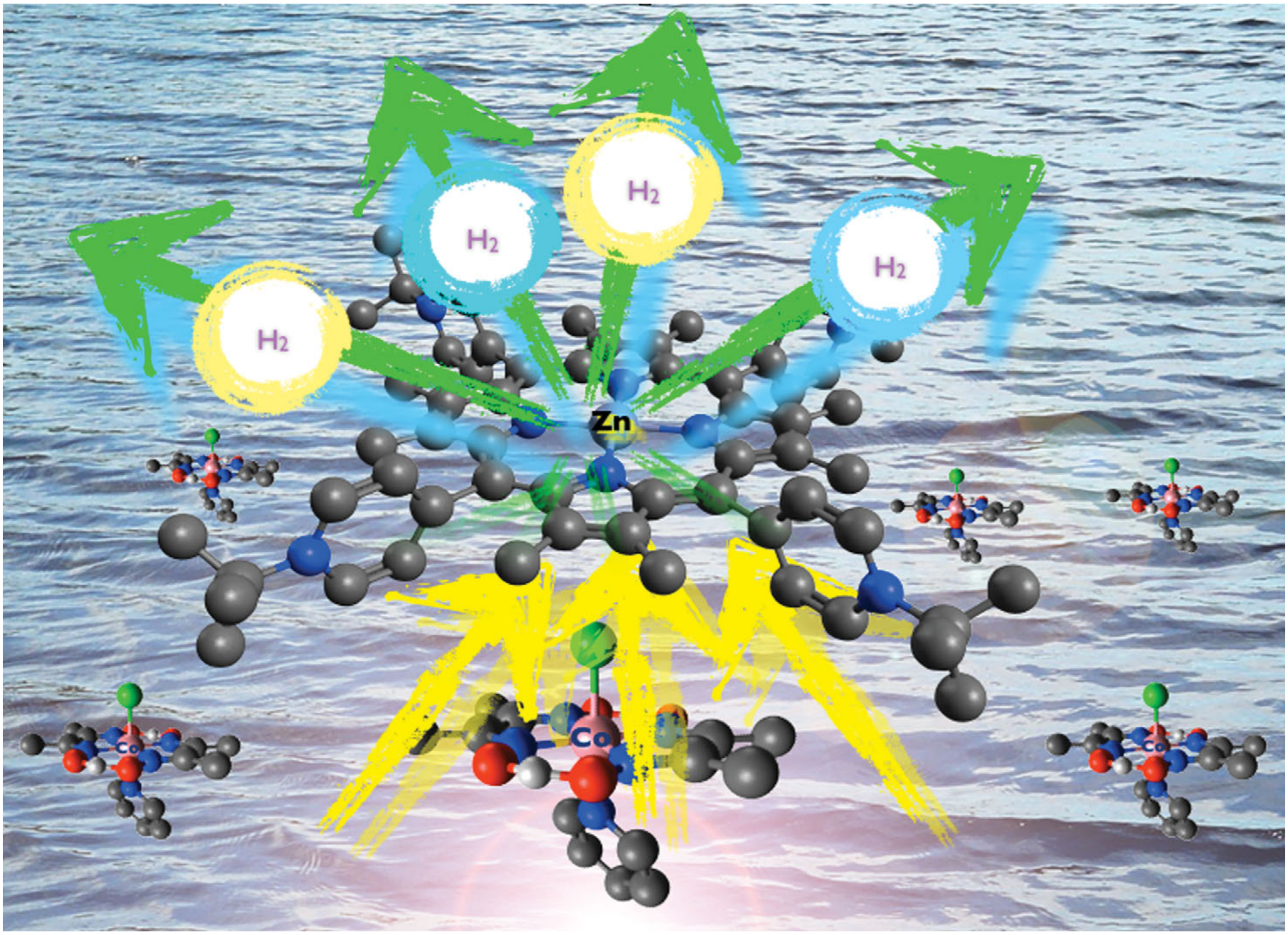

Showcasing research from the laboratories of Athanassios G. Coutsolelos, Department of Chemistry, University of Crete, Heraklion, Greece and Julia A. Weinstein, Department of Chemistry, University of Sheffield, Sheffield, UK

Photocatalytic hydrogen production from a noble metal free system based on a water soluble porphyrin derivative and a cobaloxime catalyst

Cobalt-based compounds are well-known catalysts for H_2 production, but require a photosensitizer to be powered by sunlight. This paper describers the first example of a water-soluble porphyrin to photosensitize cobaloxime catalysed H_2 production. The noble-metal free photocatalytic system works under visible light with large turnover numbers.

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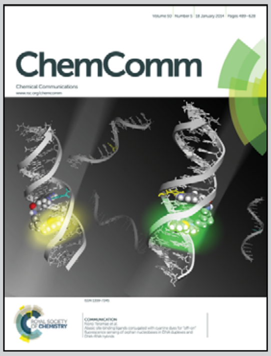

See Athanassios G. Coutsolelos and Julia A. Weinstein *et al.*, *Chem. Commun.*, 2014, **50**, 521.

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Photocatalytic hydrogen production from a noble metal free system based on a water soluble porphyrin derivative and a cobaloxime catalyst†

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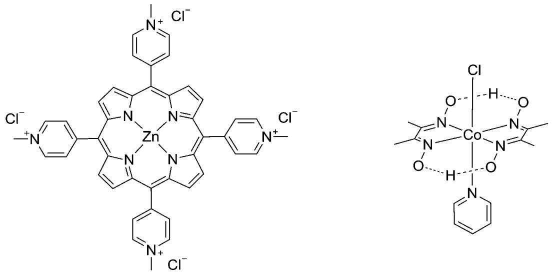
A combination of noble-metal free components, a water soluble porphyrin photosensitizer zinc *meso*-tetrakis(1-methylpyridinium-4-yl)porphyrin chloride [ZnTMPyP^{4+}]Cl$_4$ (1) with cobaloxime complex [Co^{III}(dmgH)$_2$(py)Cl] (2) as a catalyst, creates an efficient system for photochemical hydrogen production acting under visible light with 280 TONs. This is the first example of a water soluble porphyrin acting as a photosensitizer for cobaloxime catalysed H$_2$ production.

One of the major strategies for solar energy conversion that is currently under development is the light-driven splitting of water into its constituent elements.[1,2] Inspired by nature's extensive use of metalloporphyrins as solar energy harvesters and electron transfer agents, artificial porphyrins have found prominent use as photosensitizers in hydrogen[3] and oxygen[4,5] producing schemes. The photocatalytic production of hydrogen from aqueous protons, which constitutes the reductive side of water splitting, can be accomplished by systems containing a photosensitizer, an electron relay, a sacrificial electron donor and a catalyst. The great challenges that remain in the field of photocatalytic hydrogen production include the development of systems which employ earth-abundant materials, and the improvement of the activity and durability of the systems.[6,7] To this end, photocatalytic systems involving molecular catalysts based on low-cost and synthetically facile cobaloxime complexes have attracted great attention over the last few years.[8–16] Here, we report a noble metal free bioinspired photocatalytic system which uses a tetracationic water soluble Zn porphyrin, zinc *meso*-tetrakis(1-methyl-pyridinium-4-yl)porphyrin chloride, [ZnTMPyP]$^{4+}$(Cl$^-$)$_4$, **1**, as the photosensitizer and [Co^{III}(dmgH)$_2$(py)Cl] (dmgH = dimethylglyoximate and py = pyridine), **2**, as the catalyst (Fig. 1).



1 2

Fig. 1 Structures of photosensitizer **1**, [ZnTMPyP]$^{4+}$(Cl$^-$)$_4$, and catalyst **2**, [Co^{III}(dmgH)$_2$(py)Cl] (dmgH = dimethylglyoximate and py = pyridine).

Fig. 2 shows the amount of hydrogen produced over time upon irradiation (λ > 440 nm) at two different pH values of systems containing **1**, **2** and triethanolamine (TEOA) in MeCN–H$_2$O (1 : 1).

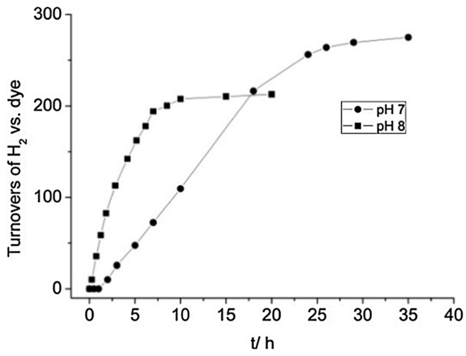


Fig. 2 Plots of hydrogen production upon irradiation (λ > 440 nm) of solutions (1 : 1 acetonitrile–water) containing **1** (4.0 × 10^{-5} M), **2** (4.9 × 10^{-4} M) and TEOA [5% (v/v)].

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At pH 8, the initial rate of H_2 generation is maintained for approximately 3 h before starting to decline until it finally ceases in about 5 h. At pH 7, hydrogen production is observed only after an induction period of 1 h with the initial hydrogen production rate being considerably slower than that at pH 8. However, at pH 7, the system shows considerably improved stability as it maintains its photocatalytic activity for more than 20 h producing in total about 280 TONs of hydrogen.

These pH values were selected on the basis of observations in related photocatalytic systems involving **2** as the catalyst and TEOA as a sacrificial donor, which show their maximum rate of hydrogen production at neutral to slightly basic pH values ($7 < \text{pH} < 8.5$).[10–12,14] Cessation of hydrogen production coincides, in all cases, with bleaching of the photolysis solutions. To regenerate the catalytic activity of the system, addition of both **1** and **2** is necessary, suggesting that both the photosensitizer and the catalyst undergo at least partial decomposition in the course of the reaction.[10–12] Control experiments at pH 7 and 8 with $\lambda > 440$ nm irradiation showed that the presence of all three components (**1**, **2** and TEOA) is necessary in order to observe H_2 production. Photolysis experiments performed under identical conditions but in the presence of 2 mL of Hg, in order to suppress any heterogeneous catalytic sites, show no appreciable change in the H_2 production rate confirming that catalysis is of truly homogeneous nature.[10] It is worth mentioning that H_2 production was also observed in experiments in which ascorbate was used as a sacrificial donor at pH 4 albeit with lower TON (50) (detailed comments are provided in ESI†).

Importantly, selective excitation of the porphyrin Q-band with 572 nm light (through a band-pass filter of ∼10 nm FWHM) in the solution containing **1**, **2** and TEOA in MeCN–H_2O (1 : 1) at pH 7 also resulted in H_2 production with 90 TONs after 120 h of irradiation.§ This experiment unambiguously confirms that the porphyrin acts as a photosensitizer for H_2 production in this system.

Addition of 25 equivalents of $[Co^{III}(dmgH)_2(py)Cl]$ or up to 700 equivalents of TEOA into a solution of **1** in MeCN–H_2O (1 : 1) at pH 7 results in quenching of the porphyrin-based fluorescence by only 5% and no appreciable quenching, respectively (Fig. S1 and S2, ESI†). No change is observed in the UV-Vis absorption spectra of **1** in both of the above cases.

These results are in agreement with what was observed in other diffusion-controlled photocatalytic systems[11,12,17] and indicate that intermolecular electron transfer to/from the singlet excited state of **1** is not favourable due to its short lifetime ($\tau = 1.6$ ns fluorescence lifetime in MeCN–H_2O (1 : 1) at pH 7). This observation is consistent with previous transient absorption studies, which showed that reductive and oxidative electron transfer occurs *via* the lowest-lying triplet excited state of **1**.[18,19]

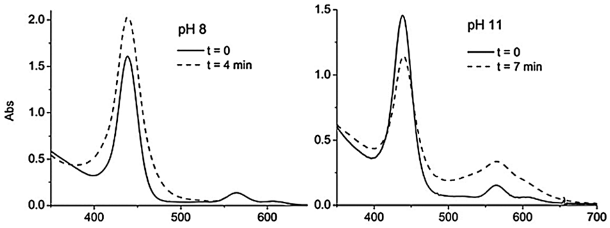

Fig. 3 UV-Vis spectra at pH 8 and pH 11 before and after irradiation of degassed solutions (1 : 1 acetonitrile–water) containing **1** (1.0×10^{-5} M), **2** (4.9×10^{-4} M) and TEOA [5% (v/v)].

To shed more light on the mechanism of photocatalytic H_2 production by the system {**1** + **2** + TEOA}, the UV-Vis absorption spectra at pH 8 and 11 before and after irradiation with visible light ($\lambda > 440$ nm) were recorded (Fig. 3). At pH 8 under H_2 producing conditions, the absorption spectrum of the initial solution is simply the sum of the spectra of its components (see individual spectra in Fig. S3, ESI†). After 4 min of irradiation the porphyrin Soret band shows considerable broadening accompanied by an increase in intensity. This can be attributed to the formation of the absorption band at 450 nm characteristic of the Co^{II} species.[8,12] When the same experiment is conducted at pH 11, where H_2 generation is greatly suppressed, a new broad absorption at 500–600 nm appears within 7 min due to the accumulation of a Co^{I} species.[12,20]

It had been proposed previously that this Co^{I} species leads to H_2 generation, *via* protonation yielding a Co^{III} hydride.[21,22] Variation of the concentration of **2** in systems {**1** + **2** + TEOA} at pH 8 reveals a linear relationship between the concentration of **2** and the initial rate of hydrogen production (Fig. S4, ESI†).

This observation is consistent with the results obtained with related photocatalytic systems and favours a H_2-generating mechanism that is first order in cobalt.[11,12,14] Thus, taking into account recent results from transient absorption studies,[21,23] we propose the mechanism shown in Scheme 1 involving the generation of a Co^{II} hydride which decomposes giving H_2 *via* a monometallic pathway.

The metal-free analogue of **1**, $[H_2TMPyP]^{4+}(Cl^-)_4$, was also tested as a sensitizer for H_2 production under the same conditions. At pH 8, only a relatively modest amount of H_2 was produced (*ca.* 60 TONs) after 9 h of irradiation ($\lambda > 440$ nm). The system containing $[H_2TMPyP]^{4+}(Cl^-)_4$ + **2** + TEOA at pH 8 (Fig. S5, ESI†) shows the formation of a Co^{II} species within the first 3 min of irradiation. The considerably slower rate of H_2 production with the metal free photosensitizer, PS, can possibly be attributed to the higher oxidation potential of the first triplet excited state of $[H_2TMPyP]^{4+}$ compared to that of $[ZnTMPyP]^{4+}$ [(−0.14 V) and (−0.45 V) in aqueous solution, respectively].[24]

To elucidate the role of the porphyrin as a photosensitizer, picosecond–microsecond transient absorption studies have been undertaken. Picosecond transient absorption studies of {**1** + **2** + TEOA} at pH 7 show the formation of the characteristic spectrum of the singlet excited state of the porphyrin and its decay to that of the triplet excited state of **1**, ^{3*}PS, with a 1.0 ± 0.1 ns

Hydrogen production

$$Co^{I} + H^+ \longrightarrow Co^{III}H$$

$$Co^{III}H + Co^{I} \longrightarrow Co^{II}H + Co^{II}$$

$$Co^{II}H + H^+ \longrightarrow Co^{II} + H_2$$

Scheme 1 Proposed reaction scheme of hydrogen production.

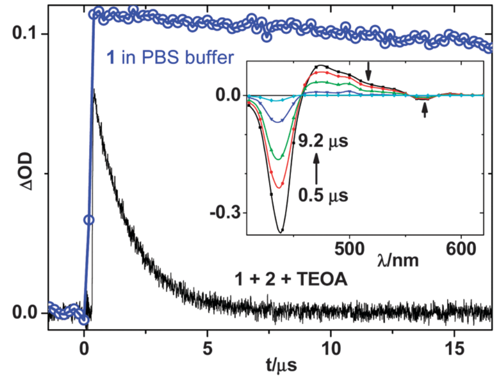

Fig. 4 Nanosecond transient absorption decay kinetics at 470 nm for {**1** + **2** + TEOA} (black) and {**1** in PBS} (blue) following 438 nm excitation. Inset: spectrum of {**1** + **2** + TEOA} at representative delay times 0.5, 0.8, 1.7, 4.1 and 9.2 μs (black, red, green, blue and cyan, respectively).

Table 1 Porphyrin triplet state lifetime under different conditions

Components[a]	pH	Lifetime (μs)
1, **2**, TEOA, water : MeCN	7	1.9 ± 0.4
1, **2**, TEOA, water : MeCN	8	2.4 ± 0.2
1, **2**, PBS : MeCN	7.4	2.4 ± 0.2
1, PBS : MeCN	7.4	130 ± 20, 490 ± 60

[a] Concentrations used: **1**, 4.0 × 10^{-5} M; **2**, 4.9 × 10^{-4} M, TEOA 5% (v/v), water or PBS buffer–MeCN in the 1 : 1 v/v ratio.

lifetime (Fig. S6, ESI†). The observed 1 ns lifetime of the singlet state is similar to that previously reported for ^{1}***1**,[18,19] indicating that this state is not participating in the photoinduced processes, and that any PS contribution to H_2-production must originate from its triplet state. No further processes have been detected on the time scale up to 4 ns.

The transient absorption spectrum of {**1** + **2** + TEOA} at pH 7 on the microsecond time scale (Fig. 4) shows characteristic features of ^{3}***1**. The decay kinetics of ^{3}***1** in the PBS–MeCN mixture are best fitted with double-exponential functions (Table 1), probably due to concentration self-quenching, or different solvation environments. If both **1** and **2** are present, addition of TEOA or a change in pH does not affect the lifetime of ^{3}***1**. Excitation at different wavelengths (438 nm, the Soret band of **1**; 560 nm, Q-band, or 490 nm, cobaloxime) to explore different **1**(PS)/**2**(Co) absorption ratios consistently produced the same results in the transient absorption experiments. **1** in the presence of TEOA alone is extremely photo-unstable and instantaneously photobleaches upon excitation, as has been reported previously.[18,19]

For all systems containing **1** and **2**, decay traces of the transient signals can be satisfactorily fitted with a single-exponential function, indicating that only one process, that of the triplet state decay, is observable on this timescale. The addition of **2** decreases the ^{3}***1** lifetime from over a hundred μs to ~2 μs (Table 1 and Fig. 4), indicating that **2** efficiently quenches ^{3}***1**. This fact directly supports the participation of ^{3}***1** in the hydrogen production pathway.

We have shown for the first time that a combination of a water soluble porphyrin $ZnTMPyP^{4+}$ (**1**) photosensitizer and the cobaloxime catalyst $[Co^{III}(dmgH)_2(py)Cl]$ (**2**) is effective in photoinduced H_2 production in MeCN–water (1 : 1) with TEOA as a sacrificial donor. The maximum performance occurs at neutral to slightly basic pH, with *ca.* 300 TONs of H_2 after 25 h of irradiation with >440 nm light.

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Notes and references

§ The lower rate of H_2 production observed under 572 nm excitation in comparison to the λ > 440 nm cut off filter is due to the considerably reduced amount of light delivered to the sample.

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