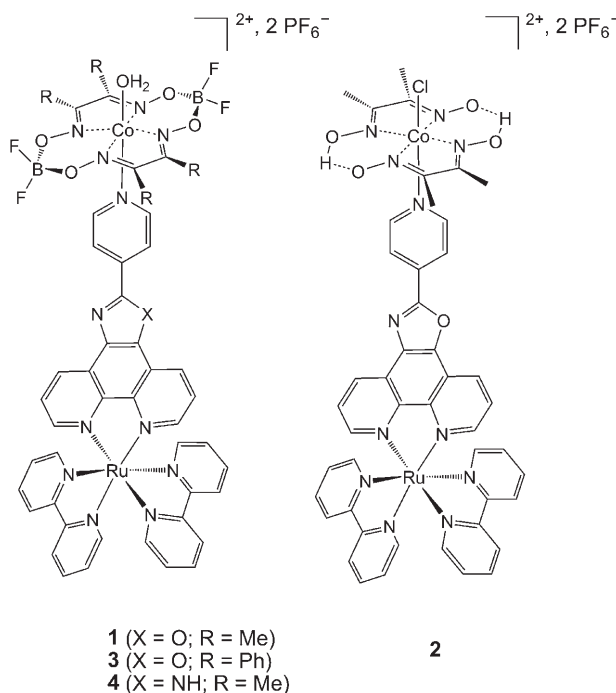


Cobaloxime-Based Photocatalytic Devices for Hydrogen Production**

Aziz Fihri, Vincent Artero,* Mathieu Razavet, Carole Baffert, Winfried Leibl, and Marc Fontecave

Dedicated to Professor P. Gouzerh on the occasion of his 65th birthday

Homogeneous light-driven catalytic systems for hydrogen production and, more generally, efficient photoactivated synthetic multielectron catalysts remain relatively scarce.^[1] Such systems^[2–4] generally consist of 1) a photosensitizer, often based on the ruthenium tris(diimine) moiety,^[5] 2) a metal-based catalytic center, and in some cases 3) an additional redox mediator. However, their efficiency remains to be improved in terms of both turnover numbers (stability) and turnover frequencies, and these systems should preferably rely on inexpensive first-row transition-metal catalysts rather than unsustainable noble metals. We and others recently reported that cobaloximes are very efficient and cheap electrocatalysts for hydrogen evolution.^[6–9] We thus decided to couple cobaloximes with ruthenium tris(diimine) moieties in order to make a supramolecular variant of the system previously studied by Lehn et al. for photochemical production of hydrogen.^[3] In such a molecular device, the intramolecular electron transfer from the photoactivated center to the catalytic center can potentially be controlled, and the charge-recombination processes limited, to an extent larger than in intermolecular systems, by fine-tuning both the distance between metal centers and the nature of the bridge.^[2,10] Such an organized assembly is found in hydrogen-evolving green algae, where the photosystem I is tightly coupled to hydrogenase enzymes.^[11] In this paper we describe the synthesis and activity of a series of novel heterodinuclear ruthenium–cobaloxime photocatalysts able to achieve the



Scheme 1. Structures of 1–4.

photochemical production of hydrogen with the highest turnover numbers so far reported for such devices.

Compounds **1–3** (Scheme 1) were synthesized in good yields^[12] by replacing one axial ligand of cobaloxime moieties with the pyridine residue of the previously reported $[(bpy)_2Ru(L-pyr)]^{2+}$ complex ($L-pyr = (4-pyridine)oxazolo-[4,5-f]phenanthroline$).^[13] NMR measurements and ESI-MS analysis are consistent with the $L-pyr$ ligand connecting the ruthenium and cobalt centers. This was further supported by cyclic voltammetry:^[12] in addition to ruthenium-centered processes, which are not significantly modified upon complexation to the cobalt center, cyclic voltammograms of **1–3** show Co^{II}/Co^I reversible processes shifted by ≈ 80 mV to more positive potentials relative to the starting cobaloximes, probably because of the overall $2+$ charge of the compounds.

We checked by cyclic voltammetry that the cobaloxime moieties retain their electrocatalytic properties for hydrogen production in all three heterodinuclear complexes: an electrocatalytic wave corresponding to proton reduction develops at -0.45 V vs. $Ag/AgCl$ upon addition of increasing amounts of p -cyanoanilinium tetrafluoroborate to a solution of **1** in CH_3CN ^[12] (electrocatalytic waves are observed at -0.9 V vs.

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AgCl for **2** in the presence of Et₃NHCl and −0.65 V vs AgCl for **3** in the presence of *p*-cyanoanilinium tetrafluoroborate).

H₂ was produced when a CdI-doped Hg light source was used to irradiate acetone solutions of **1–3** in the presence of 100 equiv of Et₃N as the sacrificial electron donor and 100 equiv of Et₃NHBF₄ as the proton source (Table 1). No

Table 1: Photocatalytic hydrogen production in acetone using Et₃N as the sacrificial electron donor. TONs are calculated based on the cobalt moiety.

Run	Photocatalyst ^[a]	Irrad. time [h]	TON ^[b]
1	1	1	32
2	1	4	56
3	1	4	60 ^[c]
4	1	8	85 ^[c]
5	1	1	16 ^[d]
6	1	15	103 ^[d]
7	1	4	22 ^[e]
8	2	4	17
9	2	4	14 ^[d]
10	3	4	12
11	—	4	<1
12	[(bpy) ₂ Ru(L-pyr)](PF ₆) ₂	4	<1
13	[Co(dmgbF ₂) ₂ (OH ₂) ₂]	4	<1
14	[Ru(bpy) ₃]Cl ₂ + 1 equiv [Co(dmgbF ₂) ₂ (OH ₂) ₂]	1	20 ^[f]
15	[Ru(bpy) ₃]Cl ₂ + 2.4 equiv [Co(dmgbH) ₂ (OH ₂) ₂] + 15.4 equiv dmgbH ₂ ^[g]	4	2 ^[f]

[a] [Ru] = 0.43 mmol L^{−1}. [b] Irradiation was performed in Pyrex glassware using a 150-W CdI-doped Hg lamp; unless otherwise stated, 100 equiv Et₃N and 100 equiv Et₃NH⁺ were added. [c] 300 equiv Et₃N and 300 equiv Et₃NH⁺ were added. [d] A UV cut-off filter was placed between the lamp and the Schlenk tube. [e] 100 equiv Et₃N and 100 equiv H₂O were added. [f] Only traces of H₂ were detected when a UV cut-off filter was used. [g] dmgb^{2−} = dimethylglyoximate dianion.

H₂ could be detected when the catalyst was omitted (run 11, Table 1) or replaced by the mononuclear ruthenium complex (run 12, Table 1) or the mononuclear cobaloxime moiety (run 13, Table 1). With up to 56 turnovers achieved over 4 h (Figure 1), **1** proved to be more active as a photocatalyst than **2** and **3** (compare runs 2, 8, and 10, Table 1). Increasing the amounts of Et₃N and Et₃NHBF₄ had only a slight effect (compare runs 2 and 3, Table 1). Prolonged irradiation led to increased H₂ production (compare runs 2 and 1, 4 and 3, and 6 and 5, Table 1). The maximum turnover frequency in the case

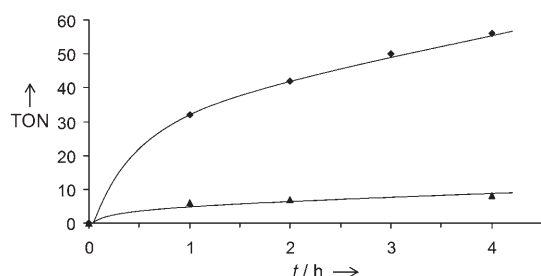


Figure 1. Photochemical production of hydrogen from acetone (◆) and acetonitrile (▲) solutions (10 mL) of Et₃N (0.043 mol L^{−1}) and Et₃NHBF₄ (0.043 mol L^{−1}) catalyzed by **1** (0.43 mmol L^{−1}).

of **1** was observed during the first hour of irradiation but hydrogen production was sustained for the following time with a turnover frequency (TOF) of 7–8 h^{−1}. Up to 85 turnovers could be obtained in an eight-hour experiment (run 4, Table 1). Lower amounts of H₂ were obtained in CH₃CN (10 turnovers within 4 h, Figure 1), MeOH (TON = 9), DMF (TON = 3), and 1,2-dichloroethane (TON = 0).^[14] When the reaction was carried out using water as the proton source instead of Et₃NH⁺, much lower turnover numbers were obtained (run 7, Table 1), probably because the pH value was too high. Compounds **1** and **2** were active when a UV cut-off filter was used (runs 5, 6, and 9, Table 1) as well. Under these conditions more than 100 turnovers (run 6, Table 1) could be achieved in 15 h. Comparison of runs 5 and 1 indicates that both UV and visible light contribute to the photochemical production of H₂ using **1** as catalyst. Finally **4**, a close analogue of **1** in which the bridging ligand was modified by replacing the central oxazole unit with an imidazole unit (Scheme 1), showed a two-fold increased photocatalytic activity with 104 turnovers achieved within 4 h in the same conditions as used in run 2.

The mechanism for cobaloxime-catalyzed hydrogen evolution is now well documented. It implies the reduction of the cobaloxime to the Co^I state followed by protonation to yield a cobalt(III) hydride intermediate.^[6,7,15] The latter is then protonated to generate dihydrogen. The resulting Co^{III} species is finally reduced either at the electrode or through a retrodisproportionation reaction with bulk Co^I. Since the observed electrocatalytic potentials are more positive than the standard potentials of the [Ru(bpy)₃]³⁺/[Ru(bpy)₃]²⁺ (E⁰ = −0.87 V vs. standard hydrogen electrode (SHE)) or the [Ru(bpy)₃]²⁺/[Ru(bpy)₃]⁺ (E⁰ = −1.28 V vs. SHE) couples,^[16] photochemical production of hydrogen mediated by compounds **1–3** is likely to proceed from the thermodynamically favorable electron transfer to the catalytic cobalt center either directly from the photoexcited ruthenium moiety (oxidative quenching) or from the reduced sensitizer resulting from reductive quenching by an electron donor. This could be confirmed by irradiation experiments carried out in the presence of Et₃N as the electron donor but without any added proton source: flashing a solution of **1** in DMF with 440-nm laser light resulted in the appearance of a broad absorption band located at 600 nm, which could be assigned to reduced cobaloxime, either described as a Co^I species or as a Co^{II} ion in interaction with a radical located on the ligand.^[9,15] Photoaccumulation of this species reached a saturation level after about 100 flashes. Addition of a great excess of *p*-cyanoanilinium tetrafluoroborate leads to recovery of the original absorption spectrum of the sample.

Measurements of luminescence lifetimes at 650 nm upon laser excitation at 532 nm were performed in deaerated acetone in order to gain more insight into the electron-transfer mechanism. All complexes displayed the classical exponential decay of the metal–ligand charge-transfer (MLCT) state (lowest triplet excited state resulting from intersystem crossing)^[12] observed for other ruthenium tris-(diimine) compounds. First-order decay lifetimes of 1.63, 1.17, and 1.72 μs were obtained for **1**, **2**, and **3**, respectively. These data are consistent with an oxidative quenching mechanism

(light-induced electron transfer from the photoexcited ruthenium moiety to the cobaloxime center). However, this process is only slightly competitive with the intrinsic decay of the MLCT (1.72 μ s) measured on [(bpy)₂Ru(L-pyr)](PF₆)₂. On the basis of the comparison of these lifetimes^[17] yields of 5 %, 32 %, and < 1 % and intrinsic time constants for electron transfer of 30 μ s, 4 μ s, and > 300 μ s, respectively, could be estimated for **1**, **2**, and **3**.^[18]

In Table 1, we also compare the photocatalytic properties of our novel supramolecular systems with those of multicomponent {[Ru(bpy)₃]²⁺/cobaloxime} systems. In the dmGH series, the multicomponent system afforded only 2 turnovers (run 15, Table 1) after 4 h, whereas 17 were obtained with **2** (run 8, Table 1). In the dmGBF₂ series, the supramolecular system was also superior but to a lesser extent (compare runs 1 and 14, Table 1). The difference became much greater when the samples were irradiated using a UV cut-off filter since under these conditions, the multicomponent systems were very slow, in agreement with previous reports,^[3] while **2** maintains its activity and **1** retains half of it.

The high catalytic activity of the supramolecular systems described here relies on the following considerations. First, the H₂-evolving catalytic center in **1** is quite stable towards both hydrolysis and hydrogenation reactions. The BF₂-bridged catalytic center is known to be more resistant towards acidic hydrolysis,^[19] and the lowered nucleophilicity of its hydride derivative^[7] limits undesired hydrogenation reactions. By contrast, addition of 6 to 15 equiv of free dmGH₂ was found to be necessary in the multicomponent system described by Lehn et al. to prevent dissociation of [Co(dmGH)₂(OH₂)₂] and replace hydrogenated ligand formed by side reactions.^[3]

Second, the Co^{II} state is more easily reducible in BF₂-bridged than in H-bridged cobaloximes, which facilitates electron transfer from the ruthenium to the cobalt center. This is demonstrated by comparison of the activity of **1** and **2** under the same conditions as well as in the multicomponent system: substituting [Co(dmGBF₂)₂(OH₂)₂] ($E^0(\text{Co}^{\text{II}}/\text{Co}^{\text{I}}) = -0.55$ V vs. Ag/AgCl) for [Co(dmGH)₂(OH₂)₂] ($E^0(\text{Co}^{\text{II}}/\text{Co}^{\text{I}}) = -0.98$ V vs. Ag/AgCl) results in a tenfold increase in hydrogen production (runs 14 and 15, Table 1).

Third, the presence of a conjugated bridging ligand facilitates the transfer of photogenerated electrons either through bonds or by an outer-sphere mechanism favored by the spatial proximity of the ruthenium center and the catalytic cobaloxime moiety. Under similar conditions, the supramolecular systems are indeed from 1.5 to 8.5 times more efficient than the multicomponent system, in which generation of the catalytically active Co^I center occurs through intermolecular electron transfer from the light-harvesting unit. When 1 equiv of pyridine was added to the systems described in runs 14 and 15 (Table 1) in order to compare catalysts with the same coordination sphere at cobalt, no effect on the photocatalytic activity was observed.

The ruthenium–cobaloxime compounds reported here are the first supramolecular photocatalysts for hydrogen production using first-row transition-metal H₂-evolving catalytic centers.^[2] Furthermore, compared to the three previously reported supramolecular systems, **1** (with up to 103 turnovers

achieved in 15 h; run 6, Table 1) provides the largest reported turnover number: the Ru–Pt photocatalyst synthesized by Sakai et al. was shown to achieve 4.8 turnovers over 10 h of irradiation in water,^[20] the Ru–Pd photocatalyst designed by Rau et al. stops after 56 turnovers over 29 h irradiation in acetonitrile,^[21] and up to 60 TON was reported for the Ru–Rh system from Brewer et al.^[22,23] Compound **1** proves also competitive with regard to [Rh₂(dfpma)₃(PPh₃)(CO)] (dfpma = bis(difluorophosphino)methylamine) which achieves 80 turnovers for H₂ production in 0.1 M HCl in THF with $\lambda_{\text{exc}} > 338$ nm.^[24]

The supramolecular compounds presented here pave the way towards efficient photocatalytic devices for hydrogen production. First of all, substituting cobalt for rare and expensive platinum, palladium, or rhodium metals in photocatalysts is a first step toward economically viable hydrogen production. Cobaloximes appear to be good candidates for H₂-evolving catalysts, and they may provide a good basis for the design of photocatalysts that function in pure water as both the solvent and the sustainable proton source. Secondly, a molecular connection between the sensitizer and the H₂-evolving catalyst seems to provide advantages regarding the photocatalytic activity. Structural modifications of this connection should allow a better tuning of the electron transfer between the light-harvesting unit and the catalytic center and thus an increase of the efficiency of the system. Further developments may eventually lead to the replacement of the rare and expensive ruthenium center by other photosensitizers such as inorganic nanoparticles (quantum dots) or nanocrystalline materials meeting all the specifications required for technological applications.

Experimental Section

See the Supporting Information for experimental details including synthetic and photocatalytic assay procedures, cyclic voltammograms of **1**, [Co(dmGBF₂)₂(dmf)₂], [(bpy)₂Ru(L-pyr)](PF₆)₂ (Figure S1), and **3** (Figure S2), electrochemical parameters for **1–3** and corresponding cobaloximes (Table S1), electrocatalytic behavior of **1** (Figure S3), and emission kinetics and steady-state emission spectra of **1–3** (Figures S4 and S5).

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