

Proton Transfer

Strong Enhancement in Cobalt(II)-TPMA Aqueous Hydrogen Photosynthesis through Intramolecular Proton Relay

Federico Droghetti⁺, Federico Begato⁺, Melvin Raulin, Gioia Musiu, Giulia Licini, Mirco Natali,^{*} and Cristiano Zonta^{*}

Abstract: Photosynthetic hydrogen generation by cobalt(II) tris(2-pyridylmethyl)amine (TPMA) complexes is mainly limited by protonation kinetics and decomposition routes involving demetallation. In the present work we have explored the effects of both proton shuttles and improved rigidity on the catalytic ability of cobalt(II) TPMA complexes. Remarkably, we demonstrate that, while a small enhancement in the catalytic performance is attained in a rigid cage structure, the introduction of ammonium groups as proton transfer relays in close proximity to the cobalt center allows to reach a 4-fold increase in the quantum efficiency of H₂ formation, and a surprising 22-fold gain in the maximum turnover number, at low catalyst concentration. The beneficial role of the ammonium relays in promoting faster intramolecular proton transfer to the reduced cobalt center is documented by transient absorption spectroscopy, showcasing the great relevance of tuning the catalyst periphery to achieve efficient catalysis of solar fuel formation.

Generation of molecular hydrogen through photochemical water splitting currently features as a fundamental reaction scheme in the context of solar energy conversion into fuels (i.e., Artificial Photosynthesis).^[1,2] Though simple at first glance, the complex mechanistic requirements associated with this reaction are such that a catalyst unit is always necessary. In this regard, following Nature's design concepts, many artificial hydrogenases have been purposely conceived which are based upon the suitable combination of catalytic metal ions and diverse ligand sets.^[3,4] The subsequent

merging of these artificial catalysts with light-harvesting sensitizers and electron donors has ultimately led to the effective generation of molecular hydrogen by direct light conversion.^[5,6] Within the plethora of metal complexes efficiently employed for this purpose, polypyridine cobalt complexes have received substantial interest in the last years, taking advantage of their ability to work under purely aqueous conditions and their enhanced stability with respect to other molecular analogues.^[7–13]

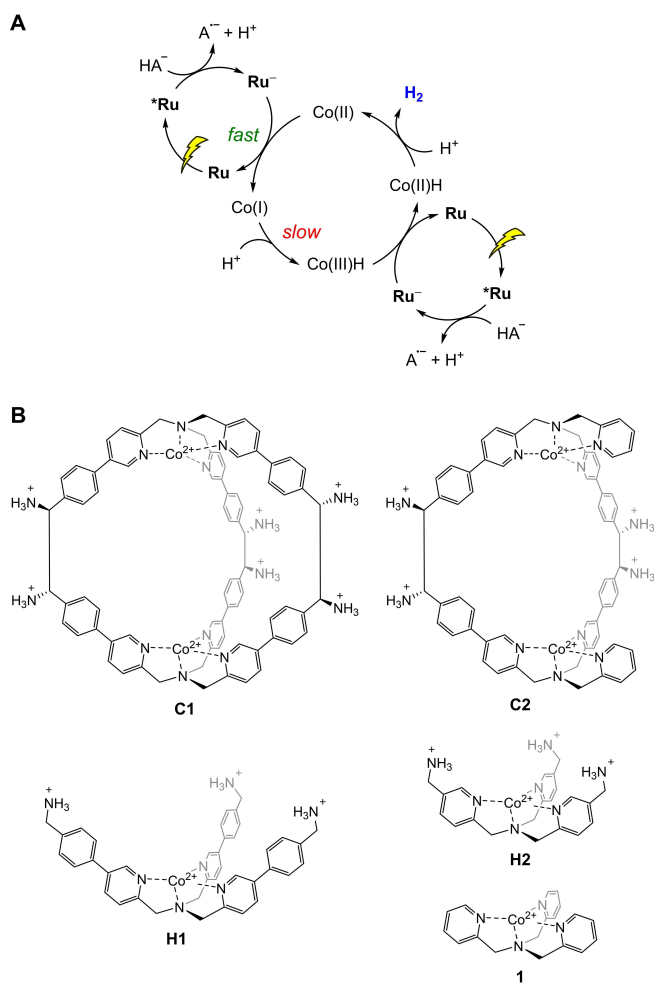
We and others have effectively exploited the tris(2-pyridylmethyl)amine (TPMA) ligand scaffold to prepare cobalt(II) complexes for promoting the hydrogen evolving reaction (HER) both under electrochemical and light-driven conditions.^[14–16] For these complexes, hydrogen production is expected to occur via a heterolytic ECEC mechanism (where E and C are a reduction and a chemical step, i.e., protonation, respectively).^[16] Interestingly, some of these complexes were efficiently applied for aqueous hydrogen photosynthesis in combination with [Ru(bpy)₃]²⁺ (where bpy = 2,2'-bipyridine) as the sensitizer (Ru) and ascorbate (HA⁻) as the electron donor.^[14,17] Within this photochemical cycle, fast electron transfer from the reduced sensitizer to the TPMA-based catalyst is observed,^[14] possibly indicating that catalyst turnover is mainly limited by proton transfer from the aqueous solution to the reduced metal center (Scheme 1A). Furthermore, slow proton transfer could also be responsible for progressive catalyst deactivation which, for these metal complexes, is expected to proceed through decoordination of the cobalt center from the polydentate chelate,^[15,18] likely assisted by aqueous protons. With these evidences in our hands, we envisioned that a considerable improvement of the light-driven catalytic activity towards aqueous proton reduction to H₂ by cobalt(II) TPMA complexes could be achieved by i) positioning a proton transfer relay in proximity to the cobalt center, possibly accelerating both formation of the cobalt(III)-hydride intermediate and hydrogen elimination, and ii) improving the rigidity of the catalytic structure, thus enhancing catalyst stability. In order to target both issues, we synthesized the two molecular cages featuring two sandwiched cobalt(II) TPMA fragments with a recently reported synthetic methodology which allows to prepare hydrolytically stable complexes also in acidic conditions.^[19] This novel structures should furnish structural rigidity, acidic stability, and ammonium acidic sites potentially working as proton transfer relays. The two binuclear complexes C1 and C2 (Scheme 1B) differ for the presence of either three or two connections between the two TPMA units, respectively. To

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Scheme 1. A) Mechanism of photochemical hydrogen production by cobalt(II) TPMA complexes with indications of the fast and slow elementary steps ($\text{Ru} = [\text{Ru}(\text{bpy})_3]^{2+}$, $\text{HA}^- = \text{ascorbate}$); B) molecular structures of the complexes studied in this work. Chloride counterions are removed for clarity.

unravel the effect of the relay position, we also prepared the two “half cages” **H1** and **H2** (Scheme 1B), both characterized by ammonium groups but located at different distances from the metal center. The novel complexes were employed as catalysts for the HER under photochemical conditions in combination with $[\text{Ru}(\text{bpy})_3]^{2+}$ (**Ru**) and ascorbate (HA^-) as the sensitizer and the electron donor, respectively, and their activity compared with that of the prototype TPMA cobalt(II) complex **1** (Scheme 1B).

In this paper we will disentangle the factors determining the efficiency of cobalt(II) TPMA complexes in photosynthetic hydrogen evolution. In particular, we will show that positioning the proton relays close to the catalytic center significantly boosts the photosynthetic performance over the prototype complex **1**.

Complexes **C1**, **C2**, **H1** and **H2** were prepared according to synthetic methodologies reported by us and others.^[19] All the synthetic details as well as the characterization of the resulting compounds with a variety of techniques are reported in the Supporting Information. The photosynthetic

performances towards hydrogen formation were investigated upon visible-light irradiation ($1 \text{ sun} = 0.1 \text{ W} \cdot \text{cm}^{-2}$) of aqueous acetate buffer solutions containing 0.5 mM Ru and 0.1 M HA^- in the presence of different amounts of catalyst. To properly investigate the series of metal complexes, comparative experiments were made considering identical concentrations of cobalt centers. Figure 1A depicts the kinetic traces at $[\text{Co}] = 0.2 \text{ mM}$ obtained at pH 5, i.e., the optimum pH for all complexes examined (see Figure S1–S6 of the Supporting Information for traces at different concentrations and pH), while Figure 1B exhibits the trend in the quantum efficiency (QE), defined as two-time the ratio between the initial rate of hydrogen production and the absorbed photon flux,^[17] at variable catalyst concentration (see Supporting Information for the definition and the complete collection of the relevant key performance indicators).

Inspection of the catalytic data shows that both the binuclear complexes **C1**, **C2** and the “half cages” **H1**, **H2** outperform the reference TPMA complex **1** under all experimental conditions, indicating the beneficial role of the introduced synthetic modifications. However, the mononuclear complexes **H1** and **H2** display enhanced QE over the

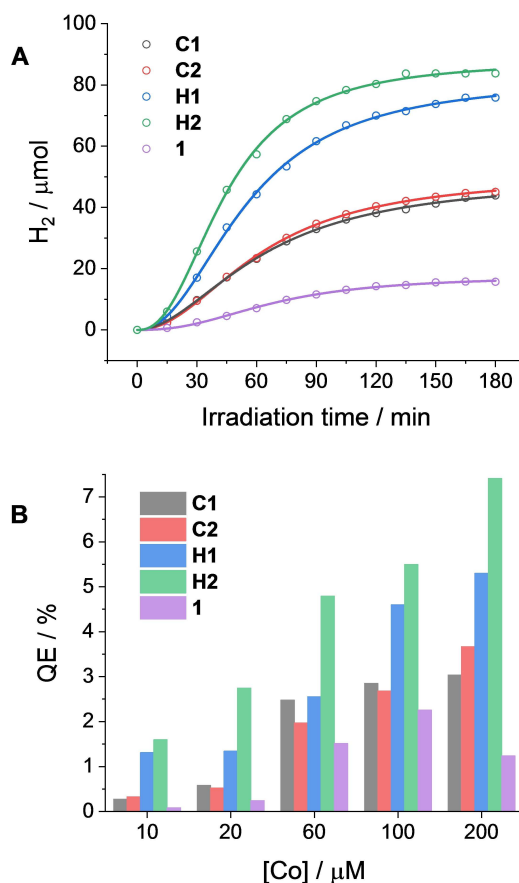


Figure 1. A) Hydrogen evolution kinetics upon visible light-irradiation ($400\text{--}800 \text{ nm}$, $0.1 \text{ W} \cdot \text{cm}^{-2}$) of 1 M acetate buffer solutions (pH 5) containing 0.5 mM Ru , 0.1 M HA^- , and catalysts **C1**, **C2**, **H1**, **H2**, or **1** (total Co concentration = 0.2 mM); B) plot of the quantum efficiency (QE) at different total Co concentrations.

binuclear cages **C1** and **C2** (Figure 1B) both when this quantity is compared as a function of the total Co content and also when the actual concentration of catalyst species is considered (see Table S1 of the SI). Although these findings possibly indicate the absence of a cooperative effect between the two metal ions within the cage and the likely involvement of only one cobalt center per molecule in the catalytic process, they unequivocally demonstrate that the rigidity imparted by the cage structure does not positively contribute to an efficient catalysis. This can be ascribed to the decrease of the ligand flexibility, possibly impacting on the complex reorganization along the catalytic cycle^[17,18] as well as the lower mobility of the ammonium functional groups that could minimize the resulting proton relay effect. Removal of a connection between the two **TPMA** units from **C1** to **C2**, likely enhancing molecular flexibility, however proves insufficient to improve the photosynthetic activity. On the other hand, the more efficient catalytic activity by complexes **H1** and **H2** within the light-activated cycle here examined clearly points to a favorable role of the ammonium relays in accelerating catalysis via intramolecular proton transfer. In this regard, the largest QEs measured with **H2** well correlate with the shortest distance between the proton relay and the cobalt center, possibly indicating enhanced proton transfer kinetics for **H2** over **H1**. The beneficial role of proton shuttles in the HER is indeed characteristic of other catalytic platforms^[4,13,20–23] and the specific position and orientation of the proton transfer relay also play an important role.^[24] Remarkably, at 0.2 mM a QE of 7.4% is measured for **H2**, which represents an unprecedented value for **TPMA** complexes.^[17] Similar QEs were only achieved using cobalt polypyridine complexes featuring chelating ligands characterized by redox-active properties.^[11,13]

A further proof of the beneficial role of the proton relay comes from the comparison of the maximum turnover number (TON) of hydrogen evolution for the series of complexes examined (Figure S7). In this regard, the maximum TON extracted at low catalyst concentrations is usually considered a key performance indicator of the stability of the catalyst within the light-activated cycle.^[20] For the model complex **1** a decrease in the total cobalt concentration leads to a progressive abatement of the maximum TON, consistent with a weak stability of the metal complex. For both cages **C1** and **C2** no net increase is apparent with lowering the concentration, only pointing to a slight improvement with respect to complex **1**. Instead, a sharp increase of the maximum TON is observed for both the “half cages” **H1** and **H2** at low catalyst loading. Remarkably, at a concentration of 10 μM , **H1** and **H2** show a ca 18- and 22-fold enhancement in the maximum TON of hydrogen generation over complex **1**, respectively. These results thus confirm a definite improvement in catalyst stability engendered by the simple introduction of proton transfer relays. As a matter of fact, the acceleration of the protonation steps required for catalyst turnover, besides speeding up the whole reaction and increasing both the rate and QE, helps in preserving the catalyst structure from parallel, unwanted deactivation pathways.

In order to get a deeper insight into the light-driven catalytic mechanism and shine light on the effective role of the proton transfer relay, we performed transient absorption studies on the three-component systems employed in the catalytic assays. Photosynthetic production of hydrogen is expected to involve excitation of the **Ru** sensitizer, reductive quenching of the excited $^*\text{Ru}$ by the HA^- donor and subsequent electron transfer from the reduced chromophore Ru^- to the catalyst (Scheme 1A).^[17] Laser flash photolysis experiments were thus conducted to monitor the reaction sequence leading to the transfer of one electron to each catalyst. Generation of Ru^- is observed within ca 1 μs upon photoexcitation of a 1 M acetate buffer solution (pH 5) containing 70 μM **Ru** and 0.1 M HA^- following its characteristic absorption at 500 nm (Figure 2A).^[13,14,25]

In the absence of the catalyst, this absorption decays towards the baseline within a few hundred μs due to charge recombination with the oxidized ascorbate radical (black trace in Figure 2A). In the presence of the catalyst, the decay of the transient absorption becomes more rapid (red and blue traces in Figure 2A for complex **H1**, see the Supporting Information for the cages **C1** and **C2**, complex **H2** and the reference **1**, Figure S10–S29). The kinetics are

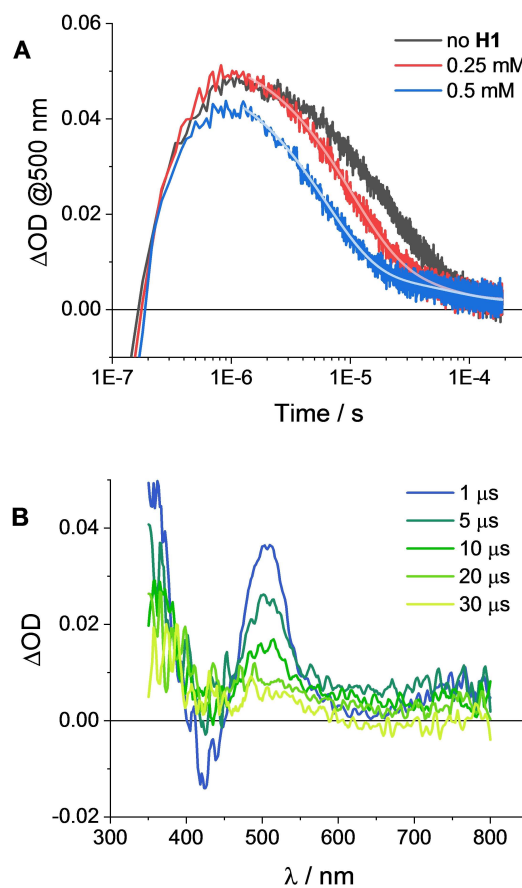


Figure 2. A) Kinetic traces at 500 nm at different concentrations of **H1** and B) transient absorption spectra between 1–30 μs time-delay with 0.5 mM **H1** obtained by laser flash photolysis (excitation at 355 nm) of 1 M acetate buffer (pH 5) solutions containing 70 μM **Ru** and 0.1 M HA^- .

satisfactorily fitted using a biexponential function where the fast (major) component accounts for the electron transfer from Ru^- to the catalyst and the second (minor) component for the decay of the generated Co(I) intermediate, expected to occur by charge recombination with the oxidized ascorbate or by protonation or a combination of both.^[26] The accuracy of the kinetic treatment here employed is validated by the spectral evolution reported in Figure 2B recorded by laser flash photolysis of a 1 M acetate buffer solution (pH 5) containing 70 μM Ru and 0.1 M HA^- in the presence of 0.5 mM H1 (see Figure S9 for the spectral evolution with H2). This experiment shows that the decay of the transient signal at 500 nm, occurring within a few μs , is followed by the development of a broad absorption between 550–700 nm, characteristic of Co(I) species.^[13,25,27,28] This latter subsequently decays towards the baseline in a longer timescale. Inspection of the kinetic data (see Table S2 for details) shows that the first decay component, associated with the electron transfer from Ru^- to the catalyst, shows a well-behaved first-order dependence on the concentration of the cobalt complex, as expected based upon the bimolecular nature of the process.^[13] From these data, rate constants of $4.6 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for C1 , $4.4 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for C2 , $2.5 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for H1 , $2.2 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for H2 , and $7.3 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for 1 can be estimated (see Supporting Information for the kinetic details). Although a slightly lower value is recorded for the prototype TPMA complex 1 , all the rate constants appreciably fall within a narrow range, thus indicating that no major differences in the catalyst activation step exists among the complexes examined. In this respect, the ca 2-times larger value measured for the binuclear complexes C1 and C2 than for the “half cages” H1 and H2 most likely reflects the statistical factor associated with the presence of two cobalt centers per molecule. Overall, these results point to a similar driving force for catalyst reduction, as expected considering the nature of the introduced chemical modifications. Besides, while clearly confirming that for the series of cobalt(II) TPMA complexes examined the electron transfer from Ru^- to the catalyst does not represent the rate-determining step in hydrogen photosynthesis, this experimental evidence implicitly showcases the active role of the proton relays in accelerating the catalysis. This conclusion is further supported by the trend observed in the second component of the decay at 500 nm associated with the fate of the Co(I) intermediate. As a matter of fact, similar kinetics are apparent in the case of complexes C1 , C2 , H1 and 1 (time-constants of ca 60 μs , see SI), suggesting that, for these latter, charge recombination between Co(I) and the oxidized ascorbate radical represents the major decay pathway associated with the Co(I) intermediate in our laser flash photolysis conditions. On the other hand, systematically faster decay rates are evidenced for complex H2 (time-constants of ca 30 μs , see SI) indicating that protonation of Co(I) most likely takes place concurrently, leading to a more rapid disappearance.^[26,27] Furthermore, the appreciable independence of this second kinetic component in the pH range 4–6 (Figure S30) speaks in favor of an intramolecular process^[29,30] and supports the attribution made.^[31] The fastest decay rate observed in the

case of the “half cage” H2 is in perfect agreement with the photochemical hydrogen evolution results and the effective role of the proton relay.

In summary, we have prepared novel cobalt complexes based on the TPMA ligand to tackle both efficiency and stability issues associated with this molecular architecture in light-driven hydrogen photosynthesis. Experimental findings show that the introduction of ammonium groups acting as intramolecular proton transfer relays results instrumental towards efficient light-driven hydrogen production. We believe that the design motif employed in this work will open new avenues in molecular catalysis of solar fuel formation where stability issues usually limit extended applications.

Supporting Information

The authors have cited additional references within the Supporting Information.^[32–39]

Acknowledgements

Financial support from the Italian MUR (PRIN 2020927WY3_001 ElectroLight4Value, to M.N.), from the European Union—Next Generation UE (PRIN2022 PNRR P2022ZSPWF PHOTOCORE to M.N., 2022CXHY3A_003 INVESTCPE to C.Z.), from the University of Ferrara (FAR2023, to M.N.), and from the Fondazione Cassa di Risparmio di Padova e Rovigo (Chiralspace, to C.Z.) is gratefully acknowledged. Open Access publishing facilitated by Università degli Studi di Padova, as part of the Wiley - CRUI-CARE agreement.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: hydrogen · cobalt · proton transfer · relay · cage

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Manuscript received: May 1, 2024

Accepted manuscript online: July 15, 2024

Version of record online: ■■, ■■

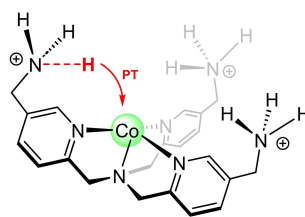
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Enhanced Hydrogen Photosynthesis

Introduction of proton relays close to the catalytic metal center boosts hydrogen photosynthesis with cobalt(II) TPMA complexes leading to a 4-fold increase in quantum efficiency and up to a 22-fold gain in turnover number.