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## Evaluation of Bis-Cyclometalated Alkynylgold(III) Sensitizers for Water Photoreduction to Hydrogen

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ABSTRACT: Well-defined gold sensitizers for hydrogen production from water remain extremely rare, despite decades of interest and are currently limited to systems based on ruthenium, iridium or platinum complexes. This report details the synthesis and characterization of a series of neutral cyclometalated gold(III) complexes of the type  $[(RC^N^CR)Au(C \equiv C - R')]$  (R = H or *tert*-butyl group; R' = aryl groups) that have been found to be good candidates to function as harvesting materials in light-induced electron transfer reactions. We established the efficacy of systems with these gold(III) complexes as photosensitizers (PSs) in the production of renewable hydrogen in the presence of [Co(2,2]]bipyridine)<sub>3</sub>]Cl<sub>2</sub> or [Rh(4,4'-di-tert-butyl-2,2'-bipyridine)<sub>3</sub>](PF<sub>6</sub>)<sub>3</sub> as a H<sub>2</sub>-evolved catalyst and triethanolamine (TEOA) as a sacrificial electron donor in acetone-water solution. All complexes are active, and there is a more than threefold increase over other candidates in photocatalytic H<sub>2</sub> generation activity. Under the optimal reaction conditions, hydrogen evolution took place through a photochemical route with the highest efficiency with a turnover number (TON) of up to 1441.5 relative to the sensitizer over 24 hours. In the initial photochemical path, the reductive quenching of the excited gold(III) complex by TEOA due to the latter's greater concentration in the system followed by electron transfer to the catalyst species is proposed to be the dominant mechanism. A photo-to-H<sub>2</sub> quantum yield of approximately 13.7% was attained when illuminated with monochromatic light of 400 nm. Such gold(III) complexes have demonstrated significant utility in solar-to-hydrogen reactions and thus represent a new effective class of light-harvesting materials. These results open possibilities for pursuing more efficient photosensitizers featuring gold(III) complexes in photocatalytic solar energy conversion.

Keywords: gold • hydrogen evolution • photochemistry • photosensitizer • water splitting

#### INTRODUCTION

The solar generation of molecular hydrogen is an inspiring technology based on the direct reduction of water that involves turning solar energy into clean chemical energy, and it has favorable long-term prospects for building a sustainable clean energy future.<sup>1</sup> Among the various approaches that have been developed toward this, artificial photosynthetic processes exploiting the principles of natural photosynthesis are particularly intriguing, and they always start with the light energy being trapped by specialized light-harvesting chromophores acting similar to photosynthetic pigments such as chlorophylls in multi-component photochemical hydrogen evolution systems.<sup>2</sup> For the efficient capture of solar energy in solar-to-fuel conversion devices,<sup>3</sup> the capability of a light harvester, which funnels the energy to the associated reaction centers (water-reduction catalyst) for conversion into chemical fuel in the form of hydrogen, plays a pivotal role.<sup>4</sup> Transition metal compounds, especially based on the d<sup>6</sup> Ru(II) metal ion with polypyridyl-based ligands as potent sensitizers, have been the focus of research due to their advantageous photophysical and photochemical properties, such as intense absorption in the visible range and long excited state lifetimes, thereby making them attractive in the context of developing the light-harvesting components of fuel-generating systems.<sup>5</sup>

Recently, Ir(III) complexes with excellent activity have emerged as exciting alternatives to be used in this process.<sup>6</sup> The potential of these complexes relies on the fact that their remarkable photoexcited states are very tunable by varying the electronic structures of the ligands or the selection of special ligands with relatively facile synthetic accessibility. Despite years of research and the achievement of significant progress in recent years,<sup>7</sup> solar fuel production is still at its experimental stage, and there are many challenges that must be met. Indeed, upon irradiation, sensitizers are often limited by their durability.<sup>8</sup> This drawback is the consequence of the fact that the ligand dissociation of the complex occurs during photolysis, hence giving rise to the functional inactivation of the complex. Against this backdrop, several solutions have already been proven but require the further design and development of novel metal complex sensitizers that show stability and activity to fulfill artificial photosynthesis.<sup>9,10</sup> Comprehensively understanding the structural features of these sensitizers that determine the electronic structures and excited-state molecular geometries is certainly important as part of the mechanistic principles behind H<sub>2</sub>O reduction catalysis to apply this knowledge to the rational molecular design of future efficient sensitizers for photosensitized reactions.

In contrast, reports of luminescent gold(III) complexes having long-lived excited states in fluid solutions, which can lead to their utilization as functional sensitizers to perform light-induced electron transfer reactions, are sparse due to the high electrophilicity of the gold(III) center and the presence of the low-energy d-d ligand field states responsible for non-emissive species.<sup>11</sup> Moreover, as a consequence of their relatively large positive reduction potentials and their consequent poor stability in

DOI: 10.1039/C6DT03044K solution, the photochemistry of cyclometalated gold(III) complexes has not yet been extensively investigated. It has been proposed that the gold(III) complexes, by use of the incorporation of both rigid cyclometalating and strongly  $\sigma$ -donating carbon ligands such as acetylide or carbone, as they raise the energies of the deactivating metal-centered d-d excited states, making them thermally inaccessible and thus leading to a reduction of non-radiative deactivation, have been observed to emit even at room temperature in various media.<sup>12-14</sup> Additionally, the presence of the  $\sigma(M-C)$  bond to a correlated gold(III) center improves the stability of the high-valent metal compounds toward reduction. By analogy to isoelectronic and isostructural alkynylplatinum(II) compounds, alkynylgold(III) complexes with longlived emissive excited states and other attractive properties, such as low toxicity, inertness and an environmentally benign nature, may open a wide range of unexplored possibilities as photosensitizers for the prospect of photocatalytic hydrogen production. Despite these prospects, gold(III) complexes are considerably less explored in such investigations. A cationic carbene-containing gold(III) complex was first found recently to lend itself to this type of application, with approximately 350 turnovers of hydrogen after 4 h of irradiation,<sup>15</sup> reinforcing the potential application of gold complexes in the relevant photocatalytic process. This demonstration of their accessibility offers opportunities for the development of new sensitizers in this series that bear new and specific structural features and might display increasing reactivity.



Scheme 1. Chemical structures of gold compounds 1–4.

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In continuation of our work on the design of transition metal complex sensitizers and their application in the chemical conversion of light energy, we now anticipate to extend it to gold(III) complexes for the construction of photochemical hydrogen production systems. In this study, we

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focused on bis-cyclometalated gold(III) complexes with acetylide co-ligands, which have been discovered to favor bright luminescence with a long lifetime in both the solid and solution states, which is crucial for triggering efficient photocatalytic processes. A class of neutral luminescent alkynylgold(III) complexes [(RC^N^CR)Au(C=C-R')] (R = H or *tert*-butyl group; R' = aryl groups) has been synthesized and characterized (Scheme 1). Theoretical investigations based on density functional theory (DFT) and time-dependent DFT (TD-DFT) methods have elucidated the electronic structures and electronic transition processes of the compounds. Their photosensitization behavior for hydrogen production was investigated by adopting a three-component catalytic system in the presence of the water reduction catalyst and triethanolamine (TEOA) as a sacrificial electron donor in a mixture of acetone and water. The results demonstrate that the change of the microenvironment of the gold(III) complex, such as the use of cyclometalating ligands with different electronic properties and ancillary ligands, generates complexes with different photophysical and photochemical characteristics and also shows different activities in photocatalytic systems for the production of hydrogen.

#### **RESULTS AND DISCUSSION**

Gold(III) complexes 1–4 were synthesized in 68.7-95.8% yields *via* a copper(I)-catalyzed route based on the literature protocol for analogous compounds as executed with related molecules.<sup>16</sup> The detailed synthetic procedures are described in the Supporting Information.





**Photophysical Properties.** The studied complexes were first assessed for their photophysical properties in air-saturated acetonitrile at ambient temperature. The UV/vis profiles of complexes 1–4 are illustrated in Figure 1. The photophysical data of complexes 1 and 3 that have previously been reported are also shown for comparison.<sup>16</sup> For all complexes, at concentrations of ca.  $5 \times 10^{-5}$  M, intense absorption bands below 340 nm in the UV spectral region with molar extinction coefficients ( $\varepsilon$ ) on the order of  $10^4$  M<sup>-1</sup> cm<sup>-1</sup> are observed and are in general assigned to the ligand-centered  $\pi \to \pi^*$  intraligand

charge transfer (ILCT) transition located on the surrounding ligands. This UV absorption is followed by a less intense vibronic-structured absorption band ( $\varepsilon$  on the order of 10<sup>3</sup> M<sup>-1</sup> cm<sup>-1</sup>) at a longer wavelength with some tailing into the visible region, giving rise to the pale-yellow to yellow colors of the complexes. The lower-energy bands contribute to the transition, incorporating a mixed state involving metal-perturbed  $\pi \to \pi^*$  IL transitions located in the tridentate C^N^C ligand and  $\pi \to \pi^*$ ligand-to-ligand charge transfer (LLCT) transitions from the peripheral phenyl moieties to the central pyridine unit. Such assignments are based on earlier reported studies of related similar gold(III) complexes. A possibility of a metal-to-ligand charge transfer (MLCT) is less feasible due to the electrophilic and redox-inactive character of the gold(III) metal center, as predicted by the below calculations. The intensity and onset of absorption in the visible spectral region account for the ability of the light-harvesting materials to capture solar energy and thus exert an influence on the photocatalytic performance.

Table 1. Photophysical a	nd electrochemical	l properties of studiec	l gold(III) comp	plexes 1-4
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Comp.	$\lambda_{em} [nm]^{[a]}$	$\tau [\mathrm{ns}]^{[\mathrm{a}]}$	$ au_{\mathrm{avg}}  [\mathrm{ns}]^{[\mathrm{a}]}$	$arPsi^{[a]}[\%]$	$E_{\mathrm{ox}}[\mathrm{V}]^{[\mathrm{b}]}$	$E_{\rm red} \left[ { m V}  ight]^{[b]}$
1	478,504	35.1 (44%)	10.1	$1.5 \times 10^{-3}$	+1.77	-1.27
2	480,625	19.6 (97%)	19.4	1.1×10 <sup>-2</sup>	+1.29	-1.27
3	488,513	106.9 (88%)	42.9	8.8×10 <sup>-3</sup>	+1.87	-1.33
4	455,478(sh)	3.8 (70%)	4.2	2.6×10 <sup>-2</sup>	+1.44	-1.35 <sup>c</sup>

[a] Measurements in a N<sub>2</sub> atmosphere in CH<sub>3</sub>CN at room temperature (relative error for  $\lambda_{em}$ : ±3 nm); Decay profiles were satisfactorily fitted by three exponential functions and only the dominant lifetime was shown (relative error for  $\tau$ : ±5%). The percentage in parentheses indicates the contribution from that component; the luminescence quantum yield was measured utilizing [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> in aqueous in solution as a standard (relative error for  $\Phi$ : ±10%). [b] Redox potentials measured in deoxygenated CH<sub>3</sub>CN with 0.1 M n-Bu<sub>4</sub>NPF<sub>6</sub> as the supporting electrolyte; potentials ( $E_{ox}$  refers to the peak potential for the irreversible oxidation waves;  $E_{red} = 1/2(E_{pa} + E_{pc})$  for the reversible reduction) measured vs Ag/AgCl coupled and converted to normal hydrogen electrode (NHE). [c] The value refers to the peak potential for the irreversible reduction wave.

For all complexes, emission was weak in the air-saturated CH<sub>3</sub>CN solutions, probably because of quenching by oxygen in air. However, in nitrogen-saturated CH<sub>3</sub>CN, using an excitation wavelength of 350 nm, all complexes (at concentrations of ca.  $5 \times 10^{-5}$  M) exhibited intense emissions with a broad, emission band with peak wavelengths of approximately 455–625 nm at room temperature, with solution photoluminescence quantum yields ( $\Phi$ ) on the order of  $10^{-2}$ . The corresponding photophysical data are collected in Table 1 and found to be qualitatively in agreement with those observed for gold(III) complexes described in the literature,<sup>16</sup> and the spectra are depicted in Figure S1. As anticipated, there was an increase in the quantum yield of the carbazole-containing complexes **2** and **4** compared to **1** and **3**. The excitation spectra of each complex recorded at the maximum emission closely resemble the corresponding electronic absorption spectra. With reference to previous studies, the luminescence was derived from the metal-perturbed triplet [ $\pi \rightarrow \pi^*$ ] IL excited state of the C^N^C ligand. The luminescence of **3** is red-shifted with respect to that observed for complex **1**. As in the absorption spectra, this is due to the involvement of slight different HOMO-1 in the related transition, as observed

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from the corresponding TD-DFT data (vide infra). Complexes 2 and 4 displayed exceptional emission profiles and wavelength maxima at wavelengths of 480 nm and 625 nm for 2, and 455 nm for 4, respectively, which probably originated from a LLCT  $[\pi(C \equiv C - R') \rightarrow \pi^*(RC^N \cap CR)]$  excited state.<sup>17</sup> The relatively weak emission peak at 480 nm persisted even after the most careful purifications of 2 by repeated recrystallization, and thus is not attributed to a possible impact of impurity but to an intrinsic electronic transition of this complex. The incorporation of *tert*-butyl groups in the C^N^C ligand resulted in a blue shift of the emission. This has also been observed in [Pt(II)C^N^N] alkynyl complex by Che and coworkers previously.<sup>18</sup> These differences in the emission maxima could arise from the varying energies of the different cyclometalating surroundings, which provide orbitals that participate to different extents in the excited state origin of the respective complexes. The spectral assignments have been further substantiated by DFT/TDDFT calculations. For each complex in nitrogen-saturated CH<sub>3</sub>CN (5×10<sup>-5</sup> M), the observed emission lifetimes ( $\tau$ ) upon excitation at 370 nm exhibit three exponential component with an average lifetime ( $\tau_{avg}$ ) on the nanosecond time scale (4.2-42.9 ns), following the order 3 > 2 > 1 > 4 (Figure S2). Three exponential components were necessary for fitting adequately the luminescence decays. This result is similar to that obtained for emissive Au(III) complexes.<sup>19</sup> The lifetime data suggested the presence of more than one emitting species in these complexes, which can not be resolved in energy in the steady-state emission spectra with our device.<sup>20</sup> In the case of complex 4, it exhibits a relatively short lifetime. This is probable the result of mixed singlet-triplet states,<sup>21,22</sup> which could contain more singlet state mixing in the emission. That such a mixing occurs is supported by the fact that the luminescence cannot be quench by oxygen. Under air saturation, the emission spectral profiles of 1-3 remain unchanged but the intensities of the luminescence, exhibiting the short lifetimes in aerated solution, were quenched an extent of ca. 20%-30%, whereas no significant quenching effect was observed for **4** (Figure S3).<sup>17</sup> The knowledge of these photophysical parameters for complexes of these types provides valuable insights in evaluating the potential applications of these materials in light-induced electron transfer reactions.

**DFT Calculations.** The above spectral/structure views are supported by the DFT/TD-DFT calculations using the molecular orbital diagrams of the systems of interest.<sup>23</sup> The spatial plots of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for each complex are illustrated in Table S1, and they are consistent with previous reports on analogous gold(III) complexes. The HOMO and LUMO are obviously separated, indicating intramolecular charge separation interactions between the separated fragments in the complex. For the four complexes, the HOMO consists primarily of the electron density on the ligand of  $\pi$ -(C=C-R'). The HOMO-1 (second-highest occupied molecular orbital) is of quite a different character, as is induced by the different characters of the molecular environments of the individual complexes. It is interesting that the C^N^C

ligand in 1 and 3 contributes a large participation to the HOMO-1 orbital, while the HOMO-1 in 2 and 4 is localized on the carbazole fragment. In contrast, the LUMO has nearly identical contours in all complexes, being spread over both the  $\pi^*$ -(RC^N^CR) with some contributions from the gold(III) center.

Based on the results of TD-DFT calculations (Table S2), the orbitals involved in the lowest energy transition ( $S_0 \rightarrow S_1$ ,  $S_0$  is the ground state) for complexes 1–4 are primarily HOMO-1 and LUMO for 1 (by 97.35% contribution) and 3 (by 96.85% contribution), while that are HOMO and LUMO for 2 (by 96.50% contribution) and 4 (by 95.04% contribution). Thus, the vertical transitions imply an electron density transfer, mainly from the one-electron excitations of HOMO-1  $\rightarrow$  LUMO (<sup>1</sup>ILCT) for 1 and 3. The presence of the carbazolyl group in 2 and 4 reduces the contribution of the C^N^C ligand and enhances the participation of the C=C-R' ligand; consequently, the origin of the first singlet transition, which is clearly different from that of 1 and 3, can be described as the one-electron excitation of HOMO  $\rightarrow$  LUMO (<sup>1</sup>LLCT, also involving HOMO-3).

Similar to the singlets, the lowest vertical triplet  $S_0 \rightarrow T_1$  transition is of the  $\pi \rightarrow \pi^*$  type, which does not correspond to the triplet excited state derived from the HOMO  $\rightarrow$  LUMO excitation but is defined by the configuration HOMO-1  $\rightarrow$  LUMO for both 1 and 3 (contribution: 82.80% for 1; 82.79% for 3), lying at similar energies. This indicates that the excited state contains predominantly a tridentate ligand with a <sup>3</sup>ILCT character, although other transitions are also involved therein. In comparison to complexes 1 and 3, complexes 2 and 4 also only differ in the ligand of RC^N^CR (for 2, R = H; for 4, R = *tert*butyl); however, owe to the large molecular architectures of these complexes, it is difficult to describe the distribution calculated for their lowest triplet  $S_0 \rightarrow T_1$  transition, which is rather complicated, both containing HOMO  $\rightarrow$  LUMO (contribution: 40.77% for 2; 10.38% for 4) and being highly multiconfigurational in character. This is likely accounted for the blue-shift of the emission band in 4 compared to that in 2. The result suggests a difference in the nature of the excited state of these complexes.

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**Electrochemical Properties**. The redox properties of all four complexes were evaluated by cyclic voltammetry, conducted in anhydrous acetonitrile solvent containing 0.1 M tetra-n-butylammonium hexafluorophosphate (n-Bu<sub>4</sub>NPF<sub>6</sub>) as the supporting electrolyte at room temperature, and the results are summarized in Table 1. The cyclic voltammograms of the four compounds exhibit an irreversible oxidative wave with anodic maxima at 1.29-1.87 V versus NHE ( $E_{pa}$ ) (Figure S4). They also show a quasi-reversible reductive wave, except **4** (irreversible wave), with a half-wave potential in a small range of -1.27 V to -1.35 V vs NHE (for **4**,  $E_{pc}$ , cathodic peak). In analogy with previously published works<sup>16</sup> and the uncoordinated ligand under identical conditions (Figure S5), on the basis of the DFT calculations, both processes could mainly be associated with ligand-centered electrochemical events,

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concomitant with minor influences from the gold(III) center. For the reduction potentials occurring at the  $\pi^*$ -(RC^N^CR) orbital with only minor influences from the gold(III) center, there is only a small variation in the cathodic peaks, indicating the limited influence of the *tert*-butyl substituents on the aryl ring of the RC^N^CR ligand in **3** and **4** on the LUMO orbitals. With reference to the other studies on the related derivatives,<sup>16</sup> the oxidation is considered the oxidation of the alkyne unit. The electronic effects of the alkynyl ligands lead to the variation of the potential for the oxidation.

**Photocatalytic Hydrogen Production**. The photocatalytic reaction activities for hydrogen generation were then examined to identify the applicability of these complexes as photosensitizers (PSs). The studies were performed by adopting a three-component catalytic system in the presence of the water reduction catalyst (WRC) and TEOA as a sacrificial electron donor in a media of an acetone/water mixture (v/v = 4:1) (for details, see the Experimental Section).<sup>24</sup> The reduction catalyst generally includes cobalt, rhodium and platinum and so on.<sup>8-10</sup> TEOA is chosen because according to the comparison of the equilibrium redox potential of TEOA with the excited-state redox potentials  $E(S^*/S^{-})$  of the gold(III) complexes, the driving force for the reductive quenching of the excited state of the complex using TEOA is generally thermodynamically favorable. The utility of acetone is due to solubility reasons, as this type of gold(III) complex is sparingly soluble in water. In an earlier study,<sup>25</sup> it was found that the performance of the catalytic system is strongly affected by the media used in the hydrogen-evolving reactions. Here, the ratio of co-solvent is adopted based on optimizing experiments previously described for similar multicomponent systems.<sup>10</sup> The reaction turnover numbers [TONs = n(H)/n(PS)] with respect to the photosensitizer were calculated according to one-electron transfer processes.

An initial series of experiments was conducted for the comparison of the activities of the four complexes in the photocatalytic production of hydrogen upon irradiating deaerated solutions containing different complexes 1–4 acting as a PS,  $[Co(2,2'-bipyridine)_3]Cl_2 (0.33 \text{ mM}) \text{ or } [Rh(dtb-bpy)_3](PF_6)_3 (dtb-bpy = 4,4'-di-tert-butyl-2,2'-bipyridine) (0.33 mM) as a WRC,<sup>8-10</sup> and TEOA (0.19 M) as a source of electrons under irradiation with a Xe-arc lamp (300 W). The conditions were identical to those used for hydrogen production according to the preceding results,<sup>10</sup> which were optimized for the catalytic performance. The pH value of the initial solution is adjusted to the desired value by the addition of hydrochloric acid prior to addition of the PS and WRC, and the pH was selected based on the optimization of the catalytic reaction to achieve the optimal performance of hydrogen production. Figure 2 displays a plot of the amount of hydrogen produced in the photolysis at a specific pH in a typical run, as quantitatively measured by gas chromatography, versus the irradiation time under UV and visible light irradiation, and the results are summarized in Table 2. No hydrogen production could be detected outside of experimental error in the control experiments in the absence of any of the$ 

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sensitizer, TEOA, or WRC in the system, demonstrating that all of the components make an essential contribution in the reaction for the production of hydrogen. Moreover, the reaction did not proceed at all when the reaction was conducted under identical reaction conditions but lacking light, suggesting that light is a necessary component to provide the electrochemical driving force for electron transfer to achieve a fuel-producing catalysis. The experimental results suggest that the systems containing the gold(III) complexes are capable of promoting the light-driven hydrogen production in the presence of an electron donor.



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**Figure 2.** Photo-induced hydrogen evolution of 1–4 (40  $\mu$ M) with (A) 0.33 mM [Co(bpy)<sub>3</sub>]Cl<sub>2</sub> (at pH 8.0) or (B) 0.33 mM [Rh(dtb-bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>3</sub> (at pH 7.0) and 0.19 M TEOA in acetone/water (4:1 v/v, 100 mL) upon irradiation (Xe arc lamp; 300 W).

In Figure 2A, for the cobalt catalyst employed (pH = 8.0), the hydrogen produced with no induction period was observed to follow the order 3 > 4 > 1 > 2. Upon maintaining these conditions for 24 h, the system with complex 3 produced up to 1716.9  $\mu$ mol of H<sub>2</sub> (TON = 858.5, ±10%), which is approximately 3.3 times as much as that produced with complex 2 (515.7  $\mu$ mol of H<sub>2</sub>). When the photoproduction of H<sub>2</sub> was accomplished in the presence of  $[Rh(dtb-bpy)_3](PF_6)_3$  (pH = 8.0), which replaced  $[Co(bpy)_3]Cl_2$  (bpy = 2,2'-bipyridine) as a WRC, the hydrogen production occurs after a measurable induction time. During the initial 4 h of irradiation (except for complex 4, with 6 h), no reaction proceeded to yield H<sub>2</sub>, but the H<sub>2</sub> produced increased with the continued irradiation time. This is indicative of the formation of an active species from the reaction during the induction time, as confirmed by the formation of the black solid after the photolysis. The observed long induction time prior to hydrogen generation in the Rh-catalyzed system is a feature about the formation of active colloidal species in the reaction.<sup>26</sup> The quenching behavior of these complexes will be further discussed in the sections below. A similar induction time was previously observed in studies of the Rh catalyst for water reduction,<sup>27</sup> with the reduction of the initial Rh(III) species to the catalytically reactive state, probably formally a colloidal Rh, which is a key species for hydrogen evolution. Similarly, under these conditions, complex 3 led to the production of more  $H_2$  (TON = 745.5) after 72 h of illumination than

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did the other complexes (Figure 2B). These results indicate that there is no clear correlation between the photophysical properties and the catalytic activity. For example, although complex **3** is by far the most effective compared to the other complexes, it has no remarkable photophysical properties, except for the excited-state lifetime compared to its analogues. The difference among the activities of these complexes is difficult to rationalize because the hydrogen evolution activity depends in a complex way on the sensitizer, the catalyst and the electron donor but also the interaction between them. It is clear that the further exploration of the utility of such complexes for photoinduced electron transfer chemistry would be helpful in understanding the underlying structure and function relationship.

Run	PS (Concn (µM))	Catalyst	pH	Time (h)	TON <sup>[a]</sup>
1	1 (40 µM)	Co(bpy) <sub>3</sub> Cl <sub>2</sub>	8.0	24	394.2
2	<b>2</b> (40 μM)	Co(bpy) <sub>3</sub> Cl <sub>2</sub>	8.0	24	257.9
3	<b>3</b> (40 µM)	Co(bpy) <sub>3</sub> Cl <sub>2</sub>	8.0	24	858.5
4	<b>4</b> (40 μM)	Co(bpy) <sub>3</sub> Cl <sub>2</sub>	8.0	24	633.1
5	<b>3</b> (5 μM)	Co(bpy) <sub>3</sub> Cl <sub>2</sub>	8.0	24	1276.2
6	<b>3</b> (10 μM)	Co(bpy) <sub>3</sub> Cl <sub>2</sub>	8.0	24	1441.5
7	<b>3</b> (20 μM)	Co(bpy) <sub>3</sub> Cl <sub>2</sub>	8.0	24	1250.2
8	1 (40 µM)	Rh(dtb-bpy) <sub>3</sub> (PF <sub>6</sub> ) <sub>3</sub>	7.0	72	610.3
9	<b>2</b> (40 μM)	Rh(dtb-bpy) <sub>3</sub> (PF <sub>6</sub> ) <sub>3</sub>	7.0	72	557.5
10	<b>3</b> (40 µM)	Rh(dtb-bpy) <sub>3</sub> (PF <sub>6</sub> ) <sub>3</sub>	7.0	72	745.5
11	<b>4</b> (40 μM)	Rh(dtb-bpy) <sub>3</sub> (PF <sub>6</sub> ) <sub>3</sub>	7.0	72	295.2
12	<b>3</b> (5 μM)	Rh(dtb-bpy)3(PF6)3	7.0	72	1246.3
13	<b>3</b> (10 μM)	Rh(dtb-bpy) <sub>3</sub> (PF <sub>6</sub> ) <sub>3</sub>	7.0	72	1057.7
14	<b>3</b> (20 μM)	Rh(dtb-bpy)3(PF6)3	7.0	72	923.4
15 <sup>[b]</sup>	<b>3</b> (20 μM)	Co(bpy) <sub>3</sub> Cl <sub>2</sub> (0.08 mM)	8.0	24	216.9
16 <sup>[b]</sup>	<b>3</b> (20 μM)	Co(bpy) <sub>3</sub> Cl <sub>2</sub> (0.17 mM)	8.0	24	443.7
17 <sup>[b]</sup>	<b>3</b> (20 µM)	Co(bpy) <sub>3</sub> Cl <sub>2</sub> (0.33 mM)	8.0	24	530.5
18	<b>3</b> (40 µM)	K <sub>2</sub> PtCl <sub>4</sub>	7.0	72	127.4

The activity of the hydrogen-evolving systems is determined by each electron transfer step which depends on the redox potentials of the involved species in the reaction mixture. Based on the estimated excited-state redox data, the excited state of gold(III) is likely to undergo an electron transfer of both

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oxidative quenching by the catalyst with electron transfer from the photoexcited sensitizer to the catalyst  $[Co(bpy)_3]^{2+} [E(Co(bpy)_3^{2+}/Co(bpy)_3^{+} = -0.95 \text{ V vs. NHE}]^{28}$  or  $Rh(dtb-bpy)_3^{3+} [E(Rh(dtb-by)_3^{+} = -0.95 \text{ V vs. NHE}]^{28}$  $bpy_{3}^{3+}/Rh(dtb-bpy)_{3}^{2+} = -0.67 V vs. NHE^{29}$  and reductive quenching by TEOA [E(TEOA<sup>+</sup>/TEOA) = +0.82 V vs. NHE].<sup>30</sup> In such multicomponent systems with catalyst as  $[Co(bpy)_3]^{2+}$  or Rh(dtb-bpy)<sub>3</sub><sup>3+</sup>, because quenching processes are certainly thermodynamically favorable, the reductive and oxidative quenching can take place at the same time. Experimentally, reductive quenching by TEOA is observed for complexes 1–3, but not for complex 4, which suggests that the much shorter-lived singlet state of the complex is not the species involved in the photoreduction event. Unlike TEOA, quenching by  $[Co(bpy)_3]^{2+}$  or Rh(dtb-bpy)\_3^{3+} is observed at relatively low concentrations for all cases, as shown in Figures. S7 and S8. All the quenching followed a linear Stern-Volmer relationship between the luminescence intensity of the complex and the quencher concentration (Figures S6-8), and the quenching constant  $(k_0)$  are presented in Table 3. Complex 3 has a smaller driving force for the respective reaction and also has a relatively long lifetime than the other gold cyclometalated species (Table 1), which make it low sensitivity to quenching by TEOA and other quenchers. The rate constant for complexes 1, 2 and 4 by  $[Co(bpy)_3]^{2+}$  or  $Rh(dtb-bpy)_3^{3+}$  is near the diffusion-limited rate (in the range of  $10^9 - 10^{10} \text{ M}^{-1} \text{s}^{-1}$ ), suggesting the presence of both static and dynamic quenching, which can be attributed to electron transfer from the excited sensitizer to the Co or Rh species.<sup>31</sup>

Table 3. Quenching Kinetics of studied gold complexes. <sup>[a]</sup>						
PS	$k_{\rm q} {\rm Co(bpy)_3}^{2+} ({\rm M}^{-1}{\rm s}^{-1})$	$k_{\rm q}  {\rm Rh} ({\rm dtb}{-}{\rm bpy})^{3+}  ({\rm M}^{-1}{\rm s}^{-1})$	$k_q$ TEOA (M <sup>-1</sup> s <sup>-1</sup> )			
1	5.94×10 <sup>10</sup>	1.81×10 <sup>9</sup>	$1.87 \times 10^{8}$			
2	6.73×10 <sup>10</sup>	1.59×10 <sup>9</sup>	1.57×10 <sup>8</sup>			
3	3.71×10 <sup>9</sup>	3.37×10 <sup>7</sup>	2.11×10 <sup>7</sup>			
4	6.37×10 <sup>10</sup>	2.24×10 <sup>10</sup>	No quenching			
[a] Measured in CH <sub>3</sub> CN at room temperature.						

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These results, combined with the fact that all complexes facilitated the hydrogen-evolution process to some degree, suggest that quenching ability is not directly correlated with catalytic reactivity. The observation showed that the presence of the  $[Co(bpy)_3]^{2+}$  or  $Rh(dtb-bpy)_3^{3+}$  in the systems of **1–3** provided an anther quenching pathway that was the oxidative electron transfer from the sensitizer to the catalyst and was fast as the reductive quenching by TEOA. To obtain the information of the excited state reaction of the cyclometalated gold complex with Co or Rh catalyst in the presence of TEOA, the lifetime of **3** in CH<sub>3</sub>CN were measured under the addition of  $[Co(bpy)_3]^{2+}$  or  $Rh(dtb-bpy)_3^{3+}$  (Figure S9). With TEOA, in the absence of the catalyst the decay time of the luminescence is almost half of that

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in the pure CH<sub>3</sub>CN solution, indicating that the quenching behavior by TEOA through electron transfer. If the  $[Co(bpy)_3]^{2+}$  or Rh(dtb-bpy)<sub>3</sub><sup>3+</sup> was added, the decay time of the luminescence reduces further, respectively. The observation showed that the presence of the  $[Co(bpy)_3]^{2+}$  or Rh(dtb-bpy)<sub>3</sub><sup>3+</sup> provided an anther quenching pathway that was the oxidative electron transfer from the sensitizer to the catalyst and was slow as the reductive quenching. In the photocatalysis, both pathway should occur in the same time and contribute to the quenching process. In the photocatalysis, it could be considered that hydrogen evolution may also occur by both pathway. However, these processes may be kinetically competitive with the hydrogen generation reaction under the existing working conditions, where the amount of TEOA is far more than that of the catalyst. Therefore, the pathway for electron transfer accounting for the production reaction of hydrogen was assumed to proceed via reductive quenching dominating over oxidative quenching. For the system containing complex **4**, the results unambiguously demonstrate that the hydrogen production appears to involve an oxidative quenching event.

Considering the aforementioned photocatalytic results, a possible photocatalytic pathway is briefly documented below based on well-established studies.<sup>32</sup> Hydrogen generation starts with the quenching of the excited-state of gold(III) of **1–3**, which is long-lived enough for electron transfer between the light harvesting and the electron donor. In the presence of an electron donor, the excited state of PS, that is  $[Au]^{3+}$  (most likely in the triplet excited state), is reductively quenched, providing a reduced sensitizer, that is  $[Au]^{2+}$ , which has a sufficiently strong reduction potential to effectively deliver an electron to the catalyst unit, where dihydrogen can be produced. With complex **4**, an oxidative quenching pathway results in hydrogen production.

However, if the reaction was carried out with  $[Co(bpy)_3]Cl_2$  or  $[Rh(dtb-bpy)_3](PF_6)_3$  under irradiation with a Xe-arc lamp (300 W), the sensitizer was unstable. Complex **3** was used for all of the subsequent light-driven hydrogen production experiments. After photoreduction reaction, the decomposition products were extracted from the mixture solution and characterized. From the ESI-MS analysis (Figure S10) for illuminated samples of the reaction mixture with **3**, no peak of complex **3** (m/z = 662.33) was observed, and the peak of RC^N^CR (R = *tert*-butyl) was found at m/z = 343.33. The results indicated that the neutral gold complex is still unstable under constant illumination. This is in part because a reductive quenching pathway drives the photochemical reaction.<sup>33</sup> In addition, when using  $[Co(bpy)_3]Cl_2$ , no solid particle was observed in the solution after the photocatalytic reaction. There was no evidence of the formation of metallic Co nanoparticles during photocatalysis for hydrogen production. The X-ray photoelectron spectroscopy (XPS) measurements were used to get information on metal oxidation state before and after the photocatalytic reaction. In Co 2p spectra, no peak appeared for the 2p transition in the sample obtained from the reaction mixture compared with that of CoCl<sub>2</sub> or  $[Co(bpy)_3]Cl_2$  (Figure S11, left),<sup>34</sup> suggesting that the occurrence of the decomposition of the catalyst

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under the photocatalytic conditions. In the case of  $[Rh(dtb-bpy)_3](PF_6)_3$ , a dark solid particle was observed after photolysis. From the XPS measurements of this particle (Figure S11, right), much broader and relative lower intensities were observed compared to the original compound. The catalytic reaction seemed to not be homogeneous, as confirmed by the quantitative poisoning experiments with carbon disulfide (CS<sub>2</sub>), which is a strong catalyst poison for rhodium(0).<sup>27b</sup> With the addition of 1 equivalents of CS<sub>2</sub>, the activity of the catalysis system was suppressed. The observation that the catalytic system is deactivated in the presence of CS<sub>2</sub> supported that the colloidal species participate in the catalysis.<sup>35</sup>



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**Figure 3.** (A) Influence of pH on photoinduced hydrogen evolution upon irradiation (300 W Xe-arc lamp) using **3** (40  $\mu$ M). (B) The apparent quantum yield (AQY) of hydrogen production of **3** *versus* the wavelength of the incident light (upon irradiation of 2 h, selected wavelengths: 350, 380, 400, 420, and 450 nm). Conditions: Co(bpy)<sub>3</sub><sup>2+</sup> (0.33 mM) and TEOA (0.19 M) in acetone-water solution (4:1, v/v, 100 mL, pH = 8.0)

In the light-induced catalytic experiments, the pH value has a strong effect on the activity of the catalytic system.<sup>36</sup> A series of photocatalytic experiments based on the system containing complex **3** by changing the pH of the solution was conducted to investigate the effect of the pH while keeping the component concentrations of 40  $\mu$ M **3**, 0.33 mM [Co(bpy)<sub>3</sub>]<sup>2+</sup> and 0.19 M TEOA. The reaction has been found to be sensitive to the pH; a clear optimum is observed at a pH value of 8.0, with an activity ~4-fold higher than that observed at pH 5.0, as shown in Figure 3A. This agrees with previous observations by others using [Co(bpy)<sub>3</sub>]<sup>2+</sup> as a catalyst in hydrogen generation systems.<sup>37</sup> At lower pH values, the activity of the H<sub>2</sub> production was decreased. This reduction in activity can be rationalized by the decrease in the pH value, which may cause the protonation of TEOA to a considerable extent. At a higher pH of 9.0, a reduced hydrogen production was also observed. The loss of activity can be attributed to that the solution in this case does not favor the formation of the cobalt hydride species or proton reduction to hydrogen at the metal center of a molecule catalyst. The effects of pH are complex, and the observed pH optimum for the photocatalytic hydrogen production sither result of the balance of these competing effects. The optimal hydrogen-production activity corresponds with the pH range at

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which the system shows its highest electron transfer ability, as confirmed by the quenching experiments of complex **3** in the presence of TEOA at different values of pH (Figure S12). Further wavelength-dependent experiments were carried out for the optimized system with complex **3** using bandpass filters at 350, 380, 400, 420, and 450 nm under otherwise identical reaction conditions (Figure 3B). The apparent quantum efficiency (AQY) of the hydrogen production was calculated to evaluate the photon-to-H<sub>2</sub> efficiency. The AQY increased with increasing wavelength to a maximum at 400 nm, which achieved a maximum AQY of 13.7%. After that, it decreased because of a decrease in the absorbance of **3** (Figure S13), and finally reached zero at the given wavelength of 450 nm.

When a 420-nm cut-off filter was used in the same xenon lamp to remove the UV irradiation, complex 3 was still active, indicating that visible light is sufficient to promote hydrogen production. However, the amount of evolved hydrogen upon visible-light irradiation decreased to 43% (530.5 µmol, TON = 530.5) after irradiation for 24 h under otherwise identical conditions [3 (20  $\mu$ M), Co(bpv)<sub>3</sub><sup>2+</sup> (0.33 mM) and TEOA (0.19 M)]. Under this condition, the decomposition of 3 is much slower, and the system durability increases, with a system lifetime of over 96 h to when the system produces minimal further H<sub>2</sub>, with a total amount of hydrogen evolved of 933.0 µmol. At the last stage of irradiation, the  $H_2$  production rate decreases dramatically, with the turnover frequency (TOF) (3.7 h<sup>-1</sup>) significantly lower than that at 24 h (22.1 h<sup>-1</sup>). The enhanced durability of the system under visible light irradiation is mainly associated with the weak absorption ability at those wavelengths. Such catalysis would proceed slowly and the process of decomposition would slow down as well. In a separate experiment, the stability of 3 during photolysis was tested. At the end of a given hydrogen-producing cycle, as shown in Figure 4, after the readdition of an extra equiv of catalyst, approximately 502.0  $\mu$ mol H<sub>2</sub> was obtained after an additional 30 h of irradiation, suggesting that the activity was almost recovered. The results imply that the catalyst deactivation was the main reason for the cessation of hydrogen evolution under illumination.



**Figure 4.** H<sub>2</sub> production as a function of time showing the stability of the system with the re-addition of catalyst after 96 h of irradiation ( $\lambda > 420$  nm). Conditions: **3** (20 µM), Co(bpy)<sub>3</sub><sup>2+</sup> (0.33 mM) and TEOA

#### (0.19 M) in acetone-water solution (4:1, v/v, 100 mL, pH = 8.0)

We also examined the concentration effect of the catalyst on the light-induced hydrogen production, while the concentrations of TEOA (0.19 M) and sensitizer (20  $\mu$ M) were kept constant in the mixed solvent solution of acetone/water (4:1 v/v, pH = 8.0) (Table 2). The amount of hydrogen production increased with the concentration of the catalyst in the range of 0.08 to 0.33 mM (Figure S14), but the initial rates of H<sub>2</sub> generation are similar for the three catalyst concentrations; an analogous phenomenon was also observed for other Co-based catalytic systems.<sup>38</sup> The H<sub>2</sub> production efficiency of the system reached its highest value, 530.5  $\mu$ mol of H<sub>2</sub> after 24 h of irradiation in the presence of 0.33 mM (Co(bpy)<sub>3</sub><sup>2+</sup>, after which the system did not produce more hydrogen as the concentration of catalyst increased further to 0.5 mM.

#### Conclusions

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In this work, a class of bis-cyclometalated gold(III) acetylide complexes containing a tridentate 2,6diphenylpyridine-based C^N^C-type ligand have been successfully utilized as sensitizers for application in photocatalytic hydrogen production in the presence of a molecular cobalt or rhodium complex as the proton reduction catalyst and TEOA as an electron donor in an acetone/water solvent mixture. These three-component systems displayed a long lifetime of greater than 96 h under the operating conditions, and a turnover number of H<sub>2</sub> production as high as 1441.5 was achieved, 4-fold higher than those reported previously for water reduction using gold complexes. The highest single-wavelength quantum yield of 13.7% for water reduction was obtained at 400 nm and compares well to the values for lightinduced H<sub>2</sub> production by other metal complexes. The photocatalytic hydrogen production process may occur through the quenching of the excited states of the neutral Au(III) complexes via both an oxidative quenching by the catalyst and a reductive quenching by TEOA, based on UV/vis and electrochemistry data, but the latter likely plays a more significant role in the photocatalysis because the amount of the catalyst is far less than that of the TEOA. On the basis of the present results, future research will focus on deepening our understanding of the structure/function relationship, as well as the further exploration of architecture-unique gold(III) complexes through modification of the ligand framework for the construction of even more efficient light-harvesting materials for use in direct solar fuel production.

#### **EXPERIMENTAL SECTION**

**Syntheses.** All of the gold complexes (1–4) were prepared via the similar procedure and were described in the Supporting Information.

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**Theoretical Calculations.** All calculations were performed using the Gaussian 09 program based on the density functional theory (DFT) method and time-dependent DFT (TD-DFT) calculations. The numerical calculations in this paper were performed on the IBM Blade cluster system at the High Performance Computing Center (HPCC) of Nanjing University.

**H<sub>2</sub> Evolution Experiments.** All H<sub>2</sub> production experiments were evaluated in a conventional closed circulating system with a side visible light irradiation using a 300 W xenon lamp (CERMAX LX–300; ILC Technology) equipped without or with a cut-off filter (radiation wavelength > 420 nm, 300 mW/cm<sup>2</sup>).<sup>1c</sup> A typical sample for the photocatalytic reaction studied herein contained 5  $\mu$ M photosensitizer, 0.33 mM catalyst and 0.19 M TEOA solution in 100 mL of acetone-water (4:1, v/v). The pH value of the mixed solution was adjusted with concentrated hydrochloric acid as required. Prior to the light irradiation, the solution should be protected from light by an Al foil, and the system was evacuated successively before being backfilled with 100% argon. Subsequently, the solution was irradiated with magnetic stirring. At this point, the hydrogen evolved from the reactions was monitored and quantified at each analysis time on an online gas chromatograph equipped with a thermally conductive detector (Shimadzu GC-8A, argon as a carrier gas and MS-5A column). The variation in hydrogen production was less than 10% upon repeated experiments.

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**Supporting Information.** Synthetic procedures, additional data and details including CVs, photocatalytic experiments and DFT calculations for all complexes in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

#### REFERENCES

(1) (a) S. Styring, *Faraday Discuss.*, 2012, **155**, 357–376; (b) Y. Tchibana, L. Vaysierres and J. R. Durrant, *Nat. Photonics*, 2012, **6**, 511–518; (c) A. Kudo and Y. Miseki, *Chem. Soc. Rev.*, 2009, **38**, 253–278; (d) V. Artero, M. Chavarot-Kerlidou and M. Fontecave, *Angew. Chem. Int. Ed.*, 2011, **50**, 7238–7266.

(2) (a) M. Wang and L. Sun, *ChemSusChem*, 2010, **3**, 551–554; (b) N. Armaroli and V. Balzani, *Angew. Chem. Int. Ed.*, 2007, **46**, 52–66.

(3) T. C. B. Harlang, Y. Liu, O. Gordivska, L. A. Fredin, C. S. Ponseca Jr, P. Huang, P. Chábera, K.

S. Kjaer, H. Mateos, J. Uhlig, R. Lomoth, R. Wallenberg, S. Styring, P. Persson, V. Sundström and K. Wärnmark, *Nat. Chem.*, 2015, 7, 883–889.

(4) (a) W. T. Eckenhoff and R. Eisenberg, *Dalton Trans.*, 2012, 41, 13004–13021; (b) S. P. Luo, E. Mejía, A. Friedrich, A. Pazidis, H. Junge, A. E. Surkus, R. Jackstell, S. Denurra, S. Gladiali, S. Lochbrunner and M. Beller, *Angew. Chem. Int. Ed.*, 2013, 52, 419–423; (c) R. S. Khnayzer, C. E. McCusker, B. S. Olaiya and F. N. Castellano, *J. Am. Chem. Soc.*, 2013, 135, 14068–14070; (d) S. Jasimuddin, T. Yamada, K. Fukuju, J. Otsuki and K. Sakai, *Chem. Commun.*, 2010, 46, 8466–8468.

(5) (a) S. Fukuzumi, T. Kobayashi and T. Suenobu, *Angew. Chem. Int. Ed.*, 2011, **50**, 728–731; (b) T. Stoll, M. Gennari, I. Serrano, J. Fortage, J. Chauvin, F. Odobel, M. Rebarz, O. Poizat, M. Sliwa, A. Deronzier and M.-N. Collomb, *Chem. Eur. J.*, 2013, **19**, 782–792.

(6) (a) J. I. Goldsmith, W. R. Hudson, M. S. Lowry, T. H. Anderson and S. Bernhard, *J. Am. Chem. Soc.* 2005, **127**, 7502–7510; (b) F. Gärtner, D. Cozzula, S. Losse, A. Boddien, G. Anilkumar, H. Junge, T. Schulz, N. Marquet, A. Spannenberg, S. Gladiali and M. Beller, *Chem. Eur. J.*, 2011, **17**, 6998–7006; (c) P. Zhang, M. Wang, Y. Na, X. Li, Y. Jiang and L. Sun, *Dalton Trans.*, 2010, **39**, 1204–1206; (d) S. Hansen, M. M. Pohl, M. Klahn, A. Spannenberg and T. Beweries, *ChemSusChem*, 2013, **6**, 92–101.

(7) D. R. Whang, K. Sakai and S. Y. Park, Angew. Chem. Int. Ed., 2013, 52, 11612–11615.

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(8) L. J. Tinker, N. D. McDaniel, P. N. Curtin, C. K. Smith, M. J. Ireland and S. Bernhard, *Chem. Eur. J.*, 2007, **13**, 8726–8732.

(9) (a) S. Metz and S. Bernhard, *Chem. Commun.*, 2010, **46**, 7551–7553; (b) B. F. DiSalle and S. Bernhard, *J. Am. Chem. Soc.*, 2011, **133**, 11819–11821.

(10) (a) Z. T. Yu, Y. J. Yuan, J. G. Cai and Z. G. Zou, *Chem. Eur. J.*, 2013, **19**, 1303–1310; (b) Y. J.
Yuan, Z. T. Yu, H. L. Gao, Z. G. Zou, C. Zheng and W. Huang, *Chem. Eur. J.*, 2013, **19**, 6340–6349; (c)
Y. J. Yuan, Z. T. Yu, J. G. Cai, C. Zheng, W. Huang and Z. G. Zou, *ChemSusChem*, 2013, **6**, 1357–1365.

(11) (a) C.-W. Chan, W.-T. Wong and C.-M. Che, *Inorg. Chem.*, 1994, 33, 1266–1272; (b) X. Zhu,
L.-L. Hung, N. Zhu, V. W.-W. Yam and H.-S. Kwok, *Chem. Commun.*, 2005, 2906–2908; (c) V. W.-W.
Yam, K. M.-C. Wong, L.-L. Hung and N. Zhu, *Angew. Chem. Int. Ed.*, 2005, 44, 3107–3110.

(12) (a) W.-P. To, K. T. Chan, G. S. M. Tong, C. Ma, W. M. Kwok, X. Guan, K.-H. Low and C.-M. Che, *Angew. Chem. Int. Ed.*, 2013, **52**, 6648–6652; (b) C.-Y. Sun, W.-P. To, X.-L. Wang, K.-T. Chan, Z.-M. Su and C.-M. Che, *Chem. Sci.*, 2015, **6**, 7105–7111.

(13) J. Fernandez-Cestau, B. Bertrand, M. Blaya, G. A. Jones, T. J. Penfold and M. Bochmann, *Chem. Commun.*, 2005, **51**, 16629–16632.

(14) (a) V. K.-M. Au, K. M.-C. Wong, D. P.-K. Tsang, M. Y. Chan, N. Zhu and V. W.-W. Yam, J.

*Am. Chem. Soc.*, 2010, **132**, 14273–14278; (b) K. M.-C. Wong, V. K.-M. Au, D. Wu and V. W.-W. Yam, *J. Am. Chem. Soc.*, 2015, **137**, 4654–4657.

(15) W.-P. To, G. S.-M. Tong, W. Liu, C. Ma, J. Liu, A. L.-F. Chow and C.-M. Che, *Angew. Chem. Int. Ed.*, 2012, **51**, 2654–2657.

(16) (a) K. M.-C. Wong, L.-L. Hung, W. H. Lam, N. Zhu and V. W.-W. Yam, *J. Am. Chem. Soc.*, 2007, 129, 4350–4365; (b) V. K.-M. Au, D. P.-K. Tsang, K. M.-C. Wong, M.-Y. Chan, N. Zhu and V. W.-W. Yam, *Inorg. Chem.*, 2013, 52, 12713–12725.

(17) A. Szentkuti, J. A. Garg, O. Blacque and K. Venkatesan, *Inorg. Chem.*, 2015, 54, 10748–10760.
(18) W. Lu, B. X. Mi, M. C. W. Chan, Z. Hui, C. M. Che, N. Zhu and S. T. Lee, *J. Am. Chem. Soc.*, 2004, 126, 4958–4971.

(19) M. P. Eng, T. Ljungdahl, J. Andréasson, J. Mårtensson and B. Albinsson, *J. Phys. Chem. A*, 2005, **109**, 1776–1784.

(20) E. C. Glazer, D. Magde and Y. Tor, J. Am. Chem. Soc., 2007, 129, 8544-8551.

(21) K. Kalyanasundaram, Coord. Chem. Rev., 1982, 46, 159–244.

(22) E. Y.-H. Hong, C. T. Poon and V. W.-W. Yam, J. Am. Chem. Soc., 2016, 138, 6368-6371.

(23) (a) E. S.-H. Lam, W. H. Lam and V. W.-W. Yam, Inorg. Chem., 2015, 54, 3624–3630; (b) G. S.

M. Tong, K. T. Chan, X. Chang and C.-M. Che, Chem. Sci., 2015, 6, 3026–3037.

(24) E. S. Andreiadis, M. Chavarot-Kerlidou, M. Fontecave and V. Artero, *Photochem. Photobiol.*, 2011, **87**, 946–964.

(25) J. G. Cai, Z. T. Yu, Y. J. Yuan, F. Li and Z. G. Zou. ACS Catal., 2014, 4, 1953–1963.

(26) L. E. Roy, G. Scalmani, R. Kobayashi and E. R. Batista, Dalton Trans., 2009, 6719-6721.

(27) (a) J. Xie, Q. Zhou, W. Wang, Y. Hou, B. Zhang and X. Wang, Inorg. Chem., 2012, 51, 6376-

6384; (b) E. D. Cline, S. E. Adamson and S. Bernhard, Inorg. Chem., 2008, 47, 10378-10388.

(28) H. A. Schwarz, C. Creutz and N. Sutin, Inorg. Chem., 1985, 24, 433-439.

(29) C. Creutz, A. D. Keller, N. Sutin and A. P. Zipp, J. Am. Chem. Soc., 1982, 104, 3618–3627.

(30) H. Sun and M. Z. Hoffman, J. Phys. Chem., 1994, 98, 11719-11726.

(31) (a) A. M. Kluwer, R. Kapre, F. Hartl, M. Lutz, A. L. Spek, A. M. Brouwer, P. W. N. M. van Leeuwen and J. N. H. Reek, *Proc. Natl. Acad. Sci. USA*, 2009, **106**, 10460–10465; (b) C. F. Wise, D. Liu, K. J. Mayer, R. M. Crossland, C. L. Hartley and W. R. McNamara, *Dalton Trans.*, 2015, **44**, 14265–14271.

(32) S. Fukuzumi, Y. Yamada, T. Suenobu, K. Ohkubo and H. Kotani, *Energy Environ. Sci.*, 2011, 4, 2754–2766.

(33) Z. Han, W. R. McNamara, M. S. Eum, P. L. Holland and R. Eisenberg, *Angew. Chem. Int. Ed.*, 2012, **51**, 1667–1670.

(34) H. Chen, Z. Sun, S. Ye, D. Lu and P. Du, J. Mater. Chem. A, 2005, **3**, 15729–15737.

(35) P. Lei, M. Hedlund, R. Lomoth, H. Rensmo, O. Johansson and L. Hammarström, J. Am. Chem. Soc., 2008, 130, 26–27.

(36) (a) P. Du, J. Schneider, P. Jarosz and R. Eisenberg, J. Am. Chem. Soc., 2006, 128, 7726-7727; (b)

C. F. Leung, S. M. Ng, C. C. Ko, W. L. Man, J. Wu, L. Chen and T. C. Lau, *Energy Environ. Sci.*, 2012, **5**, 7903–7907.

(37) (a) S. C. Marinescu, J. R. Winkler and H. B. Gray, *Proc. Natl. Acad. Sci. USA*, 2012, **109**, 15127–15131; (b) T. Lazarides, T. McCormick, P. Du, G. Luo, B. Lindley and R. Eisenberg, *J. Am. Chem. Soc.*, 2009, **131**, 9192–9194.

(38) T. M. McCormick, B. D. Calitree, A. Orchard, N. D. Kraut, F. V. Bright, M. R. Detty and R. Eisenberg, *J. Am. Chem. Soc.*, 2010, **132**, 15480–15483.

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Gold(III) acetylide complexes actively catalyzed the light-driven evolution of hydrogen in water when using [Co(2,2'-bipyridine)<sub>3</sub>]Cl<sub>2</sub> or [Rh(4,4'-di-tert-butyl-2,2'-bipyridine)<sub>3</sub>](PF<sub>6</sub>)<sub>3</sub> as a H<sub>2</sub>-evolved catalyst.