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Photocatalytic Hydrogen Evolution with a Self-Assembling Reductant–Sensitizer–Catalyst System

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Abstract: A noble-metal-free system for photochemical hydrogen production is described, based on ascorbic acid as sacrificial donor, aluminium pyridyl porphyrin as photosensitizer, and cobaloxime as catalyst. Although the aluminium porphyrin platform has docking sites for both the sacrificial donor and the catalyst, the resulting associated species are essentially inactive because of fast unimolecular reversible electron-transfer quenching. Rather, the photochemically active species is the fraction of sensitizer present, in the aqueous/organic solvent used for hydrogen evolution, as free species. As shown by nanosecond laser flash photolysis experiments, its long-lived triplet state reacts bimolecularly with the ascorbate donor, and the reduced sensitizer thus formed, subsequently reacts with the cobaloxime catalyst, thereby triggering the hydrogen evolution proc-

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ters.

ess. The performance is good, particularly in terms of turnover frequencies (TOF=10.8 or 3.6 min⁻¹, relative to the sensitizer or the catalyst, respectively) and the quantum yield (Φ = 4.6%, that is, 9.2% of maximum possible value). At high sacrificial donor concentration, the maximum turnover number (TON=352 or 117, relative to the sensitizer or the catalyst, respectively) is eventually limited by hydrogenation of both sensitizer (chlorin formation) and catalyst.

Introduction

Conversion of solar energy into fuels by photochemical water splitting is considered as an attractive potential solution to the global energy problem.^[1] Thus, large efforts are being devoted worldwide to the development of efficient molecular devices for photocatalytic hydrogen^[2-6] or oxy-gen^[1c,7-17] evolution. Various types of synthetic strategies are applied in this field, to suitably assemble molecular components (light-absorbing units, electron donors or acceptors, catalysts) into functional supramolecular systems. Among

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such strategies, "soft" methods potentially leading to self-assembling are particularly interesting from the viewpoint of

the synthetic ease and the combinatorial flexibility. One of

such soft strategies is the metal-mediated approach,^[18] by

which chromophores and other functional units, suitably

functionalized with peripheral ligand groups, are assembled

by means of coordinative bonds to appropriate metal cen-

Aluminium(III) pyridylporphyrins are interesting molecu-

lar components for the construction of functional supramolecular arrays.^[19,20] What makes them particularly attractive

is their bifunctional nature, that is, the simultaneous presence of a Lewis acid (the Al center) and a Lewis basic (the *meso*-pyridyl group) function (Figure 1). The Al center can

Figure 1. Schematic representation of the aluminium monopyridyl porphyrin pointing out the two docking sites: the Lewis acidic aluminium center (X) and the Lewis basic pyridyl group (Y).

axially bind a variety of ligands, with a particular affinity for oxygen-based functionalities, whereas the pyridyl function can coordinate to a large variety of transition metals. By using the acidic and basic functionalities and exploiting se-



lective coordination, aluminium pyridylporphyrins can be used to tackle the non-trivial problem of obtaining intrinsically asymmetric three-component supramolecular systems by self-assembly.

We have recently described the self-assembly of a triad for photoinduced charge separation based on such a platform.^[20] In that case, the Lewis acidic and basic functions were used to bind, respectively, an electron acceptor (a carboxyl derivative of naphthalene bisimide) and an electron donor unit (a ruthenium porphyrin). Selective coordination (of carboxyl to Al and of pyridyl to Ru) ensured exclusive formation of the required triad by simple mixing of the molecular components. Stepwise photoinduced charge separation was verified by ultrafast spectroscopic techniques. We report now on the implementation of the same assembling strategy to obtain a noble-metal-free system for photocatalytic hydrogen evolution. On the same aluminium porphyrin

platform, a hydrogen evolution catalyst can be bound through the *meso*-pyridyl group (see for example, in Figure 2a a cobaloxime unit).^[2] On the other hand, axial coordination at the Al center can be used to reversibly tether a variety of sacrificial oxygen-based electron donors (see for example, in Figure 2 ascorbate).



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The absorption spectrum of AlP(OH) in tetrahydrofuran is typical of metallo porphyrins, with a Soret band at λ = 425 nm and Q-bands at λ =521, 559, and 600 nm (Figure S1 in the Supporting Information).^[21] Both [Co(dmgH)(H₂O)]

Table 1.	Electrochemical	data for	the molecular	units and	dyads.[a]
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	Oxidation [V]		Reduction [V]				
AlP(OH)	1.22 ^[b]	0.96 ^[b]				-1.22 ^[b]	$-1.59^{[b]}$
Co(dmgH) ^[c]				$-0.68^{[d]}$	$-1.22^{[d]}$		
AlP(OH)-Co(dmgH)	1.21 ^[b]	$1.02^{[b]}$		$-0.63^{[d]}$	$-1.13^{[d]}$	$-1.23^{[b]}$	$-1.66^{[b]}$
AlP-Asc	1.38 ^[b]	$1.12^{[b]}$	$0.61^{[e,f]}$			$-1.20^{[b]}$	

[a] Obtained by differential pulse voltammetry in THF at 298 K, 0.1 M tetrabutylammonium hexafluorophosphate (TBA(PF₆)) as supporting electrolyte, a standard calomel electrode SCE as reference electrode, ferrocene (0.56 V vs. SCE)^[22] as internal standard, 50 mV pulse width. [b] Process attributed to the porphyrin unit. [c] For solubility reasons, [Co(dmgH)₂Cl(4-ethylpyridine)] was used as a model instead of the aquo complex. [d] Process attributed to the cobaloxime unit. [e] Process attributed to ascorbate. [f] Irreversible process.



Figure 2. Schematic representation of the target self-assembling triad for photoinduced hydrogen production.

Results and Discussion

The molecular components used for the assembling of the reductant-photosensitizer-catalyst (R–P–C) target triad system are: 1) an aluminium monopyridyl porphyrin bearing an axial hydroxo group, [5-(4'-pyridyl)-10,15,20-(3,5-di-tert-butyl)-triphenylporphyrinato-hydroxo]aluminium(III), (AIP-(OH)); 2) a cobaloxime with a chloride and a labile water ligand in the axial positions, chloro(aquo)bis-(dimethylglioximate)cobalt(III), ([Co(dmgH)(H₂O)]); and 3) ascorbic acid (AscH).

and AscH have negligible absorption at $\lambda > 400$ nm. The fluorescence of AlP(OH) ($\lambda = 615$, 663 nm, Figure S2 in the Supporting Information) has a lifetime $\tau = 6.4$ ns in THF. Relevant electrochemical data on these molecular components, as well as on their assemblies (see below), are given in Table 1.

Self-assembling of the molecular components on the aluminium porphyrin platform: The assembling of the triad system can be appropriately characterized in THF, a solvent that provides the best balance between the solubility of the three molecular units, by separately studying the formation of the two component dyads (see the Supporting Information for experimental details). The association between the aluminium porphyrin and the cobaloxime [Eq. (1)], taking place by coordination of the meso-pyridyl group of the porphyrin to the cobalt center, with displacement of the labile water ligand,^[23] can be followed both spectrophotometrically (5 nm red shift of the porphyrin Soret and Q-bands, Figure S1 in the Supporting Information) and spectrofluorimetrically (quenching of the porphyrin fluorescence by the coordinated cobaloxime, Figure S2 in the Supporting Information).

 $AlP(OH) + [Co(dmgH)(H_2O)] \rightleftharpoons AlP(OH) - Co(dmgH) + H_2O$ (1)

With both techniques, the association equilibrium in 10^{-4} M THF solution is seen to require approximately a twofold molar excess of [Co(dmgH)(H₂O)] in order to obtain complete formation of the dyad. The fluorescence quenching in the associated dyad takes place on a time scale shorter than the time resolution of the time-correlated single photon counting technique, that is, <250 ps. Time-resolved femtosecond spectroscopy shows a clean decay of the absorption of the aluminium porphyrin excited singlet state to the ground state, with a time constant of 65 ps (Figure S3 in the Supporting Information). The most likely quenching mechanism is an oxidative electron transfer [Eq. (2)], which, as estimated^[24] from the AlP(OH) singlet excited-state energy (2.04 eV) and the electrochemical data given in Table 1, is thermodynamically allowed by approximately 0.4 eV.

$$^{1*}AlP(OH) - Co(dmgH) \rightarrow AlP(OH)^{+} - Co(dmgH)^{-}$$
 (2)

The failure to observe transient accumulation of the products of Equation (2) by time-resolved spectroscopy most likely indicates that the back reaction (charge recombination) to the ground state is faster than the forward one [Eq. (2), charge separation].^[25]

The association between the aluminium pyridyl porphyrin and ascorbic acid [Eq. (3)] can also be followed spectrophotometrically (red shifts of the porphyrin B- and Q-bands, Figure S4 in the Supporting Information) and spectrofluorimetrically (quenching of the porphyrin fluorescence by the pendent ascorbate, Figure S5 in the Supporting Information).

$$AlP(OH) + AscH \rightleftharpoons AlP - Asc + H_2O$$
(3)

The association in 10^{-4} M THF solution is efficient, with approximately 70% dyad formed with stoichiometric amounts and complete formation with a tenfold excess of ascorbic acid. The quenching in the associated dyad very likely takes place by reductive photoinduced electron transfer [Eq. (4)], which, as estimated^[24] from the chromophore excited-state energy (2.04 eV) and the electrochemical data given in Table 1, is thermodynamically feasible by approximately 0.2 eV.

$${}^{1*}\text{AlP} - \text{Asc} \to \text{AlP}^{-}\text{-}\text{Asc}^{+}$$
(4)

The process in the dyad takes place on a time scale shorter than the time resolution of the time-correlated single photon counting technique, that is, <250 ps. Time-resolved femtosecond spectroscopy (Figure S6 in the Supporting Information) shows a clean decay of the absorption of the aluminium porphyrin excited singlet state to the ground state (bi-exponential, with time constants of 5 ps, 60%, and 26 ps, 40%), without apparent accumulation of significant amounts of transient intermediate products. This implies that the reductive electron transfer is largely reversible, in the sense that photoinduced charge separation is followed

by ultrafast charge recombination to reform the ground state. Oxidation of ascorbate is known from electrochemical studies^[26] to be irreversible in aqueous media, and an irreversible electrochemical behavior is also observed in THF (Table 1). The time scales of the electrochemical and time-resolved photochemical experiments are so different, however, that no extrapolation between the two domains can be made. The proof that photoinduced electron transfer is largely, but not fully reversible, derives from the observation of a permanent chemical change upon continuous visible irradiation. The spectral variations, with development of a characteristic band at $\lambda = 630$ nm (Figure S7 in the Supporting Information), indicate the formation of chlorin,^[27-30] likely originating, upon further reduction or disproportionation and protonation, from the metal porphyrin radical

anion.^[31] The quantum yield of chlorin formation in THF is estimated to be approximately 10^{-2} , an order of magnitude which is fully compatible with the failure to observe irreversibility by time-resolved spectroscopy. The results obtained on the two dyads suggest complete formation of the Asc-AlP-Co(dmgH) triad in a THF solu-

formation of the Asc–AlP–Co(dmgH) triad in a THF solution containing 10^{-4} M AlP(OH), $\geq 10^{-3}$ M AscH, and $\geq 2 \times 10^{-4}$ M [Co(dmgH)(H₂O)]. In the triad, as well as in the component dyads, the aluminium porphyrin fluorescence is completely quenched.

Energy levels and allowed processes: From the behavior of the two dyad systems, reasonable predictions can be made about plausible photochemical routes in a fully assembled triad system. Figure 3a shows the energy level diagram for an Asc-AlP-Co(dmgH) triad in THF. The energies of the various states are calculated by using the AlP(OH) singlet excited-state energy (2.04 eV) and the electrochemical data in Table 1 for the two dyads AlP-Asc (Eox values) and AlP-Co(dmgH) (E_{red} values).^[24] The diagram shows that two photoinduced charge-separation paths, of a similar driving force, are available to the triad following excitation of the aluminium porphyrin unit: 1) reductive quenching by ascorbate followed by electron shift to the cobaloxime, 2) oxidative quenching by the cobaloxime followed by hole transfer to ascorbate. Both pathways are consistent with the quenching processes observed in the two dyads, although the ultrafast measurements do not permit any decision about their relative importance in the triad. For hydrogen generation, two-electron reduction of the cobaloxime unit is required, and thus a second photoinduced electron-transfer cycle (after replacement of the oxidized ascorbate unit) should be envisioned. Figure 3b show the energy level diagram for excitation of an Asc-AlP-Co(dmgH)⁻ triad,^[24] containing a one-electron-reduced cobaloxime unit. It can be seen that, at least by a type 1) path, the second reduction step of the cobaloxime unit is thermodynamically allowed.

Hydrogen evolution experiments: The hydrogen evolution experiments were performed by irradiating deaerated solutions (5 mL) with a 175 W Xe arc-lamp and a cut-off filter at 400 nm, and by monitoring the hydrogen evolution by gas

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Figure 3. Energy levels and elementary steps potentially involved in photocatalytic cycles for hydrogen generation based on an Asc–AlP–Co-(dmgH) triad. Parts a) and b) show subsequent one-electron photoinduced charge-separation steps (charge-recombination steps omitted for clarity). For space reasons, the following short-hand notation is used: A =ascorbate, P = aluminium porphyrin, Co = cobaloxime.

chromatography (for details, see the Experimental Section). In neat THF, some hydrogen was detected upon visible irradiation of a solution containing 1×10^{-4} M AlP(OH), $3 \times$ 10^{-4} M [Co(dmgH)(H₂O)], and 1×10^{-2} M AscH. It was produced, however in small, non-catalytic amounts (0.75 µmol, corresponding to turnover number (TON) values of 0.5 relative to $[Co(dmgH)(H_2O)]$ and 1.5 relative to AlP(OH), quantum yield, ca. 4×10^{-4}). It was soon realized that a large gain in hydrogen production could be obtained by adding water to the organic solvent (Figure S8 in the Supporting Information). Therefore, optimization of the system was performed in water/organic solvent mixtures containing 1× 10^{-4} M AlP(OH), by checking the effects on hydrogen evolution of systematic changes in 1) the nature of the organic solvent, 2) the fractional amount of water, 3) the pH value of the irradiated solution, 4) the concentration of ascorbic acid, 5) the concentration of the cobaloxime catalyst, and 6) the concentration of added dimethylglyoxime ligand. Among various water/organic solvent mixtures tested, those containing acetone were found to give the best results in terms of both quantum yield (slope) and maximum chemical yield (long time asymptotic behavior) (Figure 4a). In water/



Figure 4. a) Effect of the nature of the organic solvent on the hydrogen evolution in 30:70 water/organic solvent mixtures (1×10^{-4} M AlP(OH), 3×10^{-4} M [Co(dmgH)(H₂O)], 1×10^{-2} M AscH). b) Effect of the amount of water on the hydrogen evolution in water/acetone solvent mixtures (1×10^{-4} M AlP(OH), 3×10^{-4} M Co(dmgH)(H₂O), 1×10^{-2} M AscH).

acetone solvent mixtures, the hydrogen-evolving performance first improves with increasing the water content up to 30%, but then decreases upon further addition of water (Figure 4b). Therefore, the remaining experiments were carried out in 30:70 water/acetone mixtures. The effect of the concentration of the sacrificial reductant and the pH value are intertwined as, for example, increasing the concentration of ascorbic acid from 1×10^{-2} to 5×10^{-2} M brings a change in the measured pH value from 4.5 to 3.5. The effects can be disentangled by controlling the pH upon addition of appropriate amounts of NaOH or HClO₄. At pH 6, an increase in the concentration of ascorbic acid from 1×10^{-2} to 5×10^{-2} M brings about a steady increase in both the quantum yield and the maximum chemical yield of the hydrogen evolution (Figure 5 a).

The effect of the pH is a complex one, however, with quantum yields (Figure 5b) and limiting chemical yields (Figure S9 in the Supporting Information) peaking at different pH values depending on the ascorbic acid concentration. The best hydrogen evolving conditions were obtained by working at pH 6 with 5×10^{-2} M ascorbic acid. Under these conditions, the effect of the concentration of the catalyst [Co(dmgH)(H₂O)] was then checked (Figure 6a). It can be seen that a considerable gain in performance can be obtained by increasing the catalyst concentration from 1×10^{-4} M (stoichiometric with the AlP(OH) sensitizer) up to a threefold excess (no further gain observed upon further increase). Finally, as already observed by Eisenberg and cow-

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Figure 5. a) Effect of the ascorbic acid concentration on the hydrogen evolution at pH 6 (30:70 water/acetone, 1×10^{-4} M AlP(OH), 3×10^{-4} M [Co(dmgH)(H₂O)]). b) Combined effects of the pH value and the ascorbic acid concentration on the hydrogen evolution (30:70 water/acetone, 1×10^{-4} M AlP(OH), 3×10^{-4} M [Co(dmgH)(H₂O)]).



Figure 6. a) Effect of the concentration of cobaloxime on the hydrogen evolution (30:70 water/acetone, pH 6, 1×10^{-4} M AlP(OH), 5×10^{-2} M AscH). b) Effect of added dimethylglioxime ligand on the hydrogen evolution (30:70 water/acetone, pH 6, 1×10^{-4} M AlP(OH), 3×10^{-4} M [Co-(dmgH)(H₂O)], 5×10^{-2} M AscH).

orkers in related work with cobaloxime catalysts,^[32] the addition of free dimethylglyoxime ligand (dmgH₂) brings about a further increase in the maximum chemical yield of the hydrogen evolution (Figure 6b). Following these optimization experiments, the best hydrogen evolving conditions can be summarized as follows: 1×10^{-4} M AlP(OH), 3×10^{-4} M [Co- $(dmgH)(H_2O)], 5 \times 10^{-2} M$ AscH, pH 6, and $5 \times 10^{-3} M$ dmgH₂. Under these conditions, the quantum yield of the hydrogen evolution (as measured from the slope in the initial 20 min of irradiation, see the Supporting Information) is 0.046, which, given the two-photon-two-electron nature of the photocatalytic process, amounts to approximately 9.2% of the maximum possible value. The TON values, referred to the possible limiting components (see below), are 352 relative to AlP(OH) and 117 relative to $[Co(dmgH)(H_2O)]$. The corresponding turnover frequency (TOF) values are 10.8 and 3.6 min⁻¹, respectively.

Photocatalytic mechanism: The process of the photocatalytic hydrogen evolution is certainly a complex one, involving a variety of possible photochemical and thermal steps. As to the nature of the primary photochemical process, two pathways are available to the aluminium porphyrin excited state (Figure 3): 1) oxidative quenching by the cobaloxime or 2) reductive quenching by ascorbate. The following discussion aims at an experimental discrimination between such possibilities. The first point to be emphasized is that in THF, where the association equilibria between the three molecular components are studied and the electrochemical data defining the thermodynamics of the system are obtained, practically no photocatalytic activity is observed (Figure S8 in the Supporting Information). This is no doubt the consequence of the fast charge recombination and largely reversible behavior observed by ultrafast spectroscopy in this solvent.

When the solvent is changed to water/organic solvent mixtures, efficient photocatalytic hydrogen evolution is observed (Figure 4). In such solvents, however, the association equilibria are clearly very different from the ones in THF. For instance, in a 30:70 water/acetone pH 6 solution containing 1×10^{-4} M AlP(OH) and 5×10^{-2} M AscH the porphyrin fluorescence is only quenched to an extent of 38% (Figure S10 in the Supporting Information), indicating that the axial bond is hydrolyzed under these conditions, with the porphyrin being just partially coordinated by ascorbate. A 57% quenching is observed, on the other hand, when $3 \times$ 10^{-4} M [Co(dmgH)(H₂O)] is added to such a solution (Figure S10 in the Supporting Information), implying that under these conditions coordination of the cobaloxime to the pyridyl porphyrin takes place only partially. This is likely caused by the excess of the ascorbate ligand competing efficiently with the pyridyl porphyrin for cobalt coordination. In summary, under conditions of photocatalytic hydrogen evolution, the catalyst and the sacrificial donor are only partially coordinated to the aluminium porphyrin chromophore, which is largely (ca. 43%) present in solution as a free species

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Figure 7. a) Different absorption spectra at different time delays obtained by ultrafast spectroscopy (UFS) (excitation at $\lambda = 550$ nm) on a 30:70 water/acetone solution containing 1×10^{-4} M AlP(OH) and 5×10^{-2} M AscH at pH 6, and kinetic analysis at $\lambda = 480$ nm (inset). b) Different absorption spectra at different time delays obtained by UFS (excitation at $\lambda = 550$ nm) on a 30:70 water/acetone solution containing 1×10^{-4} M AlP(OH), 3×10^{-4} M [Co(dmgH)(H₂O)], and 5×10^{-2} M AscH at pH 6, and kinetic analysis at $\lambda = 480$ nm (inset).

Under these conditions, the behavior of the aluminium porphyrin chromophore upon excitation can be investigated by ultrafast spectroscopy. It can clearly be seen that, both in the AlP(OH)/AscH (Figure 7a) and AlP(OH)/AscH/[Co-(dmgH)(H₂O)] systems (Figure 7b), a fraction of the initially formed excited singlet state (roughly corresponding to the fluorescence-quenched fraction under the same conditions) decays completely on a time scale of tens of picosecond, whereas the remaining part is appreciably constant over the whole time window of the experiment (2 ns).

By comparison with what observed in THF (Figures S3 and S6 in the Supporting Information), the fast decay of the singlet excited state can be easily assigned to rapidly reversible electron-transfer quenching taking place in the associated fraction of the aluminium porphyrin chromophore. The fate of the long-lived fraction of excited states, corresponding to the free chromophore, can be investigated by nanosecond laser flash photolysis. In the AlP(OH)/AscH system (Figure 8), the initial spectrum (100 ns time delay) can be attributed to the aluminium porphyrin triplet state, populated in a few nanoseconds by intersystem crossing from the singlet (the analogous spectrum obtained with AlP(OH) is shown for comparison in Figure S11 in the Supporting Infor-



Figure 8. Different absorption spectra at a) 0.1–5 and b) 5–100 μ s time delays obtained by laser flash photolysis (excitation at λ =532 nm) on a 30:70 water/acetone solution containing 1×10⁻⁴ M AlP(OH) and 5×10⁻² M AscH at pH 6, and c) kinetic analysis at λ =700 nm.

mation). The evolution of the spectral changes is clearly biphasic: in the earlier period $(0.1-5 \ \mu s)$, a new spectrum with a sharp maximum at $\lambda = 720$ nm develops, characteristic for the radical anion of metal tetraphenylporphyrins.^[33] Then this transient decays to the baseline on a much longer time scale with complex kinetics (from a bi-exponential fit to the black trace of Figure 9a, lifetimes $\tau = 60$ and 400 µs are obtained). This experiment provides clear evidence that free aluminium porphyrin reacts bimolecularly upon excitation with the ascorbate donor at the triplet level, giving rise to the reduced form of the sensitizer. The reaction of the aluminium porphyrin radical anion with the catalyst can then be monitored by laser flash photolysis in the AlP(OH)/ AscH/[Co(dmgH)(H₂O)] system. The transient spectral changes (Figure S12 in the Supporting Information) are qualitatively similar to those obtained for the AlP(OH)/ AscH system, except for a faster decay of the long-lived aluminium porphyrin radical anion spectrum. As expected, the decay rate shows an appreciably first-order dependence on

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Figure 10. Schematic representation of the mechanism leading to cooaloxime reduction and hydrogen generation. For clarity reasons the following abbreviations are used: AIP=aluminium porphyrin, Asc=ascorbate, and Co=cobaloxime.

Figure 9. a) Single-wavelength kinetics ($\lambda = 700 \text{ nm}$) obtained by laser flash photolysis (excitation at $\lambda = 532 \text{ nm}$) on a 30:70 water/acetone solution containing $1 \times 10^{-4} \text{ M}$ AlP(OH) $0-3 \times 10^{-2} \text{ M}$ [Co(dmgH)(H₂O)], and $5 \times 10^{-2} \text{ M}$ AscH at pH 6. b) Plot of the rate constant (obtained by mono-exponential fitting of the kinetic traces) versus the cobaloxime concentration for the calculation of the bimolecular rate constant, slope = $1.4 \times 10^8 \text{ m}^{-1} \text{ s}^{-1}$.

the [Co(dmgH)(H₂O)] concentration (Figure 9), with a calculated bimolecular rate constant of $1.4 \times 10^8 \text{ m}^{-1} \text{s}^{-1}$.

The main mechanistic conclusions from these experiments can be summarized as schematized in Figure 10. 1) Contrary to what was initially envisioned, association of the catalyst and the sacrificial donor with the sensitizer is not useful towards photocatalytic hydrogen evolution. In fact, it turns out to be detrimental, to the extent to which the associated species are rapidly quenched by largely reversible electron transfer. 2) The photocatalytic hydrogen evolution comes from a bimolecular reaction of the triplet state of the free sensitizer with the sacrificial donor. This primary photoreaction produces the reduced photosensitizer, which further reacts bimolecularly with the catalyst, thereby triggering the photocatalytic hydrogen production.[34] The reaction sequence experimentally demonstrated here is similar to that proposed by Eisenberg^[2c,32] for a number of hydrogen-evolving systems based on organic sensitizers and cobaloximes.

An interesting comparison is that between the hydrogen evolution experiments carried out at pH 6 and at natural pH (i.e., pH 3.5 with 5×10^{-2} M AscH and pH 4.5 with 1×10^{-2} M AscH). It should be remarked that at low pH a much more efficient quenching of the aluminium porphyrin fluorescence takes place (e.g., ≥ 95 % for a solution containing 1×10^{-4} M AlP(OH), 3×10^{-4} M [Co(dmgH)(H₂O)], and $1-5 \times 10^{-2}$ M AscH). Efficient coordination of cobaloxime is the main re-

sponsible for the observed quenching, as shown by a comparison between the behavior of the two AlP(OH)/[Co-(dmgH)(H₂O)] and AlP(OH)/AscH subsystems (Figure S13 in the Supporting Information). Under these conditions, with strong quenching by coordinated cobaloxime, a low triplet yield and thus a low photocatalytic activity should be expected (Figure 10). In fact, at natural pH a good hydrogen production efficiency is nevertheless observed (Figure 4), although with a prominent induction period. A key to this issue is the behavior of the aluminium porphyrin fluorescence in the early time lag of the irradiation experiments at pH 4.5 (Figure 11). The fluorescence, initially completely quenched, rises rapidly upon irradiation, reaching in a few minutes the level of emission characteristic of a two-component mixture of AlP(OH) and AscH. The likely explanation is that, in the initial stage of the irradiation, a photochemical detachment of the cobaloxime quenching unit from the aluminium pyridyl porphyrin takes place.[35,36] The blue shift (ca. 5 nm) of the Soret and Q-bands of the porphyrin that accompanies this rise in the emission (Figure S14 in the Supporting Information), symmetric to the red shift observed upon complexation in THF, confirms this hypothesis. As Co^{II} centers are generally known to be substitutionally labile,^[37,38] some detachment of the reduced cobaloxime is likely to take place, in competition with charge recombination, following oxidative quenching of the sensitizer singlet state. In the hydrogen evolution experiments carried out under these conditions (Figure 4 and, in more detail, Figure S15 in the Supporting Information), an induction period is clearly present. Part of this induction period (the first 2-3 min, according to the quenching data of Figure 11) can be accounted for by the photochemical detachment of the co-



Figure 11. a) Time-dependent fluorescence spectra obtained upon continuous irradiation (175 W Xe arc-lamp, cut-off filter at $\lambda = 400$ nm) of a 30:70 water/acetone solution containing 1×10^{-4} M AlP(OH), 3×10^{-4} M [Co(dmgH)(H₂O)], and 1×10^{-2} M AscH, at natural pH (i.e., pH 4.5), compared with the fluorescence (dashed line) of a corresponding solution lacking the cobaloxime catalyst. b) Normalized emission intensity as a function of the irradiation time.

baloxime quenching unit, whereas the remaining part (up to ca. 10 min) is as expected because an appreciable fraction of reduced cobaloxime must accumulate at stationary state before a constant hydrogen formation rate is established. It can be noticed that the induction period for the hydrogen formation is apparently absent, or much less pronounced, at higher pH (Figures 5, 6, and S9 in the Supporting Information). Two reasons can account for this observation: 1) as discussed before, the higher concentration of ascorbate chemically removes the quenching cobaloxime from the aluminium porphyrin, thus largely suppressing that part of the induction period related to the need for photochemical release of this unit and 2) the overall much higher rate is expected to compress any induction period to a time scale shorter than that of the actual measurements.^[39]

In terms of the mechanism shown in Figure 10, the effect of the cobaloxime concentration on the hydrogen production rates and yields (Figures 6a and S16 in the Supporting Information) can be easily related to the efficiency of its bimolecular reaction with the porphyrin radical anion. This reaction competes with the evolution of the latter to permanent reduction products, such as chlorins. Therefore, fast electron scavenging is expected to be crucial to minimize the photosensitizer degradation. As a matter of fact, in all the experiments an inverse relationship has been observed between the extent of chlorin product formation and the efficiency of hydrogen evolution (Figure S17 in the Supporting Information).^[40] In terms of kinetics, the dependence of the initial rate of the hydrogen production on the cobaloxime concentration is appreciably a first-order one (Figure S18 in the Supporting Information).^[41] As in similar cases,^[30c,32,42] this could be taken as an indication that, among the hydrogen evolution mechanisms available to the two-electron-reduced form of cobaloxime,^[43] a heterolytic pathway, involving protonation of the Co^{III} hydrido complex, is prevailing here.

The effect of increasing the ascorbic acid concentration on the hydrogen production rates (Figure 5a) can be mainly attributed to two effects: the above-mentioned decrease in singlet quenching by cobaloxime, with a consequent increased triplet formation yield, and an increasing efficiency of the bimolecular reaction of ascorbate with the aluminium porphyrin triplet. The bell-shaped effects of the pH value (Figure 5b) are likely the result of at least two factors playing in opposite directions as the pH is increased: the abovementioned positive effects of increasing the ascorbate concentration and the decreasing thermodynamic driving force for water reduction.

An interesting observation is that in several experiments (e.g., with 1×10^{-2} M ascorbic acid, Figures 4b and S16 in the Supporting Information) the total amount of hydrogen evolved equals the total amount of ascorbic acid present in solution. This means that, although reductive quenching of the aluminium porphyrin by ascorbate is a one-electron transfer process, each sacrificial donor molecule eventually undergoes a two-electron oxidation to dehydroascorbic acid. This most likely occurs by disproportionation^[44,45] of the ascorbate radical formed as primary product.

As far as the TON limiting reactions are concerned, as discussed above, formation of permanent reduction products of the sensitizer (chlorins) is certainly one of the main factors. Another one is clearly the consumption of the catalyst, presumably by hydrogenation of the dimethylglyoximate ligands.^[32,46,47] The improvement in performance obtained by addition of free dimethylglyoxime (Figure 6b) is consistent with this notion.

Conclusion

The sacrificial donor/sensitizer/catalyst system described here was originally conceived with the idea that self-assembly of the three components would favor the photocatalytic performance of the system. In practice, this expectation is not confirmed. In fact, association of the sensitizer with either the catalyst or the sacrificial donor leads to fast and efficient quenching of the singlet excited state of the sensitizer, with little if any net chemical change. In aqueous/organic solvent mixtures, however, a substantial amount of sensitizer is present as free, unquenched species. Under these conditions, the relevant photochemically active species is the triplet state of the sensitizer. Photocatalytic hydrogen evolution arises from a bimolecular reaction of the sensitizer triplet state with the sacrificial donor. This primary photore-

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action yields the reduced photosensitizer, which further reacts bimolecularly with the catalyst, thereby triggering the photocatalytic hydrogen production. Similar conclusions have been recently reached by Eisenberg and coworkers when comparing the photocatalytic efficiency of bound versus free fluorescein/cobaloxime systems.^[36]

A system similar to the one studied in this work has been recently described by Sun and coworkers.^[2d] It features the same cobaloxime catalyst as used here, a zinc (instead of aluminium) pyridyl porphyrin as sensitizer, and triethylamine (instead of ascorbic acid) as sacrificial donor. In that case, the mechanism was assumed to be unimolecular and thought to consist of two consecutive steps: oxidative quenching by the catalyst followed by hole transfer to the sacrificial donor. From the viewpoint of hydrogen evolution, that system (reported values in 80:20 THF/water, TON=22 in 5 h of irradiation)^[2d] is considerably less efficient than the present one.

In conclusion, a new noble-metal-free sacrificial donor/ photosensitizer/catalyst system for photochemical hydrogen production, based on ascorbic acid, aluminium pyridyl porphyrin, and cobaloxime is presented. The hydrogen evolving performance is good, particularly in terms of turnover frequencies^[48] (TOF=10.8 or 3.6 min⁻¹, with respect to the sensitizer or the catalyst, respectively) and quantum yield (Φ = 4.6%, that is, 9.2% of maximum possible value). The turnover numbers (maximum TON=352 or 117, with respect to the sensitizer or the catalyst, respectively) is limited by both the permanent reduction of the sensitizer (formation of chlorins) and the hydrogenation of the ligand of the catalyst.

Experimental Section

Materials: Solvents for spectroscopic, photophysical, and photolysis measurements were of spectroscopic grade, all the other chemicals were of reagent grade quality, and were used as received.

NMR spectroscopy: ¹H spectra were recorded at 400 MHz on a Bruker Avance 400 QNP and at 500 MHz on a Bruker Avance 500. All spectra were run at room temperature (298 K) in [D5]pyridine and [D3]acetonitrile. Proton peak positions were referenced to the peak of residual nondeuterated solvent peaks.

Electrochemical measurements: Differential pulse voltammetry (DPV) measurements were carried out with a PC-interfaced Eco Chemie Autolab/Pgstat 30 potentiostat. Argon-purged 10^{-4} M sample solutions in THF, containing 0.1 M TBAPF₆ (Fluka, electrochemical grade, 99 %, dried in an oven), were used. A conventional a three-electrode cell assembly was adopted: a saturated calomel electrode (SCE Amel) and a platinum electrode, both separated from the test solution by a glass frit, were used as reference and counter electrodes, respectively; a glassy carbon electrode was used as the working electrode. The thermodynamic reduction potentials (half-wave potentials) were calculated from the relation $E_{1/2} = E_{peak} + \Delta E/2$, where ΔE is the pulse potential.

Steady-state absorption/emission measurements: UV/Vis absorption spectra were recorded on a Jasco V-570 UV/Vis/NIR spectrophotometer. Emission spectra were taken on a Horiba-Jobin Yvon Fluoromax-2 spectrofluorimeter, equipped with a Hamamatsu R3896 tube.

Time-correlated single photon counting (TCSPC): Fluorescence lifetimes were measured by using a TCSPC apparatus (PicoQuant Picoharp 300)

equipped with sub-nanosecond LED sources (280, 380, 460, and 600 nm, 500–700 ps pulse width) powered by a PicoQuant PDL 800-B variable (2.5–40 MHz) pulsed power supply. The decays were analyzed by means of PicoQuant FluoFit Global Fluorescence Decay Analysis Software.

Ultrafast spectroscopy (UFS): Femtosecond time-resolved experiments were performed by using a pump-probe setup based on the Spectra-Physics Hurricane Ti:sapphire laser source and the Ultrafast Systems Helios spectrometer.^[49] The 550 nm pump pulses were generated with a Spectra Physics 800 OPA. Probe pulses were obtained by continuum generation on a sapphire plate (useful spectral range: 450–800 nm). Effective time resolution approximately 300 fs, temporal chirp over the white-light 450–750 nm range approximately 200 fs, temporal window of the optical delay stage 0–2000 ps. The time-resolved spectral data were analyzed with the Ultrafast Systems Surface Explorer Pro software.

Nanosecond laser flash photolysis: Nanosecond transient measurements were performed with a custom laser spectrometer comprised of a Continuum Surelite II Nd:YAG laser (FWHM 6-8 ns) with frequency doubled, (532 nm, 330 mJ) or tripled, (355 nm, 160 mJ) option, an Applied Photophysics xenon light source including a mod. 720 150 W lamp housing, a mod. 620 power controlled lamp supply and a mod. 03-102 arc lamp pulser. Laser excitation was provided at 90° with respect to the white light probe beam. Light transmitted by the sample was focused onto the entrance slit of a 300 mm focal length Acton SpectraPro 2300i triple grating, flat field, double exit monochromator equipped with a photomultiplier detector (Hamamatsu R3896) and a Princeton Instruments PIMAX II gated intensified CCD camera, using a RB Gen II intensifier, a ST133 controller and a PTG pulser. An Edmund optics notch filter centered at 532 nm was used in order to avoid eventual scattered laser by the sample to hit the detector. Signals from the photomultiplier (kinetic traces) were processed by means of a LeCroy 9360 (600 MHz, 5 Gs s⁻¹) digital oscilloscope.

Photolysis apparatus: The hydrogen evolution experiments were carried out upon continuous visible-light irradiation with a 175 W xenon CERMAX arc-lamp (cut-off filter at 400 nm) of a reactor (a 10 mm path length pyrex glass cuvette with head space obtained from a round-bottom flask) containing the solution. The measuring cell was sealed during the photoreaction: the head to which the cell is attached has indeed four ports, closed with Swagelok connections, two of them are part of a closed loop involving a GC gas inlet and a sample vent in order to analyze the head space content without an appreciable gas consumption, and the other two are for the degassing procedure (input and output). Regarding the calculation of the photoreaction quantum yields the irradiation was performed with an array of four high power Roithner Lasertechnik orange (590 nm) 350 mA LEDs instead of white light (for more details see the Supporting Information).

Gas chromatography: The gas phase of the reaction vessel was analyzed on an Agilent Technologies 490 microGC equipped with a 5 Å molecular sieve column (10 m), a thermal conductivity detector, and by using Ar as carrier gas. An aliquot of 5 mL from the headspace of the reactor was sampled by the internal GC pump and 200 nl were injected in the column maintained at 60 °C for the separation and detection of gases. The unused gas sample was then re-introduced in the reactor in order to minimize its consumption along the whole photolysis. The amount of hydrogen was quantified through the external calibration method. This procedure was performed, prior to analysis, through a galvanostatic (typically 1 mA) electrolysis of a $0.1 \text{ M }_2\text{SO}_4$ solution in an analogous cell (same volume) equipped with two Pt wires sealed in the glass at the bottom of the cell. A 100% faradaic efficiency was assumed leading to a linear correlation between the amount of H₂ evolved at the cathode and the electrolysis time.

Hydrogen evolution experiments: In a typical experiment, samples of 5 mL were prepared in 20 mL scintillation vials starting from a solution of AlP(OH) (1×10^{-4} M in water/organic solvent), and further adding AscH (as solid) and [Co(dmgH)(H₂O)] (small aliquots from a 3×10^{-2} M mother solution in acetonitrile). The change in volume upon addition of the latter can always be considered negligible (dilution ≤ 1 %). The pH of the final solution was adjusted (when required) upon further addition of different aliquots of 1 M NaOH or 1 M HClO₄ solution (total volume

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changes are negligible). The solution was then put in the reactor, degassed by bubbling Ar for 30 min, and thermostated at 15 °C. The cell was then irradiated and the solution continually stirred during the photolysis. The gas phase of the reaction was analyzed through GC and the amount of hydrogen was quantified.

Synthesis of molecular components and models

AlP(OH):^[19,20] 5-(4'Pyridyl)-10,15,20-(3,5-di-*tert*-butyl)-triphenylporphyrin (P) was synthesized and purified according to literature methods.^[50] Compound P (300 mg, 2.82 mmol) was then dissolved in dry toluene (100 mL) and trimethylaluminium (0.2 mL, 2.0 M in toluene, 5.6 mmol) was added under a N₂ atmosphere. The solution was stirred at room temperature, under a N₂ atmosphere, for 4 h, after which time H₂O (5 mL) was added and stirring was continued overnight. The toluene was removed and the violet solid thus formed was re-dissolved in CH₂Cl₂. The solution was filtered, dried over Na₂SO₄, and passed over a column of alumina to give the product (265 mg, 85%). ¹H NMR (400 MHz, [D5]pyridine): δ =9.28 (m, 6H; β₄, β₃, β₂), 9.12 (m, 4H; β₁, py_{Ha}), 8.2 (brd, 6H; *oH*, *oH'*), 8.15 (d, 2H; py_{Hb}), 7.84 (brd, 2H; *pH*, *pH'*), 1.54 (s, 36H; *t*Bu), 1.52 ppm (s, 18H; *t*Bu).

[Co(dmgH)(EtPy)]: $[Co(dmgH)_2Cl(4-ethylpyridine)]$ was synthesized according to literature procedures.^[51]

 $[Co(dmgH)(H_2O)]$: CoCl₂-6H₂O (1.10 g, 5 mmol) and dmgH₂ (dimethylglioxime, 1.18 g, 11 mmol) were dissolved in 95% ethanol (50 mL), and the solution was heated to 70 °C. A 1_M NaOH solution (5 mL, 5 mmol) was then added to the whole mixture and the solution was stirred for 1 h at 70 °C. After cooling to room temperature, a stream of air was blown through the solution for 30 min. The solution was filtered to remove sidereaction products and concentrated to allow precipitation. The so obtained brown crystals were collected by filtration on a Büchner funnel and washed with water (5 mL) and then with diethyl ether (10 mL). The solid was then dried at room temperature to yield the product (590 mg, 35%). ¹H NMR (400 MHz, [D3]acetonitrile): δ =18.40 (brs, 2H; OHO), 2.45 ppm (s, 12H; CH₃).

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- analogue such as [Co(dmgH)(EtPy)] (EtPy=4-ethylpyridine) is used as cobaloxime component of the reaction mixture. An alternative check could be performed, in principle, by substituting the AlP(OH) sensitizer with a tetraphenylporphyrin analogue lacking the pyridyl anchoring group. Such an experiment cannot be performed under comparable conditions, however, because of solubility problems.
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- [39] In related work with organic triplet sensitizers, sacrificial donors, and cobaloxime as catalyst, induction periods are either very short^[2c] or not experimentally detected.^[32]
- [40] In some instances,^[29] chlorins have been reported to show catalytic activity comparable to that of the parent porphyrin. The inverse correlation with the hydrogen yields observed here seems to rule out, in the present case, such a possibility.
- [41] Initial rates are calculated from the slope of the linear part of the kinetic experiments. Experiments with a cobaloxime concentration lower than 2×10^{-4} M are not considered in the plot because of the evident degradation of the sensitizer observed under those conditions. In such cases, the dependence of the rate of hydrogen generation on the [Co(dmgH)(H₂O)] concentration is not mechanistically meaningful.
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