Photocatalytic Hydrogen Production from a Noble Metal Free System Based on a Water Soluble Porphyrin Derivative and a Cobaloxime Catalyst

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Citation Details
Lazarides, T.; Delor, M.; Sazanovich, I. V.; McCormick, T. M.; Georgakaki, I.; Charalambidis, G.; Weinstein, J. A.; Coutsolelos, A. G. “Photocatalytic hydrogen production from a noble metal free system based on a water soluble porphyrin derivative and a cobaloxime catalyst” Chemical Communications. 50 (5), 521-523, 2014.

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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 [ZnTMPyP4+]Cl4 (1) with cobaloxime complex [CoIII(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 H2 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 hydrogen3 and oxygen4,5 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, [ZnTMPyP4+]Cl4, 1, as the photosensitizer and [CoIII(dmgH)2(py)Cl] (dmgH = dimethylglyoximate and py = pyridine), 2, as the catalyst (Fig. 1).

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–H2O (1 : 1).

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3cc45025b
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Fig. 1 Structures of photosensitizer 1, [ZnTMPyP4+]Cl4, and catalyst 2, [CoIII(dmgH)2(py)Cl] (dmgH = dimethylglyoximate and py = pyridine).
At pH 8, the initial rate of H₂ 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 < pH < 8.5). Cessation of hydrogen production coincides, in all cases, with bleaching of the photosolysis 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. Control experiments at pH 7 and 8 with λ > 440 nm irradiation showed that the presence of all three components (1, 2 and TEOA) is necessary in order to observe H₂ production. Photosolysis 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 H₂ production rate confirming that catalysis is of truly homogeneous nature. It is worth mentioning that H₂ 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 ESIF).

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–H₂O (1 : 1) at pH 7 also resulted in H₂ production with 90 TONS after 120 h of irradiation. This experiment unambiguously confirms that the porphyrin acts as a photosensitizer for H₂ production in this system.

Addition of 25 equivalents of [CoII(dmgH)₂(py)Cl] or up to 700 equivalents of TEOA into a solution of 1 in MeCN–H₂O (1 : 1) at pH 7 results in quenching of the porphyrin-based fluorescence by only 3% and no appreciable quenching, respectively (Fig. S1 and S2, ESIF). 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 and indicate that intermolecular electron transfer to/from the singlet excited state of 1 is not favourable due to its short lifetime (τ = 1.6 ns fluorescence lifetime in MeCN–H₂O (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.

To shed more light on the mechanism of photocatalytic H₂ production by the system {1 + 2 + TEOA}, the UV-Vis absorption spectra at pH 8 and 11 before and after irradiation with visible light (λ > 440 nm) were recorded (Fig. 3). At pH 8 under H₂ 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, ESIF). After 4 min of irradiation

![Scheme 1](image-url)
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>
<thead>
<tr>
<th>Components</th>
<th>pH</th>
<th>Lifetime (μs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, TEOA, water : MeCN</td>
<td>7</td>
<td>1.9 ± 0.4</td>
</tr>
<tr>
<td>1, TEOA, water : MeCN</td>
<td>8</td>
<td>2.4 ± 0.2</td>
</tr>
<tr>
<td>1, PBS : MeCN</td>
<td>7.4</td>
<td>2.4 ± 0.2</td>
</tr>
<tr>
<td>1, PBS : MeCN</td>
<td>7.4</td>
<td>130 ± 20, 490 ± 60</td>
</tr>
</tbody>
</table>

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.

Table 1 Porphyrin triplet state lifetime under different conditions

The observed 1 ns lifetime of the singlet state is similar to that previously reported for 3⁺1,18,19 indicating that this state is not participating in the photoinduced processes, and that any PS contribution to H₂-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 ZnTMPyP³⁺ (1) photosensitizer and the cobaloxime catalyst [Co³⁺(dmgH)₂(py)Cl] (2) is effective in photoinduced H₂ 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 H₂ after 25 h of irradiation with >440 nm light.

We thank the European Commission FP7-REGPOT-2008-1, BIOSOLENUTI No 229927, Heraclitos and Thales MIS 377252 grant from Ministry of Education, GSRT; EPSRC (UK), E-Futures DTC and the University of Sheffield and its Strategic Development fund for support. Prof. R. Eisenberg is gratefully acknowledged for fruitful discussions and encouragement of this work.

Notes and references

§ The lower rate of H₂ 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.