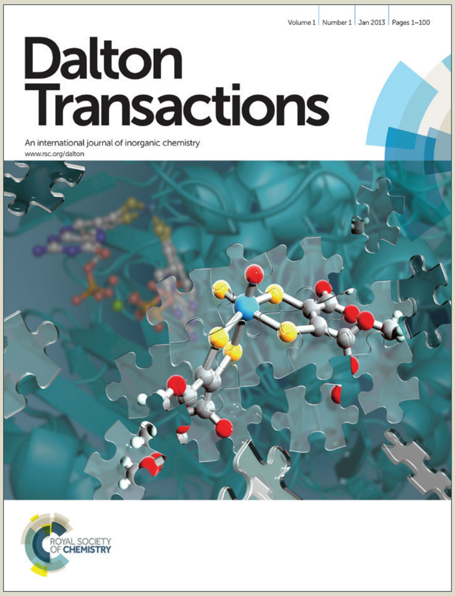
Dalton Transactions

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/dalton

Journal Name

RSCPublishing

ARTICLE

Photoinduced hydrogen evolution by a pentapyridine cobalt complex: elucidating some mechanistic aspects.

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

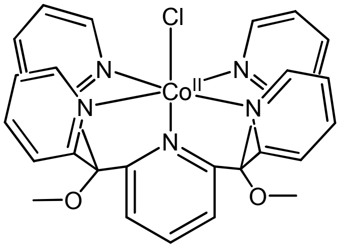
Elisa Deponti,[‡a] Alessandra Luisa,[‡b] Mirco Natali,*[a] Elisabetta Iengo*[b] and Franco Scandola*[a]

A new hydrogen evolving cobalt catalyst **1** based on a pentapyridine ligand has been synthesized and characterized. Its photocatalytic activity in the presence of a $Ru(bpy)_3^{2+}$ sensitizer and ascorbic acid as sacrificial electron donor has been screened in purely buffered aqueous solutions showing TONs and TOFs strongly dependent on both catalyst concentration and pH with the best results obtained at 50 μM **1** and at pH 4 (TON = 187, TOF = 8.1 min^{-1}). The photochemical mechanism, as revealed by flash photolysis, involves reaction of the excited sensitizer with ascorbic acid to yield $Ru(bpy)_3^{+}$ as primary photo-generated reductant, capable of electron transfer to **1** with a remarkable rate (bimolecular rate constant $k = 5.7\ (\pm 0.7) \times 10^9\ M^{-1}s^{-1}$). For hydrogen generation, two one-electron photochemical reduction steps of **1** are needed, along with hydride formation and protonation. Under the experimental conditions used, hydrogen evolution is mainly limited by partial decomposition of both sensitizer and catalyst. Moreover, accumulation of the oxidation product of the ascorbic acid donor, dehydroascorbic acid, is observed to strongly decrease the hydrogen production yield. As shown by flash photolysis, this species is capable of quenching the reduced ruthenium species ($k = 4.4\ (\pm 0.5) \times 10^7\ M^{-1}s^{-1}$) thus competing with electron transfer to the catalyst.

Introduction

Artificial photosynthesis, *i.e.* conversion of solar energy into chemical fuels, is one of the most attracting and promising research fields which can potentially provide an alternative and renewable energy supply in order to tackle the global energy issue of the current century.[1] Among several possibilities, one of the most challenging reaction schemes is represented by water splitting with formation of hydrogen as a clean and renewable fuel. To this aim large effort has been devoted worldwide to the discovery and development of molecular catalysts for photoinduced water oxidation[2-8] and reduction[9-14] and for their integration into more complex supramolecular assemblies.[9g,13c,15-17] As far as the hydrogen evolving reaction (HER) is concerned, during the last years particular attention has been given to cobalt complexes, as convenient noble-metal-free catalysts. Among these, macrocyclic cobalt complexes such as porphyrins[11a,d] and cobaloximes[9,18] have been particularly investigated. Although the activity of such compounds in sacrificial cycles was quite remarkable, the stability under turnover conditions, mainly due to catalyst self-hydrogenation,[9c] was recognized as one of the major drawbacks for this class of compounds. More recently, polypyridine cobalt complexes have emerged as competent catalysts for the HER,[19-26] combining both stability under photocatalytic conditions and outstanding activity. One of the first cobalt polypyridine complexes was introduced by Long and Chang[19a] taking advantage of differently functionalized pentapyridine ligands which were studied in sacrificial photocatalytic cycles using either $Ru(bpy)_3^{2+}$ or GaP nanowires as photosensitizer and ascorbic acid as reductant. Subsequently, Webster and Zhao reported the use of a pentadentate ligand, namely the DPA-bpy, for the construction of a molecular cobalt catalyst achieving TON up to 4400 upon continuous visible irradiation in the presence of the standard $Ru(bpy)_3^{2+}$/ascorbic acid couple.[20] Other cobalt complexes based on different pentadentate ligands were also prepared by Castellano, Long, and Chang,[19b] Alberto,[22] and Lloret-Fillol[21] and studied for photoinduced hydrogen production in the presence of ruthenium-, rhenium-, and iridium-based photosensitizers, respectively, with remarkable results in terms of both turnover numbers (TON) and frequencies (TOF). Several cobalt complexes based on the 1,1-di(pyridin-2-yl)-N,N-bis(pyridin-2-ylmethyl)methanamine pentadentate ligand were prepared by Wang by suitably changing the axial ligand and studied in light activated experiments with $Ru(bpy)_3^{2+}$ and ascorbic acid as photosensitizer and sacrificial electron donor, respectively.[24] In this report an enhanced photocatalytic activity

Chart 1. Molecular catalyst **1.**



was observed in the presence of external added NaCl which was ascribed to an "unexpected role" of one of the pyridines of the ligand capable of dissociating from the cobalt center, thus enabling and stabilizing the formation of the cobalt hydride catalytic intermediate. Tetradentate ligands based on polypyridine/amine moieties were also employed by Castellano, Long, and Chang,[19c] Lomoth and Ott,[25] and Thummel[23] for the preparation of cobalt complexes showing remarkable activity in photocatalytic experiments in the presence of $Ru(bpy)_3^{2+}$ as photosensitizer and ascorbic acid as sacrificial electron donor. Finally, a tetradentate quaterpyridine ligand were used by Lau[26] for the preparation of a cobalt catalyst capable of efficient hydrogen production in a mixed acetonitrile/water environment by taking advantage of a cyclometalated iridium complex and triethanolamine as photosensitizer and sacrificial electron donor, respectively.

Herein we report on a deep investigation of cobalt(II) complex **1** (Chart 1), based on the 6-(bis(bis-2-pyridyl)-methoxymethane)pyridine pentadentate ligand and a chloride to complete the octahedral coordination of the metal. The related aquo complex was recently reported by Berlinguette[27] as an active electrocatalyst for the oxygen evolving reaction (OER). Electrochemical investigation and photocatalytic studies in the presence of the standard $Ru(bpy)_3^{2+}$/ascorbic acid couple have been performed. Additional mechanistic studies of the photocatalytic system have been also undertaken to elucidate some key features of the HER mechanism. This is one of the few examples[26] of how the same metal-ligand combination can be used to trigger water splitting both at the oxidative and reductive level.

Results and discussion

Electrochemical investigation

Cyclic voltammetry (CV) analysis of **1** (1 mM) in acetonitrile solution (0.1 M $LiClO_4$) in both anodic and cathodic regions shows the presence of two redox processes involving the cobalt center (Figure 1a). Upon anodic scan, a poorly reversible process (ΔE = ca. 300 mV) with a potential of $E_{1/2} = 0.49$ V vs. SCE can be observed and assigned to the Co(III)/Co(II) redox couple. Upon cathodic scan a poorly reversible wave can be detected at a potential of $E_{1/2} = -1.31$ V vs. SCE which can be ascribed to the metal-centered Co(II)/Co(I) redox pair. Addition of different aliquots of trifluoroacetic acid (TFA) triggers the appearance of a catalytic wave due to proton reduction which precedes the Co(II)/Co(I) process and increases in intensity with increasing TFA concentration (Figure 1). This clearly establishes that hydrogen production catalyzed by **1** requires the reduction of Co(II) to Co(I) and protonation, yielding a Co(III)-H intermediate, occurring as a single, concerted PCET process.[28] Protonation of Co(I) is likely to occur either after releasing of the apical chloride anion or, as tentatively

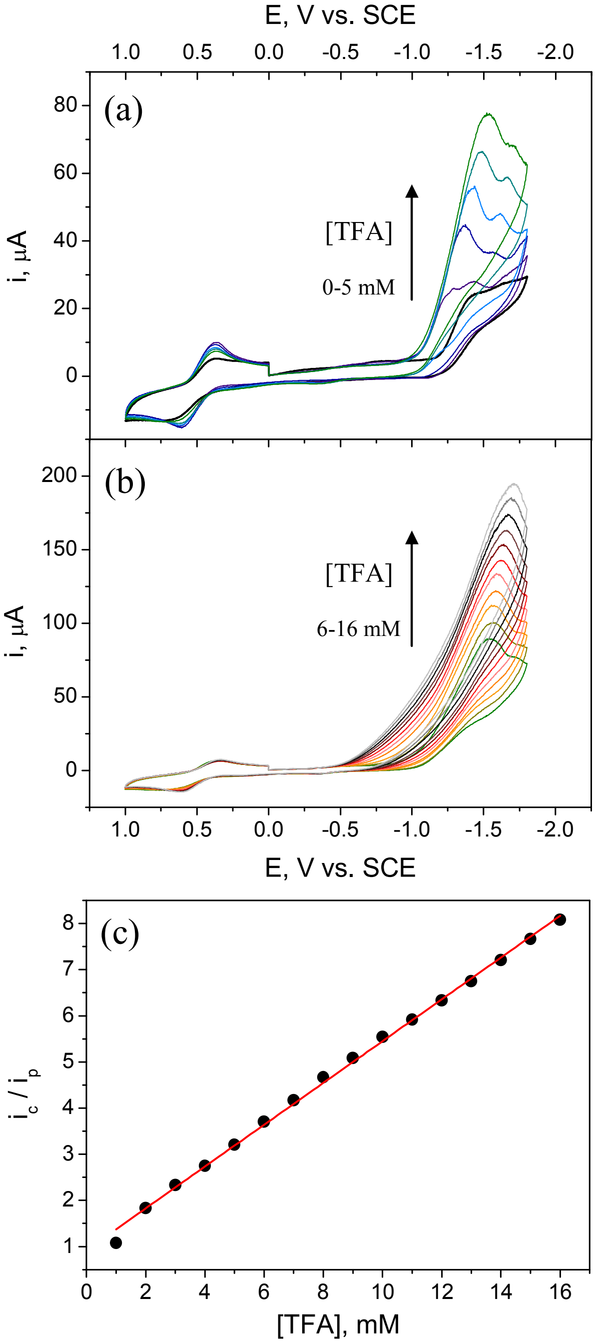
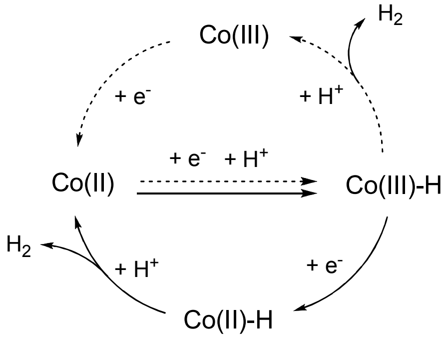


Fig. 1. Cyclic voltammetry at 298 K of a 1 mM **1** in 0.1 M $LiClO_4$ acetonitrile solution (black trace) upon addition of (a) 0-5 mM and (b) 6-16 mM TFA. Working electrode: glassy carbon (7 mm^2 surface area), counter electrode: Pt, reference electrode: SCE, scan rate 100 mV/s. (c) Plot of i_c/i_p vs. TFA concentration.

Scheme 1. Possible catalytic mechanisms of hydrogen production by **1**: low TFA concentration (solid lines) and high TFA concentration (dashed lines).



suggested by Wang,[24] after detachment of one of the pyridine of the pentadentate ligand. Analysis of the onset of the catalytic wave as a function of TFA concentration allows shedding more light into the catalytic mechanism of hydrogen production by **1**. In particular, when the concentration of external acid is kept lower than 5 mM (Figure 1a) the onset of the catalytic wave remains almost constant at ca. −1.00 V vs. SCE, meaning that under these conditions, an additional reduction of the Co(III)-H intermediate is most probably required before hydrogen evolution.[28] On the other hand, when the TFA concentration is increased up to 16 mM (Figure 1b) the onset of the catalytic wave shifts progressively towards less negative potentials. Under these conditions proton concentration is likely high enough to cause direct protonation of the Co(III)-H and thus catalytic hydrogen evolution by **1** may also take place through a different mechanism.[10e,28] The overall set of processes is summarized in Scheme 1.

As a final remark on the electrochemical experiments, a plot of the i_c/i_p ratio vs. TFA concentration (Figure 1c) is linear and this may indicate a second-order dependence of the hydrogen evolving reaction on proton concentration.[29,30]

Photocatalytic hydrogen evolution

The capability of **1** to foster hydrogen evolution in light-activated experiments was tested upon continuous visible irradiation (175 W Xenon arc lamp, cut-off at $\lambda > 400$ nm) of 1 M acetate buffer solutions at pH 4 (5 mL) containing different concentrations of **1** in the presence of 0.5 mM $Ru(bpy)_3Cl_2$ as photosensitizer and 0.1 M ascorbic acid as sacrificial electron donor and checking the headspace of the reactor by gas chromatography (see Experimental Section for additional details). The pH value was chosen by literature comparison[19c,20,22-25] and experimental evidence (*vide infra*).

Photocatalytic hydrogen production was indeed observed (Figure 2): It generally occurs at an almost constant rate, dependent on catalyst concentration, between 0 and 20-30 min (linear behavior) and levels off after approximately 1 hour of continuous irradiation (plateau). Notably, in the hydrogen evolution kinetics a small induction period (few minutes) is also present, which can be reasonably ascribed to the required lag-time so that an appreciable fraction of the catalytically-active doubly-reduced species of **1** is accumulated at stationary state before a constant hydrogen production rate is established.[10c,11d,15b] Going more into details, significant photocatalytic activity is detected when the concentration of **1** is kept higher than 10 µM achieving turnover numbers (TONs) after 3 h irradiation between 100 and 187 and turnover frequencies (TOFs) in the range 3.9-8.1 min^{-1} (Table S1) with the highest value (187 and 8.1 min^{-1}, respectively) obtained at 50 µM **1**.

Comparisons between different photocatalytic systems in terms of TON and TOF should always be taken with caution, because of possible differences in the experimental conditions used. Within these limitations, however, a comparison of the hydrogen evolving activity obtained with photocatalytic systems reported in the literature based on cobalt polypyridine catalysts, with $Ru(bpy)_3^{2+}$ as photosensitizer and ascorbic acid as sacrificial electron donor,[19-26] shows that **1** is more active than both the pentapyridine cobalt complexes reported by Long and Chang,[19a] producing ≤ 20 µmol of H_2 at 50 µM concentration, and the pentadentate complexes reported by Wang,[24] which at the best conditions give only 12 µmol of H_2 at 50 µM concentration, but less active than the pentadentate cobalt complex reported by Webster and Zhao[20] yielding a TON of 450 at 50 µM concentration. Still larger activity with respect to **1** was also observed for some of the cobalt complexes studied by Castellano, Long, and Chang[19b,c] for which TONs up to ca. 2000 were measured at 20 µM concentration.

Differently to what happens for some of the polypyridine catalysts mentioned before, in the present system the TONs are relatively insensitive to catalyst concentration (Figure 2 and Table S1). In particular, the sharp increases in TON at low catalyst concentration observed for other systems[19b,c,20] are not obtained here. This can be in part explained considering the different irradiation source (and thus the different power) used

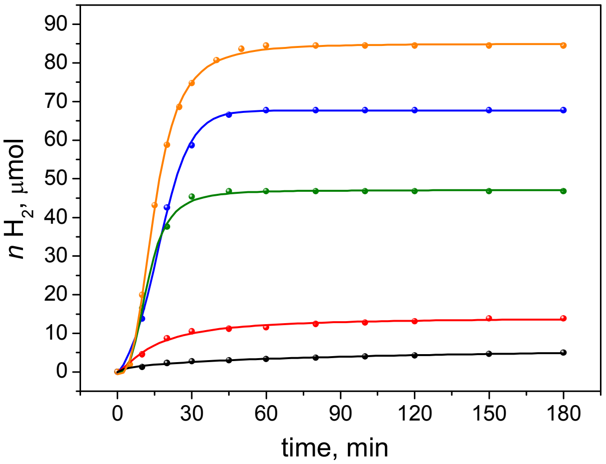


Fig. 2. Hydrogen evolution kinetics obtained upon continuous visible irradiation ($\lambda > 400$ nm) of 1 M acetate buffer pH 4 solutions (5 mL) containing 0.5 mM $Ru(bpy)_3^{2+}$, 0.1 M ascorbic acid, and **1** at 10 µM (black trace), 25 µM (red trace), 50 µM (green trace), 75 µM (blue trace), and 100 µM (orange trace) concentration.

in those experiments, usually monochromatic LEDs at 450 nm,[19b,c,20] compared to the white light used herein. It is indeed very likely that, at high light intensities and low catalyst concentration, the rate of production of reduced photosensitizer (see below for a mechanistic discussion) is too fast relative to electron scavenging by the catalyst. This may cause the build-up of substantial stationary-state concentrations of reduced sensitizer, with enhancement of unproductive routes involving the chromophore.¶

At 50 µM **1** hydrogen evolving activity is also observed to be strongly dependent on pH (Table S2 and Figure S1 of the ESI) with the best values in terms of TON obtained at pH 4 and 5 (187 and 205, respectively), but with a slightly larger TOF achieved at pH 4 (8.1 $\mathrm{min^{-1}}$ at pH 4 and 7.4 $\mathrm{min^{-1}}$ at pH 5). This is likely the result of several factors playing together towards hydrogen generation such as (i) the stability of the sensitizer under continuous irradiation, likely related to protonation of its reduced form,[11c] decreasing with increasing acidity (Figure S2 of ESI), (ii) the thermodynamic driving force for the HER, and (iii) the protonation of the Co(I) species which is more favoured at lower pH.

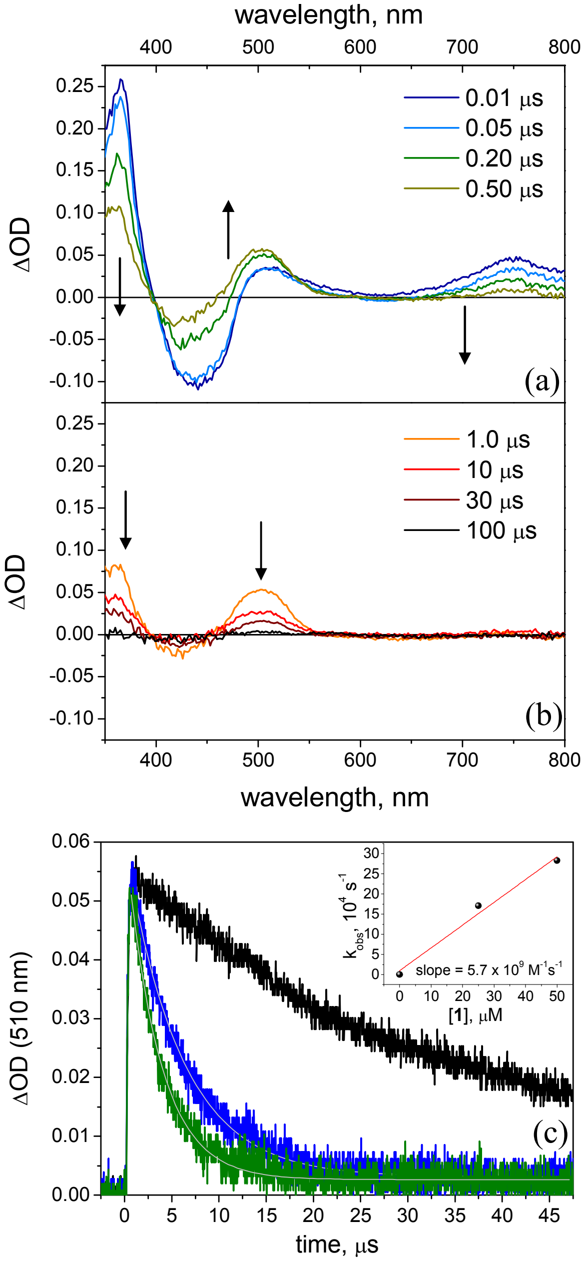


Fig. 3. Laser flash photolysis experiments (excitation at 355 nm, FWHM 6-8 ns): transient spectra obtained upon excitation of a 1 M acetate buffer (pH 4) solution containing 0.1 mM $\mathrm{Ru(bpy)_3^{2+}}$ and 0.1 M ascorbic acid at (a) 0.01-0.50 µs and (b) 1-100 µs time delays; (c) kinetic analysis of the $\mathrm{Ru(bpy)_3^{+}}$ decay at 510 nm in the absence (black trace) and in the presence of 25 µM (blue trace) and 50 µM **1** (green trace), (inset) plot of the pseudo-first order rate vs. catalyst concentration for the estimation of the bimolecular rate constant (slope).

Concerning the mechanism, two photochemical pathways are in principle available to the excited sensitizer for the reduction of **1** and eventual hydrogen production: (i) an oxidative quenching route,[10b,i,13c,15a] involving first oxidative quenching of the $\mathrm{Ru(bpy)_3^{2+}}$ triplet state by the catalyst, followed by hole shift to the ascorbic acid electron donor, or (ii) a reductive quenching route,[15b,18-25] where the excited sensitizer is primarily quenched by the donor and the so-formed $\mathrm{Ru(bpy)_3^{+}}$ reductant subsequently transfers the electron to the catalyst. In order to check for such possibilities, Stern-Volmer analyses of the $\mathrm{Ru(bpy)_3^{2+}}$ triplet state quenching by both **1** and ascorbic acid were performed. It is found that in 1 M acetate buffer (pH 4) the emission of the $\mathrm{Ru(bpy)_3^{2+}}$ excited state is quenched by **1** (Figure S3 of ESI) with a bimolecular rate constant $k = 3.1 \times 10^8$ $\mathrm{M^{-1}s^{-1}}$,§ and by the ascorbic acid donor (Figure S4) with a bimolecular rate constant $k = 1.0 \times 10^7$ $\mathrm{M^{-1}s^{-1}}$, consistent with previous findings.[20b] However, despite the difference of one order of magnitude in rate constants, under the photocatalytic conditions the concentration of the sacrificial electron donor and catalyst are such that reductive quenching by the ascorbic acid donor (0.1 M, pseudo-first order rate $k = 1.0 \times 10^6$ $\mathrm{s^{-1}}$) dominates over oxidative quenching by **1** (10-100 µM, pseudo-first order rate $k = 3.1\text{-}31 \times 10^3$ $\mathrm{s^{-1}}$). The electron transfer process from the reduced sensitizer to the catalyst can be easily followed by laser flash photolysis experiments.[11c,15b,19c,20b,25] Upon excitation of 1 M acetate buffer (pH 4) solutions containing 100 µM $\mathrm{Ru(bpy)_3^{2+}}$ and 0.1 M ascorbic acid formation of the reduced $\mathrm{Ru(bpy)_3^{+}}$ species, occurring in few hundred ns after electron transfer from the donor to the triplet excited state, is observed from the build-up of the characteristic absorption at 510 nm (Figure 3a).[31] This species in the absence of any catalyst undergoes slow bimolecular recombination with the oxidized ascorbate (Figure 3b). When **1** is introduced in solution similar spectroscopic variations are observed, however the decay of the 510-nm absorption becomes more rapid due to electron transfer from $\mathrm{Ru(bpy)_3^{+}}$ to the catalyst and under pseudo-first order kinetic conditions (Figure 3c) the bimolecular rate constant for this electron transfer can be estimated as $k = 5.7\ (\pm 0.7) \times 10^9$ $\mathrm{M^{-1}s^{-1}}$.† This value is considerably high, close to the diffusion limit, and falls within the same order of magnitude of bimolecular electron transfer rates from the reduced $\mathrm{Ru(bpy)_3^{+}}$ species to polypyridine cobalt complexes[19c,20b,25] and to a cationic cobalt porphyrin.[11c] It should be pointed out that the electron transfer rate from the reduced sensitizer to **1** is one of the most important parameter affecting the photocatalytic performance. A fast electron scavenging by the catalyst is indeed required in order to minimize alternative decomposition pathways involving the reduced species of the chromophore (one of the major reasons for the ceasing of the hydrogen evolving activity).[15b,20]

After the first photochemical reduction step, before hydrogen evolution, protonation of the so-formed reduced species of the catalyst is required yielding a Co(III)-H catalytic intermediate. On the basis of the above discussed electrochemical data (Figure 1 and Scheme 1) it is likely that at the pH 4 used in the photocatalytic experiments an additional reduction to a Co(II)-hydride species may take place. The first-order dependence of the initial rate of hydrogen production vs. catalyst concentration (Figure S5 of the ESI) is as expected for a heterolytic mechanistic pathway of hydrogen evolution.[10e,f]

As far as the turnover limiting reactions are concerned, decomposition of both the $Ru(bpy)_3^{2+}$ sensitizer and **1** can be regarded on the basis of the following experimental results. Upon addition of either $Ru(bpy)_3^{2+}$ (0.5 mM) or **1** (100 μM) to a photolyzed mixture (after 1 h photolysis of a 1 M acetate buffer solution at pH 4 containing 0.5 mM $Ru(bpy)_3^{2+}$, 100 μM **1**, and 0.1 M ascorbic acid) very low hydrogen evolving activity is recovered, 6% and 12% in terms of TON, respectively (Figure 4). On the other hand, a larger increase in hydrogen production is obtained if both catalyst and sensitizer are added to the photolyzed mixture (Figure 4), consistent with the partial decomposition of both components before their addition. In this latter case, however, the hydrogen evolving capability of the system is not restored completely, with an improvement of only 23% of the initial activity.

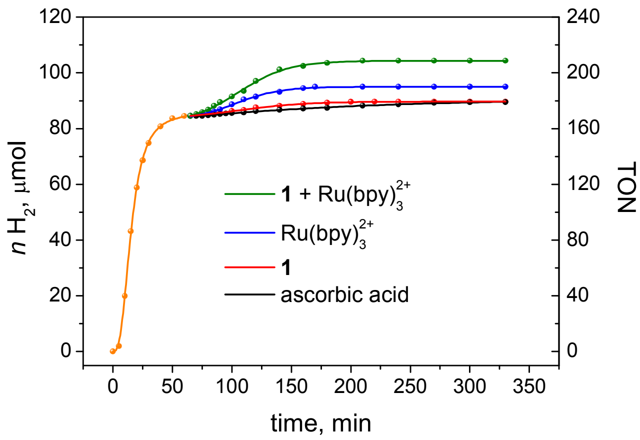


Fig. 4. Effect of addition of different components after 1 h photolysis on a 1 M acetate buffer (pH 4) solution containing 100 μM **1**, 0.5 mM $Ru(bpy)_3^{2+}$, and 0.1 M ascorbic acid (orange line): addition of 0.1 M ascorbic acid (black line), 100 μM **1** (red line), 0.5 mM $Ru(bpy)_3^{2+}$ (blue line), and both 100 μM **1** and 0.5 mM $Ru(bpy)_3^{2+}$ (green line).

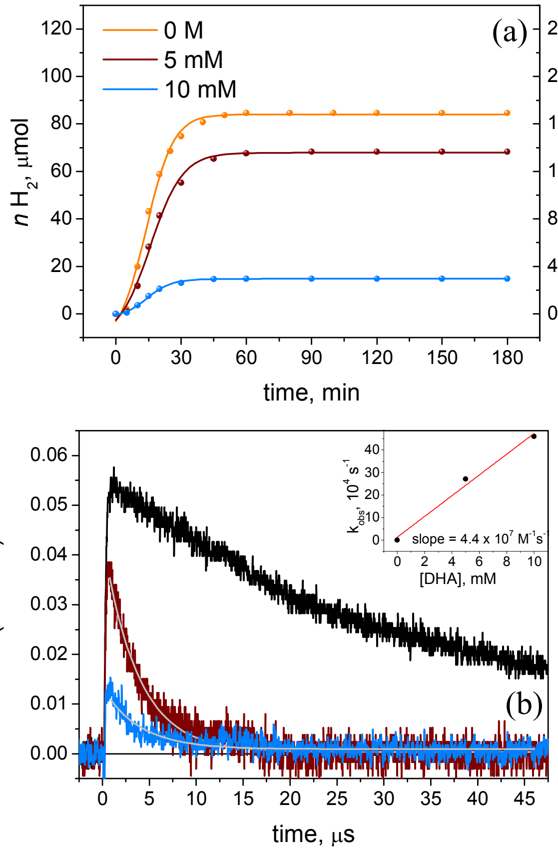
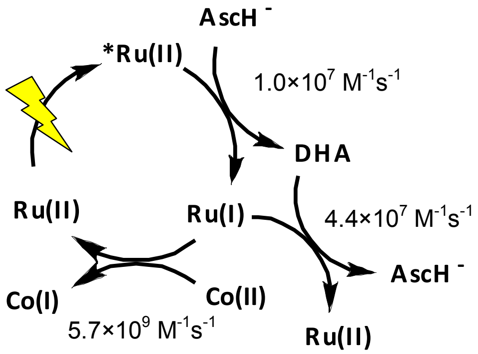


Fig. 5. (a) Effect of added external dehydroascorbic acid (0-10 mM) on the hydrogen evolution kinetic of a 1 M acetate buffer (pH 4) solution containing 100 μM **1**, 0.5 mM $Ru(bpy)_3^{2+}$, and 0.1 M ascorbic acid; (b) kinetic traces at 510 nm obtained by laser flash photolysis (excitation at 355 nm) on 1 M acetate buffer (pH 4) solution containing 1 mM $Ru(bpy)_3^{2+}$ and 0.1 M ascorbic acid, in the absence (black trace) and in the presence of 5 mM (brown trace) or 10 mM (light blue trace) dehydroascorbic acid (DHA). The difference in the prompt concentration of $Ru(bpy)_3^{+}$ at different dehydroascorbic acid content is mainly related to competition in 355-nm excitation light absorption between $Ru(bpy)_3^{2+}$ and dehydroascorbic acid.

Several reasons may in principle account for this result. The consumption of sacrificial electron donor can be definitely ruled out by experimental evidence (Figure 4, black trace) and considering the overall hydrogen yield after 1 h irradiation. Another source of inefficiency could be ascribed to the formation of decomposition products of the $Ru(bpy)_3^{2+}$ sensitizer, likely involving either protonation of the reduced bipyridine or dechelation of a bpy ligand with insertion of ascorbate[19c] or acetate,[20a] competing in the absorption of light with the fresh, undegraded sensitizer.[19c]

It must also be pointed out that once ascorbic acid is oxidized by photoinduced electron transfer with $Ru(bpy)_3^{2+}$ the one-electron oxidized species undergoes disproportionation producing ascorbic acid and dehydroascorbic acid.[32] When high substantial amounts of hydrogen are produced, as in the experimental conditions of Figure 4, a substantial amount of dehydroascorbic acid is produced as well.¥ As this oxidized product accumulates in solution, it may behave as a quencher of the reduced $Ru(bpy)_3^{+}$ species, thus inhibiting electron transfer to the catalyst and therefore hydrogen production. As a matter of fact, the hydrogen evolving activity of the photocatalytic mixture based on 100 μM **1**, 0.5 mM $Ru(bpy)_3^{2+}$, and 0.1 M

Scheme 2. Summary of the primary photochemical processes occurring upon light irradiation of the photolysis mixture containing $Ru(bpy)_3^{2+}$, **1**, and ascorbic acid. The following abbreviations have been used: Ru(II) = $Ru(bpy)_3^{2+}$, *Ru(II) = $*Ru(bpy)_3^{2+}$, Ru(I) = $Ru(bpy)_3^{+}$, $AscH^-$ = ascorbic acid, DHA = dehydroascorbic acid, Co(II) = **1**, and Co(I) = $\mathbf{1}^-$.



ascorbic acid in 1 M acetate buffer (pH 4) was found to be markedly affected by the addition of external dehydroascorbic acid (Figure 5a). At 10 mM dehydroascorbic acid concentration (which is roughly the amount of product formed without its external addition in the present experimental conditions) the final TON achieved after 3 h irradiation is ca. 20% of that obtained without external addition, well-correlating with the poor recovery in hydrogen evolving activity observed after addition of both $Ru(bpy)_3^{2+}$ and **1** after 1 h photolysis (see above, Figure 4). Additional, direct experimental evidence of this short-circuit by the dehydroascorbic acid side-product is obtained from laser flash photolysis experiments (Figure 5b) where, in the absence of any catalyst added, the transient absorption at 510 nm of the reduced $Ru(bpy)_3^{+}$ species, produced via photoinduced electron transfer from ascorbic acid to the triplet excited state of the chromophore, is observed to decay more rapidly when external dehydroascorbic acid is added. Under pseudo-first order kinetic conditions, estimation of the bimolecular rate constant of this short-circuiting process can be performed, yielding a $k = 4.4\ (\pm 0.5) \times 10^7\ M^{-1}s^{-1}$. This rate constant is considerably lower (by ca. two orders of magnitude) than that observed for the electron transfer from $Ru(bpy)_3^{+}$ to **1**, but the process may become important as long as hydrogen is produced and dehydroascorbic acid is stepwise accumulated. The whole set of primary photochemical processes occurring upon excitation of $Ru(bpy)_3^{2+}$ within the photocatalytic mixture is summarized in Scheme 2.

Altogether, these results suggest that ascorbic acid is less than ideal as a "sacrificial" electron donor, and that the use of the standard $Ru(bpy)_3^{2+}$/ascorbic acid pair is probably not the most suitable to evaluate univocally the hydrogen evolving activity of a molecular catalyst in homogeneous photocatalytic systems, in particular under conditions where copious amounts of hydrogen are produced.♠ Similar findings were also pointed out recently by Alberto[33] for a system involving a cobalt catalyst, a rhenium(I) polypyridine sensitizer, and ascorbic acid. In that case the short-cut process, by which the photogenerated reduced rhenium species was intercepted by the dehydroascorbic acid, proceeds with a slightly slower rate (bimolecular rate constant k = ca. $10^7\ M^{-1}s^{-1}$),[33] most likely as a result of the reduced rhenium species (−1.13 V vs. SCE)[34] being a less powerful reductant than the reduced ruthenium species (−1.28 V vs. SCE).[35]

As a final remark, oxidation of the reduced Co(I) species by both the transiently formed oxidized ascorbate and the accumulated dehydroascorbic acid product are other side-reactions potentially interfering towards an efficient hydrogen production. To this respect the choice of the right pH, affecting the protonation equilibria and rates of the Co(I) species, is a fundamental requirement to achieve a higher photocatalytic efficiency. However, the decrease of the pH to lower values is limited by the decreased stability of the reduced sensitizer under increased acidic conditions (see above and Figure S2).[11c]

Experimental section

Materials.

Acetonitrile for electrochemical experiments was of electrochemical grade. Milli-Q Ultrapure water and related buffer solutions were used for the spectroscopic and photolysis experiments. Ascorbic acid, dehydroascorbic acid, and $Ru(bpy)_3Cl_2.6H_2O$ were purchased from Sigma-Aldrich, and used as received. All the other chemicals were of reagent grade quality, and used as received.

Synthesis.

2,6-(bis(bis-2-pyridyl)-methoxymethane)pyridine (**Py5**) ligand was sythesized and purified according to literature procedures.[36] [Co(II)(**Py5**)Cl]Cl (**1**) was obtained by reaction of equimolar amounts of **Py5** and $CoCl_2{\cdot}6H_2O$ in refluxing methanol under Ar atmosphere, following a slightly adapted literature procedure.[37] See also ESI for additional details.

Electrochemical Meaurements.

Cyclic voltammetry (CV) measurements were carried out on a PC-interfaced Eco Chemie Autolab/Pgstat 30 Potentiostat. Argon-purged sample solutions in acetonitrile, containing 0.1 M $LiClO_4$, were used. A conventional three-electrode cell assembly was adopted: a saturated calomel electrode (SCE Amel) and a platinum electrode, both separated from test solution by a glass frit, were used as reference and counter electrodes, respectively; a glassy carbon electrode was used as the working electrode.

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.

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 - 8ns) 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. Signals from the photomultiplier (kinetic traces) were processed by means of a LeCroy 9360 (600 MHz, 5 Gs/s) 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 pathlength pyrex glass cuvette with head space obtained from a round-bottom flask) containing the solution. The measuring cell is sealed during the photoreaction: the head to which cell is attached has indeed four ports, closed with Swagelok® connections, two of them are part of a closed loop involving GC gas inlet and sample vent in order to analyze head space content without an appreciable gas consumption, and the other two are for the degassing procedure (input and output).

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 using Ar as carrier gas. 5 mL from the headspace of the reactor are sampled by the internal GC pump and 200 nL are injected in the column maintained at 60°C for separation and detection of gases. The unused gas sample is then reintroduced 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 M H_2SO_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 H_2 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 $Ru(bpy)_3^{2+}$ mother solution (5 mM), and further adding ascorbic acid (as solid) and **1** (0.4 mM mother solution). The solution was then put in the reactor, degassed by bubbling Ar for 20 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 quantified.

Conclusions

A new hydrogen evolving catalyst **1** has been synthesized and characterized. Its photocatalytic activity towards the HER in the presence of a $Ru(bpy)_3^{2+}$ sensitizer and ascorbic acid as sacrificial electron donor has been screened. In purely buffered aqueous solutions TONs and TOFs strongly dependent on both catalyst concentration and pH are observed with the best results at 50 μM **1** and at pH 4 (TON = 187 and TOF = 8.1 min^{-1}). Hydrogen production is triggered by excitation of the $Ru(bpy)_3^{2+}$ sensitizer which reacts at the excited state level with the ascorbic acid donor yielding a photogenerated reductant capable of electron transfer to **1** with a remarkable rate (bimolecular rate constant $k = 5.7\ (\pm 0.7) \times 10^9\ M^{-1}s^{-1}$). Hydrogen evolution is mainly limited by partial decomposition of both sensitizer and catalyst. Moreover, when high amounts of hydrogen are produced, the accumulation of dehydroascorbic acid, i.e., the oxidation product of the ascorbic acid donor, namely, is observed to strongly affect hydrogen production yield. This species quenches the reduced ruthenium species (bimolecular rate constant $k = 4.4\ (\pm 0.5) \times 10^7\ M^{-1}s^{-1}$), thus preventing electron transfer to the catalyst. This evidence points out that a straightforward evaluation of the photocatalytic activity of a molecular catalyst within homogeneous systems involving ascorbic acid can be misleading without a complete knowledge of the overall phenomena occurring within the three-component donor/sensitizer/acceptor system.

Acknowledgements

Financial support from the Italian MIUR (PRIN 20085ZXFEE and FIRB RBAP11C58Y ‘‘NanoSolar’’) and COST action CM1202 *PERSPECT-H₂O* are gratefully acknowledged.

Notes and references

[a] Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Ferrara, Via Fossato di Mortara 17-19, and Centro Interuniversitario per la Conversione Chimica dell’Energia Solare, sezione di Ferrara, Via L. Borsari 46, 44121 Ferrara, Italy. E-mail: mirco.natali@unife.it, snf@unife.it.

[b] Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Trieste, Via L. Giorgieri 1, 34127 Trieste, Italy. E-mail: eiengo@units.it.

‡ These authors contributed equally to the paper.

¶ These findings underline how a straightforward comparison between different photocatalytic systems studied in different laboratories must be taken with caution in order to establish the most active catalyst.

§ Quenching of $Ru(bpy)_3^{2+}$ emission by **1** can be in principle ascribed to both electron and energy transfer, as cobalt complexes display low energy d-d states potentially accessible from the triplet excited state of the sensitizer. Regardless of the mechanism, this quenching route is not sufficiently fast to compete with reductive quenching by the ascorbic acid donor.

† The incomplete decay (residual ΔOD ≈ 0.002 after ca. 50 μs) of the kinetic traces in the presence of **1** is consistent with electron transfer and reduction of the catalytic moiety as Co(I) species display broad absorption in the 500-700 nm region, as observed in similar cases.[19c,25]

¥ Hydrogen and dehydroascorbic acid concentration are interrelated, since in summary two electrons are withdrawn from one ascorbic acid molecule and used to produce one hydrogen molecule from two protons, yielding one dehydroascorbic acid molecule as a product.

♠ Ascorbic acid recycling by means of a secondary sacrificial electron donor was recently suggested to overcome this intrinsic resctriction.[38]

Electronic Supplementary Information (ESI) available: synthetic details, photolysis data, hydrogen evolving kinetics at different pH, comparison of aborption spectra before/after photolysis, Stern-Volmer plot of $^*Ru(bpy)_3^{2+}$ reductive quenching by ascorbic acid and oxidative quenching by **1**, plot of the initial hydrogen production rate vs. catalyst concentration. See DOI: 10.1039/b000000x/

1 (a) N. S. Lewis and D. G. Nocera, *Proc. Natl. Acad. Sci. U.S.A.*, 2006, **103**, 15729; (b) H. B. Gray, *Nat. Chem.*, 2009, **1**, 7; (c) D. Gust, T. A. Moore and A. L. Moore, *Faraday Disc.*, 2012, **155**, 9; (d) J. H. Alstrum-Acevedo, M. K. Brennaman and T. J. Meyer, *Inorg. Chem.*, 2005, **44**, 6802; (e) N. Armaroli, N., V. Balzani and N. Serpone, *Powering Planet Earth: Energy Solutions for the Future*, Wiley, New York, 2012; (f) R. Eisenberg and H. B. Gray, *Inorg. Chem.*, 2008, **47**, 1697; (g) D. G. Nocera, *Inorg. Chem.*, 2009, **48**, 10001; (h) J. J. Concepcion, R. L. House, J. M. Papanikolas and T. J. Meyer, *Proc. Natl. Acad. Sci. U.S.A.* 2012, **109**, 15560.

2 (a) K. J. Young, L. A. Martini, R. L. Milot, R. C. Snoeberger III, V. S. Batista, C. A. Schmuttenmaer, R. H. Crabtree and G. W. Brudvig, *Coord. Chem. Rev.*, 2012, **256**, 2503; (b) A. Sartorel, M. Bonchio, S. Campagna and F. Scandola, *Chem. Soc. Rev.*, 2013, **42**, 2262.

3 (a) Y. V. Geletii, Z. Huang, Y. Hou, D. G. Musaev, T. Lian and C. L. Hill, *J. Am. Chem. Soc.*, 2009, **131**, 7522; (b) F. Puntoriero, G. La Ganga, A. Sartorel, M. Carraro, G. Scorrano, M. Bonchio and S. Campagna, *Chem. Commun.*, 2010, **46**, 4725; (c) M. Orlandi, R. Argazzi, A. Sartorel, M. Carraro, G. Scorrano, M. Bonchio and F. Scandola, *Chem. Commun.*, 2010, **46**, 3152; (d) M. Natali, M. Orlandi, S. Berardi, S. Campagna, M. Bonchio, A. Sartorel and F. Scandola, *Inorg. Chem.*, 2012, **51**, 7324.

4 (a) N. S. McCool, D. M. Robinson, J. E. Sheats and G. C. Dismukes, *J. Am. Chem. Soc.*, 2011, **133**, 11446; (b) G. La Ganga, F. Puntoriero, S. Campagna, I. Bazzan, S. Berardi, M. Bonchio, A. Sartorel, M. Natali and F. Scandola, *Faraday Discuss.*, 2012, **155**, 177; (c) S. Berardi, G. La Ganga, M. Natali, I. Bazzan, F. Puntoriero, A. Sartorel, F. Scandola, S. Campagna and M. Bonchio, *J. Am. Chem. Soc.*, 2012, **134**, 11104; (d) F. Evangelisti, R. Güttinger, R. Moré, S. Luber and G. R. Patzke, *J. Am. Chem. Soc.*, 2013, **135**, 18734; (e) P. F. Smith, C. Kaplan, J. E. Sheats, D. M. Robinson, N. S. McCool, N. Mezle and G. C. Dismukes, *Inorg. Chem.*, 2014, **53**, 2113; (f) G. La Ganga, V. Mollica Nardo, M. Cordaro, M. Natali, S. Vitale, A. Licciardello, F. Nastasi and S. Campagna, *Dalton Trans.*, 2014, DOI: 10.1039/c4dt01785d.

5 M.-P. Santoni, G. La Ganga, V. Mollica Nardo, M. Natali, F. Puntoriero, F. Scandola and S. Campagna, *J. Am. Chem. Soc.*, 2014, **136**, 8189.

6 (a) E. Pizzolato, M. Natali, B. Posocco, A. Montellano López, I. Bazzan, M. Di Valentin, P. Galloni, V. Conte, M. Bonchio, F. Scandola and A. Sartorel, *Chem. Commun.*, 2013, **49**, 9941; (b) A. Montellano López, M. Natali, E. Pizzolato, C. Chiorboli, M. Bonchio, A. Sartorel and F. Scandola, *Phys. Chem. Chem. Phys.*, 2014, **16**, 12000.

7 (a) Z. Huang, Z. Luo, Y. V. Geletii, J. W. Vickers, Q. Yin, D. Wu, Y. Hou, Y. Ding, J. Song, D. G. Musaev, C. L. Hill and T. Lian, *J. Am. Chem. Soc.*, 2011, **133**, 2068; (b) M. Natali, S. Berardi, A. Sartorel, M. Bonchio, S. Campagna and F. Scandola, *Chem. Commun.*, 2012, **48**, 8808; (c) J. W. Vickers, H. Lv, J. M. Sumliner, G. Zhu, Z. Luo, D. J. Musaev, Y. V. Geletii and C. L. Hill, *J. Am. Chem. Soc.*, 2013, **135**, 14110; (d) X.-B. Han, Z.-M. Zhang, T. Zhang, Y.-G. Li, W. Lin, W. You, Z.-M. Su and E.-B. Wang, *J. Am. Chem. Soc.*, 2014, **136**, 5359.

8 (a) E. A. Karlsson, B.-L. Lee, T. Åkermark, E. V. Johnston, M. D. Kärkäs, J. Sin, Ö. Hansson, J.-E. Bäckvall and B. Åkermark, *Angew. Chem. Int. Ed.*, 2011, **50**, 11715; (b) R. Al-Oweini, A. Sartorel, B. S. Bassil, M. Natali, S. Berardi, F. Scandola, U. Kortz and M. Bonchio, *Angew. Chem. Int. Ed.*, 2014, DOI: 10.1002/anie.201404664.

9 (a) V. Artero, M. Chavarot-Kerlidou and M. Fontecave, *Angew. Chem. Int. Ed.*, 2011, **50**, 7238; (b) H. Ozawa and K Sakai, *Chem. Commun.*, 2011, **47**, 2227; (c) W. T. Eckenhoff and R. Eisenberg, *Dalton Trans.*, 2012, **41**, 13004; (d) W. T. Eckenhoff, W. R. McNamara, P. Du and R. Eisenberg, *Biochim. Biophys. Acta*, 2013, **1827**, 958.

10 (a) P. Du, K. Knowles and R. Eisenberg, *J. Am. Chem. Soc.*, 2008, **130**, 12576; (b) A. Fihri, V. Artero, M. Razavet, C. Baffert, W. Leibl and M. Fontecave, *Angew. Chem., Int. Ed.*, 2008, **47**, 564; (c) T. M. McCormick, B. D. Calitree, A. Orchard, N. D. Kraut, F. V. Bright, M. R. Detty and R. Eisenberg, *J. Am. Chem. Soc.*, 2010, **132**, 15480; (e) J. L. Dempsey, B. S. Brunschwig, J. R. Winkler and H. B. Gray, *Acc. Chem. Res.*, 2009, **42**, 1995; (f) J. L. Dempsey, J. R. Winkler and H. B. Gray, *J. Am. Chem. Soc.*, 2010, **132**, 1060; (g) F. Lakadamyali, A. Reynal, M. Kato, J. R. Durrant and E. Reisner, *Chem. Eur. J.*, 2012, **18**, 15464; (i) T. Lazarides, M. Delor, I. V. Sazanovich, T. M. McCormick, I. Georgakaki, G. Charalambidis, J. A. Weinstein and A. G. Coutsolelos, *Chem. Commun.*, 2014, **50**, 521.

11 (a) C. Hoon Lee, D. K. Dogutan, and D. G. Nocera, *J. Am. Chem. Soc*. 2011, **133**, 8775; (b) W. R. McNamara, Z. Han, P. J. Alperin, W. W. Brennessel, P. L. Holland and R. Eisenberg, *J. Am. Chem. Soc.*, 2011, **133**, 15368; (c) W. R. McNamara, Z. Han, C.-J. Yin, W. W. Brennessel, P. L. Holland and R. Eisenberg, *Proc. Natl. Acad. Sci. U.S.A.*, 2012, **109**, 15594; (d) M. Natali, A. Luisa, E. Iengo and F. Scandola, *Chem. Commun.*, 2014, **50**, 1842.

12 (a) D. Streich, Y. Astuti, M. Orlandi, L. Schwartz, R. Lomoth, L. Hammarström and S. Ott, *Chem. Eur. J.*, 2010, **16**, 60; (b) S.-P. Luo, E. Mejìa, A. Friedrich, A. Pazidis, H. Junge, A.-E. Surkus, R. Jackstell, S. Denurra, S. Gladiali, S. Lochbrunner and M. Beller, *Angew. Chem. Int. Ed.*, 2013, **52**, 419.

13 (a) M. P. McLaughlin, T. M. McCormick, R. Eisenberg and P. L. Holland, *Chem. Commun.*, 2011, **47**, 7989; (b) Z. Han, W. R. McNamara, M.-S. Eum, P. L. Holland and R. Eisenberg, *Angew. Chem., Int. Ed.*, 2012, **51**, 1667; (c) Z. Han, L. Shen, W. W. Brennessel, P. L. Holland and R. Eisenberg, J. Am. Chem. Soc., 2013, **135**, 14659; (d) M. A. Gross, A. Reynal, J. Durrant and E. Reisner, *J. Am. Chem. Soc.*, 2014, **136**, 356.

14 (a) H. Ozawa, M. Haga and K. Sakai, *J. Am. Chem. Soc.*, 2006, **128**, 4926; (b) S. Rau, B. Schäfer, D. Gleich, E. Anders, M. Rudolph, M. Friedrich, H. Görls, W. Henry and J. G. Vos, *Angew. Chem. Int. Ed.*, 2006, **45**, 6215; (c) M. Elvington, J. Brown, S. S. Arachchide and K. J. Brewer, *J. Am. Chem. Soc.*, 2007, **129**, 10644; (d) T. Stoll, M. Gennari, J. Fortage, C. E. Castillo, M. Rebarz, M. Sliwa, O Poizat, F. Odobel, A. Deronzier and M.-N. Collombe, *Angew. Chem. Int. Ed.*, 2014, **53**, 1654.

15 (a) P. Zhang, M. Wang, C. Li, X. Li, J. Dong and L. Sun, *Chem. Commun.*, 2010, **46**, 8806; (b) M. Natali, R. Argazzi, C. Chiorboli, E. Iengo and F. Scandola, *Chem. Eur. J.*, 2013, **19**, 9261; (c) K. Peuntinger, T. Lazarides, D. Dafnomili, G. Charalambidis, G. Landrou, A. Kahnt, R. P. Sabatini, D. W. McCamant, D. T. Gryko, A. G. Coutsolelos and D. M. Guldi, *J. Phys. Chem. C*, 2013, **117**, 1647; (d) M. Natali, M. Orlandi, C. Chiorboli, E. Iengo, V. Bertolasi, F. Scandola, *Photochem. Photobio. Sci.*, 2013, **12**, 1749; (e) J. C. Manton, C. Long, J. G. Vos and M. T. Pryce, *Dalton Trans.*, 2014, **43**, 3576; (f) J. Bartelmess, W. W. Weare and R. D. Sommer, *Dalton Trans.*, 2013, **42**, 14883; (g) J. Bartelmess, A. Francis, K. A. El Roz, F. N. Castellano, W. W. Weare and R. D. Sommer, *Inorg. Chem.*, 2014, **53**, 4527.

16 (a) X. Li, M. Wang, S. Zhang, J. Pan, Y. Na, J. Liu, B. Åkermark and L. Sun, *J. Phys. Chem. B*, 2008, **112**, 8198; (b) A. P. S. Samuel, D. T. Co, C. L. Stern and M. R. Wasielewski, *J. Am. Chem. Soc.*, 2010, **132**, 8813; (c) P. Poddutoori, D. T. Co, A. P. S. Samuel, C. H. Kim, M. T. Vagnini and M. R. Wasielewski, *Energy Environ. Sci.*, 2011, **4**, 2441.

17 T. Yu, Y. Zeng, J. Chen, Y.-Y. Li, G. Yang and Y. Li, *Angew. Chem. Int. Ed.*, 2013, **52**, 5631.

18 (a) B. Probst, A. Rodenberg, M. Guttentag, P. Hamm and R. Alberto, Inorg. Chem., 2010, **49**, 6453; (b) B. Probst, M. Guttentag, A. Rodenberg, P. Hamm and R. Alberto, *Inorg. Chem.*, 2011, **50**, 3404.

19 (a) Y. Sun, J. Sun, J. R. Long, P. Yang and C. J. Chang, *Chem. Sci.*, 2013, **4**, 118; (b) M. Nippe, R. S. Khnayzer, J. A. Panetier, D. Z. Zee, B. S. Olaiya, M. Head-Gordon, C. J. Chang, F. N. Castellano and J. R. Long, *Chem. Sci.*, 2013, **4**, 3934; (c) R. S. Khnayzer, V. A. Thoi, M. Nippe, A. E. King, J. W. Jurss, K. A. El Roz, J. R. Long, C. J. Chang and F. N. Castellano, *Energy Environ. Sci.*, 2014, **7**, 1477.

20 (a) W. M. Singh, T. Baine, S. Kudo, S. Tian, X. A. N. Ma, H. Zhou, N. J. DeYonker, T. C. Pham, J. C. Bollinger, D. L. Baker, B. Yan, C. E. Webster and X. Zhao, *Angew. Chem., Int. Ed.*, 2012, **51**, 5941; (b) B. Shan, T. Baine, X. A. N. Ma, X. Zhao and R. H. Schmehl, *Inorg. Chem.*, 2013, **52**, 4853.

21 A. Call, Z. Codolà, F. Acuna-Parés and J. Lloret-Fillol, *Chem. Eur. J.*, 2014, **20**, 6171.

22 C. Bachmann, M. Guttentag, B. Spingler and R. Alberto, *Inorg. Chem.*, 2013, **52**, 6055.

23 L. Tong, R. Zong and R. P. Thummel, *J. Am. Chem. Soc.*, 2014, **136**, 4881.

24 J. Xie, Q. Zhou, C. Li, W. Wang, Y. Hou, B. Zhang and X. Wang, *Chem. Commun.*, 2014, **50**, 6520.

25 W. M. Singh, M. Mirmohades, R. T. Jane, T. A. White, L. Hammarström, A. Thapper, R. Lomoth and S. Ott, *Chem. Commun.*, 2013, **49**, 8638.

26 C.-F. Leung, S.-M. Ng, C.-C. Ko, W.-L. Man, J. Wu, L. Chen and T.-C. Lau, *Energy Environ. Sci.*, 2012, **5**, 7903.

27 (a) D. J. Wasylenko, C. Ganesamoorthy, J. Borau-Garcia and C. P. Berlinguette, *Chem. Commun.*, 2011, **47**, 4249; (b) D. J. Wasylenko, R. D. Palmer, E. Schott and C. P. Berlinguette, *Chem. Commun.*, 2012, **48**, 2107.

28 J. T. Muckermann and E. Fujita, *Chem. Commun.*, 2011, **47**, 12456.

29 A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2nd ed.; John Wiley and Sons: New York, 2001.

30 J. P. Bigi, T. E. Hanna, W. H. Harman, A. Chang and C. J. Chang, *Chem. Commun.*, 2010, **46**, 958.

31 L. A. Kelly and M. A. J. Rodgers, *J. Phys. Chem.*, 1994, **98**, 6377.

32 (a) B. H. J. Bielski, D. A. Comstock and R. A. Bowen, *J. Am. Chem. Soc.*, 1971, **93**, 5624; (b) C. Creutz, N. Sutin and B. S. Brunschwig, *J. Am. Chem. Soc.*, 1979, **101**, 1298.

33 M. Guttentag, A. Rodenberg, R. Kopelent, B. Probst, C. Buchwalder, M. Brandstätter, P. Hamm and R. Alberto, *Eur. J. Inorg. Chem.*, 2012, 59.

34 M. Casanova, E. Zangrando, E. Iengo, E. Alessio, M. T. Indelli, F. Scandola and M. Orlandi, *Inorg. Chem.*, 2008, **47**, 10407.

35 P. Ceroni, G. Bergamini and V. Balzani, *Angew. Chem. Int. Ed.*, 2009, **48**, 8516.

36 R. T. Jonas and T. D. P. Stack, *J. Am. Chem. Soc.*, 1997, **119**, 8566.

37 R. J. M. Klein Gebbink, R. T. Jonas and T. D. P. Stack, *Inorg.Chem.*, 2002, **41**, 4633.

38 C. Bachmann, B. Probst, M. Guttentag and R. Alberto, *Chem. Commun.*, 2014, **50**, 6737.