Metalloporphyrins Catalyse the Photo-reduction of Water to H_2

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Summary The highly efficient (>350 turnovers/h) catalytic reduction of water by zinc(II) metalloporphyrins has been observed in a defined 'model system' containing zinc porphyrin (10^{-5} M), colloidal platinum (10^{-6} M), methylviologen (10^{-3} M), and ethylenediaminetetra-acetic acid or *N*-phenylglycine (10^{-2} M), and a mechanism is proposed on the basis of the intermediates observed.

WORK on conversion of solar energy into chemical energy has been highlighted by recent successes in catalytic water photo-reduction,[1–6] and photo-oxidation.[7–9] For example, Lehn first demonstrated catalytic photo-reduction of water[1] by trisbipyridylruthenium(II) [$Ru(bipy)_3^{2+}$]. Subsequent work by Kagan, *et al.*[2] and others [3–6,10] suggested similar schemes for the photo-reduction of water to H_2 and clearly defined the role of the various system components (Pt, amine, pH *etc.*). These schemes are properly viewed as 'model systems' for water splitting, since the electrons consumed are ultimately supplied by an organic donor, rather than by water itself. Recent work by Lehn[8] and Grätzel[7,9] has indicated that the organic donors may even be replaced by water in the presence of a specific catalyst (*e.g.* RuO_2).

Surprisingly, all the systems noted above employ the well studied $Ru(bipy)_3^{2+}$ as the photocatalyst.[4b] Since the catalytic properties of the photocatalyst may be drastically altered by metal, or ligand, substitution, it is of both fundamental and practical interest to explore the catalytic activity of non-ruthenium systems. Work in this area has been limited,[11–13] despite the realization that many metal ligand systems exhibit excited-state electron-transfer chemistry.[14,15] A particularly intriguing class of potential catalysts are the metalloporphyrins which possess many ideal photocatalyst properties: high thermal and photostability, broad spectral response, long-lived excited-states, and high excited-state redox-potential.[16,17] Indeed, the metalloporphyrin derivative chlorophyll is the paradigm for solar energy-chemical energy transformation. Here we report the highly efficient photocatalysis of water reduction by synthetic metalloporphyrins: zinc(II)tetra(*N*-methylpyridyl)porphyrin (ZnTMPP) and zinc(II)tetra(sulphonatophenyl)porphyrin (ZnTPPS). To test for photocatalytic activity, a previously defined[2,3,6,10] model system was used, which contains ethylenediaminetetra-acetic acid (EDTA) as the electron donor (10^{-2} M, pH 4—5), colloidal $Pt(OH)_2$ (10^{-6} M) to mediate water reduction, methylviologen (MV,10^{-3} M) as an electron acceptor/mediator, and ZnTMPP (10^{-5} M) as the photocatalyst (excited-state electron-donor). When such a system is irradiated with visible light (λ 540—650 nm) vigorous gas evolution is immediately observed. Gas chromatography demonstrates that H_2 (and CO_2) are evolved.[†] Replacement of H_2O by D_2O gives >95% D_2 by mass spectrometry. The maximum quantum yield for H_2 production, based on a Reinecke's salt actinometer,[18] of ϕ 0·06 mol/einstein of H_2 evolution for a 1 h period corresponds to a maximum of 350 turnovers/h [2 × (mol H_2) (mol porphyrin)$^{-1}$ h^{-1}] of porphyrin. The generality of this reaction is demonstrated by substituting ZnTPPS as the photocatalyst (and *N*-phenylglycine as the electron donor). H_2 is produced at a rate of *ca.* 50 turn-

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[†] Evolution of CO_2 could be explained by the following reactions.

$$R^1R^2\ddot{N}\text{–}CH_2CO_2H \xrightarrow[-\,e]{Ru(bipy)_3^{2+}} R^1R^2\overset{+\bullet}{N}\text{–}CH_2CO_2H \xrightarrow[pH\,\geqslant\,5]{-\,H^+} R^1R^2\overset{+\bullet}{N}\text{–}CH_2CO_2^-$$

$$R^1R^2\overset{+\bullet}{N}\text{–}CH_2CO_2^- \xrightarrow[-e]{MV^{2+}} R^1R^2\overset{+}{N}{=}CH_2 + CO_2 \xrightarrow{H_2O} CH_2O + R^1R^2NH$$

This explanation has precedent in an analogous hydrogen production scheme using triethanolamine rather than EDTA (K. Kalyansundaram, J. Kiwi, and M. Grätzel, *Helv. Chim. Acta*, 1978, **61**, 2720).

overs/h Under similar conditions the previously studied Ru(bipy)$_3^{2+}$ system gives approximately 4 turnovers/h [2,10] If any components are omitted, H_2 evolution does not occur and in the absence of Zn porphyrin, or organic donor, no net chemical change is observed If only Pt is omitted, however, the solution turns blue immediately on irradiation The spectrum of this product (λ_{max} 600 nm) is identical with that of the methylviologen radical ($MV^{\cdot+}$) Spectroscopic measurement of $MV^{\cdot+}$ formation during irradiation gives a steady state concentration of about 10^{-4} M, corresponding to about 200 turnovers/h of ZnTMPP Independent fluorescence measurements show that MV^{2+} effectively quenches the Zn porphyrin excited state (λ_{em} *ca* 633 nm) On the basis of all this information, a simple mechanism can be postulated for the photocatalysis (Figure) Such a mechanism is analogous to that proposed[2,10] for the similar Ru(bipy)$_3^{2+}$ system Finally, we note that if methylviologen is excluded from the system H_2 is still produced, although in much lower yield (2—4% of initial yield) We believe this production arises *via* an independent path the well known photo-reduction of porphyrins by H donors [17,19] In these reactions, photoexcited porphyrin is reduced to a dihydroporphyrin[17,19] which has long been presumed unstable to dehydrogenation [17] We have verified this instability, as addition of Pt to the photo-reduced porphyrin solution generates H_2 In principle, this reductive catalysis provides a separate potential route for water reduction In practice, however, it is unlikely that the amine could be replaced by water as a hydrogen donor in a reductive scheme For the oxidative (methylviologen dependent) catalysis, replacement of organic donor by RuO_2–H_2O is probably feasible [7,9]‡

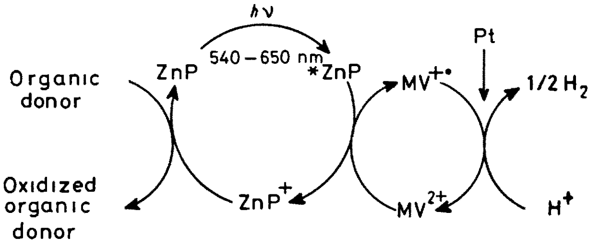

FIGURE Proposed mechanism for hydrogen production in zinc porphyrin systems P is TMPP or TPPS, MV^{2+} is methyl viologen, and the organic donor is ethylenediaminetetra-acetic acid or *N*-phenylglycine Pt is the colloidal platinum catalyst

In summary, we have shown that metalloporphyrins can catalyse the photo-reduction of water in an appropriate model system with an efficiency far exceeding that of the well studied Ru(bipy)$_3^{2+}$ The many desirable physical properties of the porphyrin systems make them extremely attractive targets for more extensive investigation, which is in progress

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‡ The work of Lehn (ref 8) and Gratzel (ref 7) indicates that any sufficiently oxidizing species ($E° > 1$ V) can mediate water oxidation of RuO_2 Such potentials can be obtained by porphyrin cation radicals (ref 16)

Added in proof Since the submission of this manuscript, Gratzel has reported similar experiments to those reported here (M Gratzel, personal communication, K Kalyanasundaram and M Gratzel, *Helv Chim Acta* , 1980, **63**, 478)

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