Topical Issue on Catalysis

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Photocatalytic Hydrogen Evolution by tris-dithiolene tungsten complexes

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Abstract: Herein, we report on the homogeneous photocatalytic evolution of hydrogen by using as reductive catalysts the prismatic symmetric tris – dithiolene complexes of the tungsten, namely [W(S2C2(Ph)2)]3 (1) and its monoanion [W(S2C2(Ph)2)(TBA)] (2). Complex 2 is fully characterized by elemental analysis, ESI-MS, IR, UV-Vis and fluorescence spectrophotometry as well as cyclic voltammetry. The photocatalytic system consists of [ReBr(CO)3(bpy)] as a photosensitizer, triethanolamine as a sacrificial electron donor and acetic acid as the proton source. Although the activity of the photocatalytic system is rather small (TON=18), it indicates that the homoleptic tris dithiolene complexes can act as proton reductive catalysts with their monoanion form to be more active in accordance with the findings for the bis - dithiolene complexes.

Keywords: homogeneous, photocatalysis, reductive catalysts, tungsten; dithiolenes, rhenium(I), hydrogen

1 Introduction

Conversion of solar energy into chemical energy remains a critical issue as far the development of clean and renewable energy is concerned [1]. The visible light driven splitting of water in its constituent elements remains a continuing challenge for the effective utilization of solar energy. Even though water photocatalysis has been a working area for the last forty years with great results especially in the area of the photosensitizers, a number of issues still remain to be addressed. In particular, there is still a need to develop efficient, stable and cheap catalysts allowing proton reduction to hydrogen at high yields.

Nowadays, light-driven hydrogen production include a series of chromophores [2, 3] and catalysts e.g. cobaloximes [4-19]. Among the chromophores, [Ru(bpy)3]2+ plays an important role, although it is well known that after some hours of irradiation it decomposes [20]. Another interesting group of chromophores are the Re complexes mainly because of their many oxidation states [3, 21]. Especially, Re(I) complexes show significant photophysical and photochemical properties [2, 10, 22-26] and they find applications as anion sensors [27], DNA probes [28-30], photosensitizers in solar cells [31, 32], luminescence probes and molecular parts in supramolecules [33, 34]. Additionally, Re(V) complexes have been examined as catalysts for oxygen transfer reactions and indicate biological activity both in dark and after illumination [35].

Within the last decade, there has been significant and accelerating progress in developing first-row transition metal catalysts carrying 1,2 – dithiolene ligands for proton reduction to hydrogen [36-41]. This is because of their low cost, the flexibility of their standard potentials, and their solubility in many solvents [42, 43]. Furthermore, the
electronic properties and the reactivity of the dithiolene complexes are based on the substituents on the dithiolene ligand [38, 41, 44-46].

Besides the first row – dithiolene complexes [41], tungsten complexes could also act as catalysts for proton reduction in electrocatalysis or photocatalysis especially since they can transfer reversible up to three electrons. It is quite surprising that so little has been done to evaluate the potential of molecular systems based on W, especially since tungsten is a non-precious metal, relatively abundant and therefore much cheaper than platinum. Actually there is only one report in the literature referring that the monoanion of the tris–[1–(4–methoxyphenyl)–2–phenyl–1,2– ethylenedithiolenic–S,S′] tungsten(VI) complex acts as a proton reductive catalyst in the presence of an electron donor namely, the free radical of methyl-viologen, in mixed water – acetone [47]. On the other side, the neutral form of this complex is a good photosensitizer/catalyst for water splitting, although it decomposes, leading to both \( \text{H}_2 \) and \( \text{O}_2 \) evolution in the presence of methylviologen, with an average quantum yield of about 4% in visible [48] without adding any further catalyst.

Furthermore, four other complexes, namely tris-[1-(4-dimethylaminophenyl)-2-phenyl-1,2-ethylenedithiolenic-S,S′] tungsten, tris-[1-(4-methoxyphenyl)-2-phenyl-1,2-ethylenedithiolenic-S,S′] tungsten, tris-[1-(4-methoxyphenyl)-1,2-ethylenedithiolenic-S,S′] tungsten, tris-[1-(phenyl)-1,2-ethylenedithiolenic-S,S′] tungsten, were used as photosensitizers with good quantum yields [49].

To our knowledge, no tris – dithiolene -tungsten complex has been reported as a proton reductive catalyst in a photocatalytic system. In the light of the aforementioned issues, we decided to explore the possibility of the use of the tris dithiolene complexes as catalysts. Thus, we studied a photocatalytic system consisting of \([\text{ReBr(CO)}_3(bpy)]\) as a photosensitizer, triethanolamine as a sacrificial electron donor and \(\text{AcOH}\) as a proton source whereas the tris – dithiolene complexes, namely \(\text{[W(S,C_2(Ph)2)2]}\) (1) and \(\text{[W(S,C_2(Ph)2)3]} (\text{TBA}) (2)\) (structures are shown in Scheme 1) were used as proton reductive catalysts. These complexes were selected because of carrying no electron donating or electron accepting substituent and at the same time they keep their trigonal prismatic structure; a requirement for the \(\text{d}^2\) orbital of the metal to be attacked by the \(\text{H}^+\) [3, 50]. Moreover herein, we present the characterization of complex 2 by ESI · MS, FT · IR cyclic voltammetry and fluorescence, since to our knowledge no detailed description of these properties of 2 are referred before in the literature.

## 2 Experimental

### 2.1 Materials and methods

We performed all the reactions in a pure argon atmosphere. Solvents were purified prior to use by standard procedures [51]. The chemicals \(\text{NaBH}_4\), \(\text{TBABr}\), pentasulfide phosphorus, \(2,2\)-bipyridine (bpy), \([\text{ReBr(CO)}_3]\), were purchased by Aldrich and used as received. The complexes \([1]\) [47] and the \([\text{ReBr(CO)}_3(bpy)]\) \([3, 27, 52, 53]\) were prepared according to literature procedures. Their physical properties are consistent with those reported.

For recording the absorption spectra, we used a Hitachi U-2000 UV Spectrophotometer with built-in computer, at 25±0.2 C. 190-1100 nm wavelength range, 2 nm bandpass, stray light 0.05 or less. This is a stand-alone system with an accuracy of 0.4 nm and reproducibility of 0.2 nm.

We recorded the \(^1\text{H}-\text{NMR}\) spectra on a Varian UNITY Plus spectrometer operating at 300 MHz with chemical shifts reported in ppm. Samples were run in a 5 mm probe with deuterated solvents as internal lock and reference.

We recorded the FT-IR spectra on IRAffinity-1 Shimadzu spectrometer using KBr pellets. The elemental analysis was conducted on a LECO-183 CHNS analyzer. The ESMS spectra were recorded on a Fisons VG Quattro instrument with a VG Biotech Electrospray source, having an hexapole lens. Nitrogen 99.99%, was used as the nebulizing and bath gas at flow rates 20 and 150 dm\(^3\) min\(^{-3}\), respectively. The samples were injected in the flow of solvent of a Varian 9012 solvent delivery system, via a Fisons interface with a Rheodyne 7125 injector. The capillary voltage was optimum at about 3 kV for the negative anions. The focus and skimmer lenses voltages were 40 and 45 V, respectively. HPLC grade acetone and double-distilled water were used as solvent. Special care was taken to make sure that the source and the capillary had not been contaminated with impurities. Blank spectra in the positive and negative mode were obtained prior to the experiments.

### Scheme 1: Structures of the catalysts 1 and 2 presented in this study.
Cyclic voltammetry was carried out with a Biopotentiostat AFCBP1 from Pine Instrument Company and controlled with the AfterMath software. Experiments were performed using a platinum (5 mm diameter) disk and an Ag/AgCl/KCl (sat.) as a working and reference electrode, respectively. We used a thin Pt gauge (8 cm², Sigma-Aldrich) as counter electrode. The working electrode was polished using successively 6, 3, 1 μm alumina paste on a DP-Nap polishing cloth (Struers, Westlake, OH), washed with water, acetone and air-dried. The potential sweep rate varied between 50–400 mV/s. A 3 mM solution of (1), (2) complexes in 0.5 M [TBA]PF₆ in acetone, under N₂, was measured and all potentials are reported versus the ferrocenium/ferrocene (Fc/Fc⁺) couple.

Excited-State Emission Quenching Experiments were carried out with a RF–5301PC (Spectrofluorophotometer) of Shimadzu, with Xe lamp, 100 W. A 0.4 mM solution of [ReBr(CO)₃(bpy)] was prepared in Acetone. One milliliter of this solution was used to prepare a solution of the desired W complex (1), (2), so that [W] equaled 3 mM, the solution was degassed with Ar. Three milliliters of the [ReBr(CO)₃(bpy)] solution was added to a quartz cuvette fitted with a septum and degassed with Ar. The effect of the W complex on the emission of [ReBr(CO)₃(bpy)] was monitored by collecting emission spectra between additions of aliquots of the W complexes/[ReBr(CO)₃(bpy)] solution. We recorded the spectra after exciting the chromophore at 361 nm with scanning from 400 to 800 nm. Both emission and excitation slits were set to 5 nm. We followed the same procedure by adding TEOA instead of tungsten dithiolene complex.

Gas chromatograms were recorded using a Bruker (430–GC) gas chromatograph with nitrogen as the carrier gas and a column: 5 Å molecular sieves. The gas flow was set 10 ml/min. The oven was operated at 80 °C (Injector). The 5 μL gas samples were injected using a Hamilton 3 microliter syringe. The gases were allowed the precipitate to dry after having washed it with warm water and ether. Yield is 39.4%. The monoanion W: C: 60.40, H: 5.77, S: 21.12; found: C: 60.31, H: 5.58, S: 21.19. ¹H-NMR (300 MHz, CDCl₃): δ 7.21–7.36 (m, 30H, aromatic). FT-IR dithiolene ring: ν(C-C)=1449 cm⁻¹, ν(C-S)=1165 cm⁻¹, ν(C-C-S)=870 cm⁻¹, aromatic ring: ν(C=C)=1594 cm⁻¹, 1490 cm⁻¹, δ C-H= 745 cm⁻¹, 693 cm⁻¹.

2.2.2. Synthesis of [W{S₂C₂(Ph)₂}3(TBA)] (1).

We synthesized the complex 2 with a procedure slightly different from the literature one [54]. We dissolved a total of 0.055 mmol of the neutral complex 1 in 35.00 mL dichloromethane and then we degassed the solution with Ar. Then, we added 2.64 mmol of NaBH₄ dissolved in distilled 34.00 mL MeOH to the solution under stirring and the green emerald solution gradually turned into a dark green solution. The solution was stirred for 10 min, and then 1.32 mmol TBABr (tetra-n-butylammonium bromide) dissolved in distilled 10.00 mL MeOH were added. The solution was left stirring and after 10 min a precipitate was observed. We filtered the mixture on a Buchner and allowed the precipitate to dry after having washed it with warm water and ether. Yield is 39.4%. The monoanion complex is paramagnetic, and thus we received no NMR spectra. Anal. calcd for C₆₅H₄₂S₃W: C: 60.40, H: 5.77, N: 1.21, S: 16.68; found: C: 60.31, H: 5.92, N: 1.25, S: 16.51 FT-IR dithiolene ring: ν(C-C)=1450 cm⁻¹, ν(C-S)=1166 cm⁻¹, ν(C-C-S)=871 cm⁻¹, aromatic ring: ν(C=C)=1593 cm⁻¹, 1490 cm⁻¹, δ C-H= 762 cm⁻¹, 745 cm⁻¹, 690 cm⁻¹.
3 Results and discussion

3.1 Synthesis

We synthesized the neutral complex 1 using the benzoin / \( P_4 S_{10} \) method of Schrauzer, as modified by Bui et al. [55], whereas we prepared the monoanion complex 2 (Scheme 1) with a slight modification of the literature procedures [54]. Elemental analysis, ES-MS, IR and NMR data are in accordance with the molecular forms of the synthesized complexes. It is known that the neutral dithiolene complexes give negative ions in the electrospray [55]. Actually both complexes give in the negative mode of the electrospray no tungsten species other than the original ones at \( m/z = 910.0 \). The isotopic distributions of the metal containing species are given as inserts in Fig. 1. Dithiolenes with double negative charge do not appear and samples seem to be very pure. The complexes exhibit IR vibrations typical of similar complexes [47]. We observed the \( \nu(C-C) \) at 1449 cm\(^{-1}\) and the \( \nu(C-S) \) at 1166 cm\(^{-1}\) for the neutral complex. Examination of the spectra of the monoanion complex 2 indicates that upon reduction of the complex 1 these vibrations shifts upfield. In the next section we discussed the complexes’ spectrophotometric and CVs data.

3.2 Electronic absorption and emission spectroscopy

Fig. 2, 3 and Table 1 indicate the electronic absorption spectra of the complex and the corresponding data in various solvents (acetone, \( CH_2Cl_2 \), DMF, THF). All complexes exhibit absorption spectra similar to those reported earlier for similar tungsten tris(dithiolene) complexes [47, 54]. The spectra for the neutral complex 1 exhibit two major bands around 414 and 659 nm with the former to correspond to MLCT transition and the latter to MLLCT transition [47, 54]. This behavior is also observed in the complex 2, with the difference that the bands were shifted downfield at 459 and 681 nm, respectively.

Excitation of the complexes 1 and 2 resulted in different data in acetone at room temperature. Complex 1 showed two weak emission bands with a peak maximum at 508 nm (excitation at 414 nm) and a peak at 473 nm (excitation at 441 nm) corresponding to MLCT and CT respectively (Fig. 4). On the other side, complex 2 showed only one weak emission band at 531 nm (excitation at 457 nm) corresponding to MLCT (Fig. 5).

3.3 Electrochemistry

We performed the cyclic voltammetric study on a platinum electrode, in acetone. For the complex 2, we observed...
two well-defined, reversible reduction waves. The first at $E_{1/2} = -1.05 \text{ V (} i_{p,c}/i_{p,a} = 1, \Delta E_p = 67 \text{ mV)}$, assigned to 0/-1 process and the second at $E_{1/2} = -0.495 \text{ V (} i_{p,c}/i_{p,a} = 1.1, \Delta E_p = 60 \text{ mV)}$ assigned to -1/-2 process [56]. The current $i_p$ is linearly correlated to $v^{1/2}$ for both processes (Fig.6). Also, since the cathodic – anionic peak separations ($\Delta E_p$) were 67 mV and 60 mV for the two processes respectively, and the ration $i_{p,c}/i_{p,a}$ was equal to 1, the redox processes are completely reversible.

### 3.5 Photochemical Studies. Light-Driven Hydrogen Production.

#### 3.5.1 Changing the catalyst in the photocatalytic system

Photochemical reactions were carried out using [ReBr(CO)₃(bpy)] as the photosensitizer, the [W(S₂C₂(PH)₂)₃] (1), [W(S₂C₂(PH)₂)₃](TBA) (2) as the molecular catalysts (Scheme 1), the TEOA as the sacrificial electron donor and acetic acid as a proton source. We compared 1 and 2 to their catalytic activity towards the hydrogen evolution. The data in Fig.7 and Table 2 indicate that the monoanion 2 is a better catalyst than its neutral form. According to the literature, kinetics studies reveal that the dithiolene complexes act as catalysts in their monoanion state for water reduction regardless of the metal ion; [11, 36, 37, 39, 40, 43, 47] besides herein, we prove that also the neutral of the tungsten complex, 1, can react as catalyst, though lower yield is achieved (Table 2).

#### 3.5.2 Efficiency of the photocatalytic system based on its components

In order to evaluate the influence of each component on the performance of the photocatalytic system, we implemented a series of experiments changing the concentration of each one of the compounds in the system.
while keeping all the other parameters constant. For our study, we used the most efficient catalyst from the previous reported, therefore as a catalyst was used the complex 2. We performed a series of blank experiments to see if there was any evolution of hydrogen. No addition of photosensitizer resulted to no hydrogen, whereas in the absence of the catalyst 2 the system achieved 0.3 TON_{cat} (0.1 mL) of H_{2} after 24 h, small quantities compared to the system efficiency (TON_{cat.} = 18.2 and 0.8 mL of H_{2}), which are attributed to the decomposition of TEOA [2, 57].

In order to evaluate the influence of the concentration of the catalyst on the hydrogen evolution activity, an increasing concentration of the catalyst 2 was used, keeping all the other parameters constant, in a solution of (0.5 mM) [ReBr(CO)_{3}(bpy)], 1M TEOA and 0.1M AcOH in acetone (30 mL). The degassed samples were illuminated with light λ > 400 nm. The system with 64 μM of the catalyst 2 gave 18.2 TON_{cat} after 24 h irradiation, while further increase of the concentration of 2 resulted to the decrease of the system’s efficiency (Fig. 8, Table 3). This is attributed to the high molar extinction coefficient of 2 in the spectrum area < 400 nm, which in high concentrations of 2 results to less photons to be absorbed by the photosensitizer. Because of this, the photocatalytic system produces less hydrogen.

Additionally, we studied the efficiency of the system by varying the concentration of the photosensitizer [ReBr(CO)_{3}(bpy)]. The system with 0.25 mM of the [ReBr(CO)_{3}(bpy)] gave 16.2 TON_{cat} (after 5 h irradiation), while further increase of the concentration of [ReBr(CO)_{3}(bpy)] followed by the decrease of the system’s efficiency (Fig. 8). The latter is mainly attributed to the loss of the labile Br under photocatalytic conditions and thus to the limitation of the long-term activity of the process by the [ReBr(CO)_{3}(bpy)].

Increasing the concentration of AcOH we noticed that the system reached at a maximum amount of produced hydrogen (16.2 TON_{cat}) at [AcOH] = 0.1M whereas the system evolved less hydrogen thereafter. It is worth to mention that for [AcOH] > 0.2M we observed no hydrogen but the formation of a white precipitation. The latter can be attributed to the formation of the protonated form of TEOA, HTEOA^{+}, which is insoluble in acetone. This results to the loss of the electron donor and as a result, the photocatalytic cycle ends. Interestingly, catalysis also took place without any acetic acid with the system to evolve 0.35 mL of hydrogen. According to the literature responsible for this process are the remaining protons of water and the decomposition of TEOA [2, 57] (Fig.10).

In order to understand better the system under study, we monitored the photocatalytic system by receiving UV-Vis spectra for 26 h. After illumination of 5 min, the main band of the catalyst 2 at 669 nm shifted to 682 nm and the absorption was reduced. After 30 min a new product has started to form, because two new peaks in the visible region of the spectra (at 617 nm and 530 nm) were appeared and the peak corresponding to the photosensitizer [ReBr(CO)_{3}(bpy)] wasn’t visible in UV range. This can attributed to the quantitative loss of Br according (vide supra) [57]. Apparently, acetic acid accelerates the loss of

![Figure 7: Hydrogen evolution with catalyst 1 (black) or catalyst 2 (red) 64μM/ [ReBr(CO)_{3}(bpy)] 0.25mM/ TEOA 1M/ AcOH 0.1M in acetone, after 0-24h irradiation.](image)

![Figure 8: Hydrogen evolution with 0.25mM [ReBr(CO)_{3}(bpy)] / 0.1M AcOH / 1M TEOA in degassed acetone with different concentrations of the catalyst 2: (16μM, 32μM, 64μM, 96μM), at room temperature.](image)

| PS (0.5mM) | Cat. (6.4 μM) | D (1M) | Solvent | Acid (0.1M) | H_{2} (ml) | TON_{cat.} |
|------------|---------------|--------|---------|-------------|------------|------------|
| [ReBr(CO)_{3}(bpy)] | 1 | TEOA | acetone | AcOH | 0.8 | 18.2 |
| [ReBr(CO)_{3}(bpy)] | 2 | | | | 0.7 | 16.3 |
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Br⁻ from [ReBr(CO)₃(bpy)], possibly via formation of an acetate or a solvate complex. Thus, we assume that the reaction between 2 and the Br results to the production of the new product (Fig. 11) which can also act as a catalyst even in lower rate since hydrogen is evolved at least up to 24 hours (Fig. 12).

Finally, in order to ensure that our system remains homogeneous, we performed two experiments. Two solutions (0.5mM PS, 64 μM catalyst 2, 1M TEOA, 0.1 M AcOH, in degassed acetone) with and without approximately 1 mL of elemental mercury were irradiated. The shapes of the curves [H₂] vs time were identical with and without mercury (Fig. 12). If tungsten nanoparticles

Table 3: Hydrogen evolution with 0.25mM [ReBr(CO)₃bpy] and 0.1M AcOH, 1M TEOA, DMF and argon with different concentrations of Catalyst (2), λ>400 nm (after 0-24 h irradiation) at room temperature.

| [Cat.] | t_irr. (h) | 16μM | 32μM | 64μM | 96μM |
|--------|------------|------|------|------|------|
|        |            | TON₄m | mL H₂ | TON₄m | mL H₂ | TON₄m | mL H₂ | TON₄m | mL H₂ |
| 0      | 0          | 0    | 0    | 0    | 0    | 0     | 0     | 0     | 0     |
| 3      | 6          | 0.06 | 3.1  | 0.067| 10.9| 0.47  | 1.5   | 0.10  |
| 5      | 10         | 0.11 | 4.2  | 0.09 | 16.2| 0.7   | 1.7   | 0.11  |
| 24     | 12.2       | 0.13 | 10.8 | 0.23 | 18.2| 0.8   | 6.2   | 0.40  |

Figure 9: Hydrogen evolution with 64μM 2, 0.1M AcOH, 1M TEOA in degassed acetone with different concentrations of [ReBr(CO)₃bpy]: (0.25mM, 0.5mM, 0.8mM), during irradiation time 0-5h, at room temperature.

Figure 11: UV-Vis of the system (2) (64μM) / PS: [ReBr(CO)₃bpy] (0.5mM) / TEOA (1M) / AcOH (0.1M) in acetone, before (black) and during irradiation.

Figure 10: Hydrogen evolution with 0.5mM [ReBr(CO)₃bpy], 64μM 2, 1M TEOA, in acetone with different concentrations of AcOH (0M, 0.01M, 0.05M, 0.1M, 0.2M, 0.5M), after 2h of irradiation at room temperature.

Figure 12. Hydrogen evolution from the systems [ReBr(CO)₃bpy] 0.5mM/ (2) 64μM / TEOA 1M / AcOH 0.1M (black) / Hg (red) in acetone after 0-24h irradiation, at room temperature.
were formed under the reducing conditions, then the formation of an amalgam would be expected along with severely decreased catalytic activity, something that we did not notice. Given these results, it seems that the system remains homogeneous, and the decomposition products of the catalyst are not responsible for the catalysis.

3.6 Quenching of Excited-State Emission.

It is well known from the literature, that photosystems with [ReL(CO)\textsubscript{3}(NN)]\textsuperscript{0/+} as photosensitizers, cobaloximes as catalysts and TEOA as sacrificial electron donor \cite{56} proceed to water reduction through a reductive quenching pathway \cite{13, 58}. Using the literature values for the excited state lifetime of complex [ReBr(CO)\textsubscript{3}(bpy)] ($\tau_{re} = 51$ ns (25 $^\circ$C)) \cite{13}, we perform a series of quenching excited states experiment for our systems.

Fig. 13 indicates that TEOA quenches $[^{1}\text{Re}](\text{TEOA})$ following Stern–Volmer behavior with $k_{q} = 3.1 \times 10^{10}$ M$^{-1}$ s$^{-1}$, which is near the diffusion control limit. Catalysts 1 and 2 are also found to quench $[^{1}\text{Re}](\text{TEOA})$ following Stern–Volmer behavior with greater rate constants than TEOA's. These values are $k_{q} = 6.4 \times 10^{10}$ M$^{-1}$ s$^{-1}$ and $k_{q} = 1.9 \times 10^{11}$ M$^{-1}$ s$^{-1}$, respectively (Fig.14, 15), higher than the normal value for dynamic quenching in acetone (ca. $10^{10}$ M$^{-1}$ s$^{-1}$) \cite{59}. These values indicate that the catalysts 1 and 2 quench the chromophore through a static quenching mechanism in accordance with our findings from the UV-Vis spectra (\emph{vide supra}) \cite{59}. Additionally, from the $k_{q}$ values it seems that the catalyst 1 is a better quencher than the catalyst 2 in the contrary of their catalytic activity.

**Figure 13:** Emission spectra of [ReBr(CO)\textsubscript{3}bpy] with added [TEOA] in acetone, Inset: $K_{q}$ as calculated from the Stern-Volmer plot and $\tau_{re} = 51$ ns (25°C).

**Figure 14:** Emission spectra of [ReBr(CO)\textsubscript{3}bpy] with added [1] in acetone, Inset: $K_{q}$ as calculated from the Stern-Volmer plot and $\tau_{re} = 51$ ns (25°C).

**Figure 15:** Emission spectra of [ReBr(CO)\textsubscript{3}bpy] with added [2] in acetone, Inset: $K_{q}$ as calculated from the Stern-Volmer plot and $\tau_{re} = 51$ ns (25°C).

**Scheme 2:** Proposed mechanism for photoreduction of H$^{+}$ by light where PS is the photosensitizer [ReBr(CO)\textsubscript{3}bpy], D is the sacrificial electron donor TEOA and HA is acetic acid.
Despite the fact that catalysts 1 and 2 quench the photosensitizer with a rate constant that is 4 order of magnitude larger than that for TEOA, reductive quenching by TEOA is the main route in our system because of the larger concentration of TEOA (1 M) suggesting a mechanism as indicated Scheme 2.

4 Conclusions

In this work, we present a series of photocatalytic experiments using the prismatic symmetric tris-dithiolene tungsten complexes namely [W(S₂C₆(Ph)₃)₂] (1) and [W(S₂C₆(Ph)₃)₃](TBA) (2) as proton reductive catalysts. We also report on the photochemical and electrochemical properties of 2 The chromophore of our photocatalytic system is the complex [ReBr(CO)](bpy)]. We have proved that the most efficient catalyst is 2, which is the monoanion of 1. This reveals the necessity of the sulfur atoms to be electron rich in order their protonation to be effective and to result to hydrogen evolution. Our experiment results indicate that [ReBr(CO)](bpy)] limits the performance of our system because of the dissociation of Br.

Our mechanistic experiments indicate that the reaction follows first order dependence on the concentration of the chromophore. Moreover, the data from the fluorescence experiments reveal the reductive quenching of the [ReBr(CO)](bpy)] by TEOA as the main route of the mechanism as well as the limitation of the use of catalyst 2 because of its high molar extinction coefficient at the same area of the visible spectra where the photosensitizer absorbs.

To improve further this system a more stable photosensitizer and electron donor is required. We are already working towards this goal.

Conflict of interest: The authors declare no conflict of interest.

Ethical approval: The conducted research is not related to either human or animals use.

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