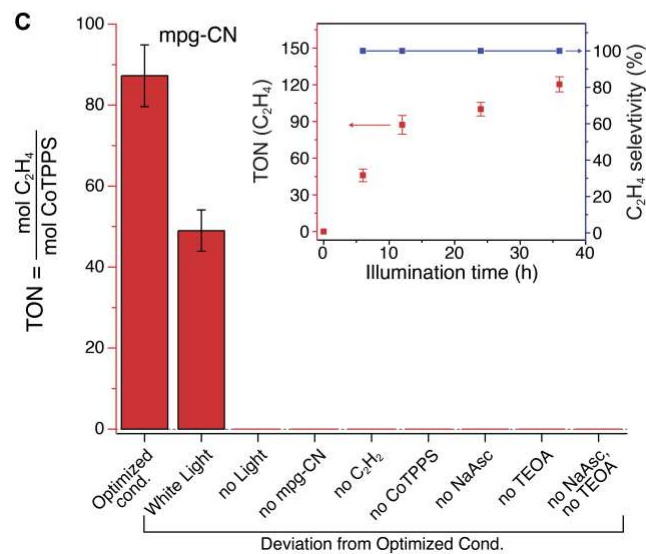
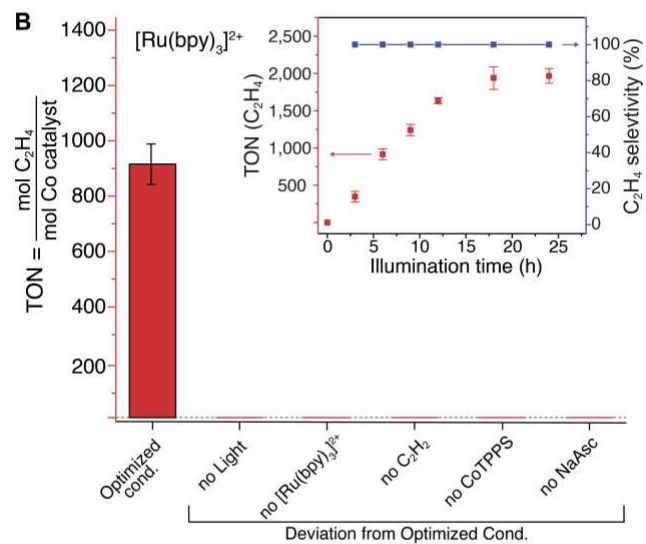
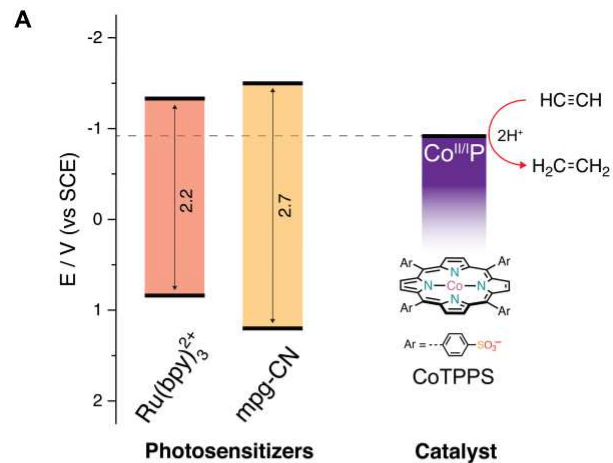


Fig. 2. Sensitizers and catalysts used in this study for the photoreduction of C₂H₂ to C₂H₄ and their performance. (A) Tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate ([Ru(bpy)₃]²⁺) or mesoporous graphitic carbon nitride (mpg-CN) photosensitizers and [*meso*-tetra(4-sulfonatophenyl)porphyrinato}cobalt(III)] (CoTPPS) catalyst. Redox potentials are shown. (B) TON (C₂H₄) by the [Ru(bpy)₃]²⁺/CoTPPS system under C₂H₂ (≥99.5 vol.%) irradiated (450 nm) for 6 h, and with conditions that differ from the optimized conditions, as indicated in the axis labels. (**Inset**) TON (C₂H₄) and S_{C₂H₄} as a function of irradiation time (450 nm) by the [Ru(bpy)₃]²⁺/CoTPPS system. (C) TON (C₂H₄) by the mpg-CN/CoTPPS system under C₂H₂ (≥99.5 vol.%) irradiated (450 nm) for 12 h, and with conditions that differ from the optimized conditions, as indicated in the axis labels. (**Inset**) TON (C₂H₄) and S_{C₂H₄} as a function of irradiation time (450 nm) by the mpg-CN/CoTPPS system. Experimental details are in the supplementary materials. Error bars are calculated from two to three runs; uncertainty is ≤10%.

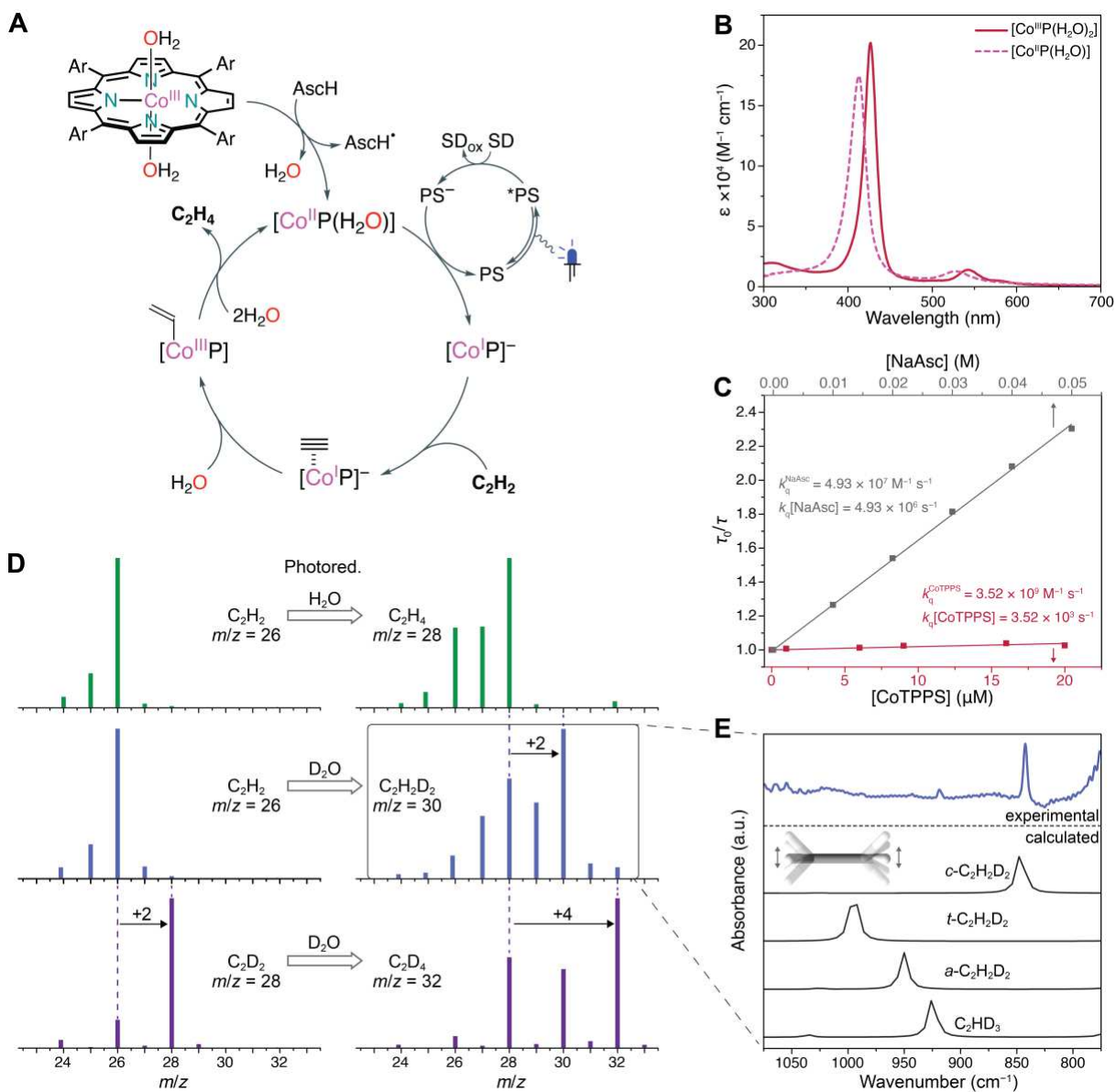


Fig. 3. Mechanistic analysis for the photoreduction of C_2H_2 to C_2H_4 . (A) Proposed mechanism for the photoreduction of acetylene to ethylene by the $[Ru(bpy)_3]^{2+}/CoTPPS$ system. (B) The Co^{III} -porphyrin is reduced by $AscH^-$ to Co^{II} . (C) Stern-Volmer plots for the quenching of the $[Ru(bpy)_3]^{2+*}$ emission lifetime (at 610 nm) by NaAsc or CoTPPS. (D) GC-MS spectra of acetylene (left) feedstock and ethylene (right) product for the irradiated (450 nm) $[Ru(bpy)_3]^{2+}/CoTPPS$ system under C_2H_2 (5 vol.%, He balance) in MilliQ H_2O (green) or in D_2O (blue, purple). The shift $m/z +2$ in H_2O corresponds to incorporation of two hydrogens to produce

C₂H₄ when starting with C₂H₂. The shifts $m/z +4$ in D₂O correspond to incorporation of two deuteriums to produce C₂H₂D₂ when starting with C₂H₂ (blue) or of two deuteriums to produce C₂D₄ when starting with C₂D₂ (violet). (E) Experimental gas phase IR spectrum of C₂H₂D₂ product (blue) for the irradiated (450 nm) [Ru(bpy)₃]²⁺/CoTPPS system in D₂O (blue in (D)), compared with the DFT calculated gas-phase spectra (black).

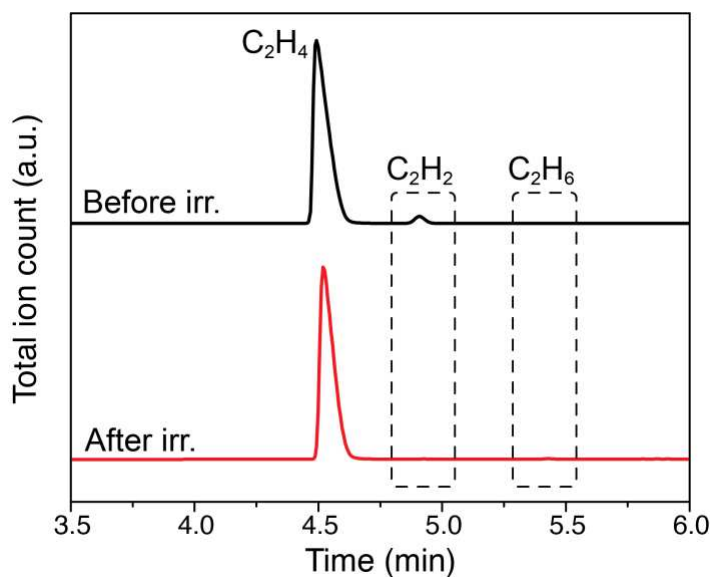


Fig. 4. Typical GC-MS chromatograms observed before and after photoreduction of the ethylene/acetylene mixture. Gas chromatograms (retention times of C_2H_2 , C_2H_4 and C_2H_6) with total ion count before and after irradiation (450 nm) for 18 h of the $[Ru(bpy)_3]^{2+}/CoTPPS$ system under C_2H_2/C_2H_4 (1 vol.% C_2H_2 , 30 vol.% C_2H_4 , He balance) mixture.

Supplementary Files

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