Supporting Information - Photocatalytic H_2 Production from Water with Rhenium and Cobalt Complexes.

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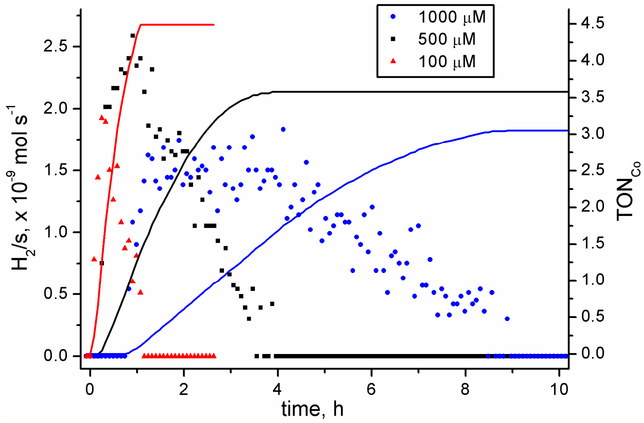

Figure SI 1. H_2 production for different concentrations of **10** (mol/s, left scale, dots; TON_{Co} ,right scale, solid lines). Conditions: 30 µM **1**, 100, 500 or 1000 µM **10**, 1 M TEOA, 0.1 M HBF_4, H_2O, 10 ml, 380 nm, $q_{n,p}$ = 1.75 x 10^{-7} einstein/s.

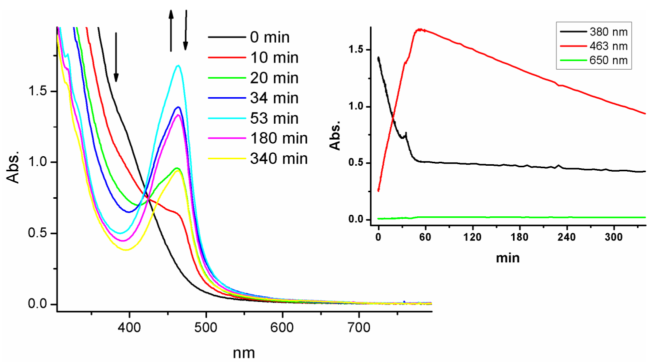

Figure SI 2. Typical absorption change during photolysis (30 µM **1**, 500 µM **10**, 1 M TEOA, 0.1 M HBF_4, H_2O, 3 ml, 380 nm, $q_{n,p} \approx 10^{-9}$ einstein/s).

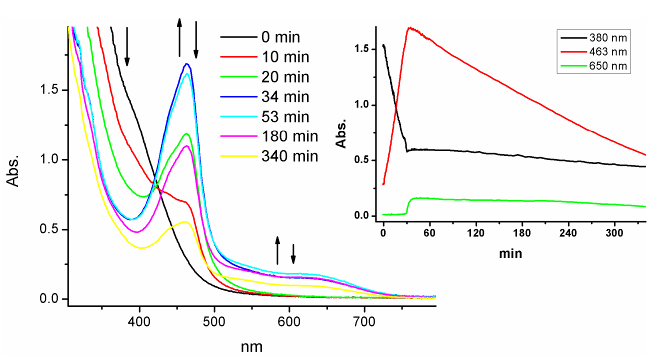

Figure SI 3. Typical absorption change during photolysis (30 µM **1**, 500 µM **10**, 1 M TEOA, 1 mM HBF_4, H_2O, 3 ml, 380 nm, $q_{n,p} \approx 10^{-9}$ einstein/s).

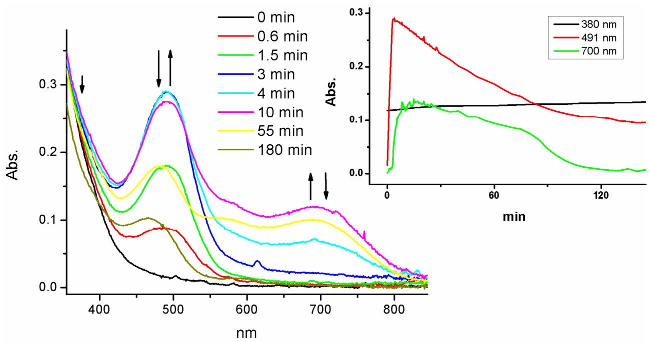

Figure SI 4. Typical absorption change during photolysis (30 µM **1**, 100 µM **15**, 1 M TEOA, 100 mM HBF_4, H_2O, 3 ml, 380 nm, $q_{n,p} \approx 10^{-9}$ einstein/s).

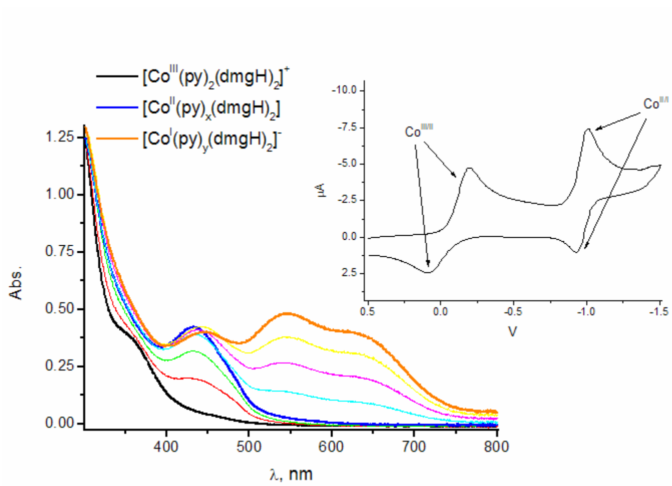

Figure SI 5. Absorption change observed in a OTTLE cell upon applying a potential of -1.2 V on a 2.5 mM solution of $[Co(py)_2(dmgH)_2]PF_6$ in DMF (selected traces, 0.1 M $[TBA]PF_6$, Ar, Pt mesh WE, Pt CE, Ag/AgCl RE, d = 0.2 mm). Inset: cyclic voltametry on a 1 mM solution of the latter complex (0.1 M $[TBA]PF_6$, DMF, Ar, 0.1 V/s), showing the irreversible $Co^{III/II}$ couple (upon reduction one axial pyridine is lost) and the reversible $Co^{II/I}$ couple (reversibility on the CV timescale does not necessarily mean reversibility in the bulk experiment, eg. it is possible that the d^8 species $[Co(dmgH)_2]^-$ is formed in the spectro-electrochemical experiment).

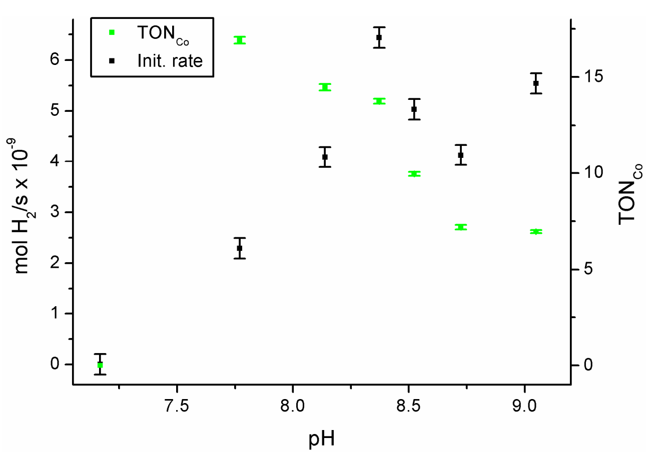

Figure SI 6. Initial H_2 production rates (left scale, ■, mol/s) and end TON_{Co} (right scale, ■) as a function of pH. Conditions: 30 µM **1**, 500 µM **11**, 1 M TEOA, varying HBF_4, H_2O, 10 ml, 380 nm, $q_{n,p} = 1.75 \times 10^{-7}$ einstein/s.

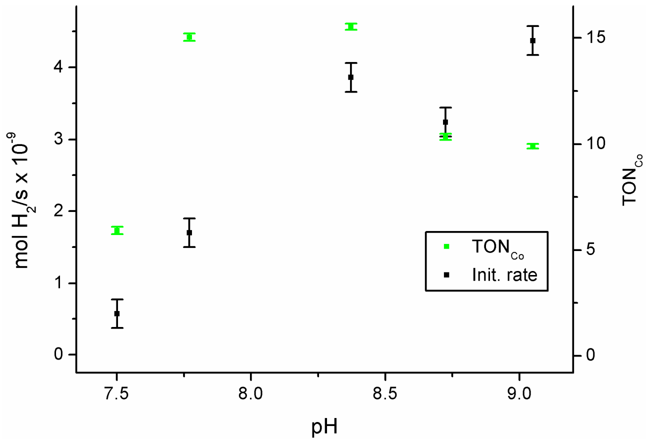

Figure SI 7. Initial H_2 production rates (left scale, ■, mol/s) and end TON_{Co} (right scale, ■) as a function of pH. Conditions: 30 µM **1**, 500 µM **15**, 1 M TEOA, varying HBF_4, H_2O, 10 ml, 380 nm, $q_{n,p} = 1.75 \times 10^{-7}$ einstein/s.

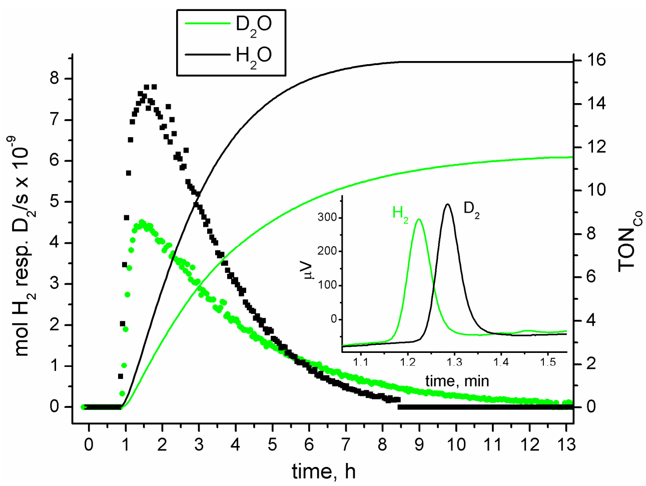

Figure SI 8. Comparison of catalytic performance in D_2O vs H_2O for **15** (mol/s, left scale, dots; TON_{Co}, right scale, solid lines; 30 µM **1**, 0.5 mM **15**, 1 M TEOA, 0.1 M HBF_4, H_2O resp. D_2O, Ar, 10 ml, 380 nm, $q_{n,p} = 1.75 \times 10^{-7}$ einstein/s). Inset: raw GC/TCD chromatograms showing the H_2 (green) resp. the D_2 (black) signals recorded 100 min after the start of the resp. experiment.

Table SI 1. Comparison of experiments with **10**, **11**, **11** + 1 eq. pyridine and **15** in H_2O versus D_2O.[a]

compound	TON_{Co} (H_2 resp. D_2 per WRC)	$TOF_{init.}$ (x 10^{-9} mol/s)
10, H_2O	3.3 ± 0.1	2.3 ± 0.3
10, D_2O	2.4 ± 0.1	2.6 ± 0.2
11, H_2O	7.4 ± 0.2	5.6 ± 0.3
11, D_2O	7.7 ± 0.2	5.7 ± 0.2
11 + py[b], H_2O	7.8 ± 0.2	6.4 ± 0.3
11 + py[b]	9.0 ± 0.2	6.9 ± 0.2
15, H_2O	11 ± 0.3	4.0 ± 0.3
15, D_2O	15.9 ± 0.4	7.8 ± 0.2

[a]: 30 µM **1**, 0.5 mM WRC, 1 M TEOA, 0.1 M HBF_4, H_2O resp. D_2O, Ar, 10 ml, 380 nm, $q_{n,p} = 1.75 \times 10^{-7}$ einstein/s. [b]: 1 eq. of pyridine, quantitative formation of [CoBr(py)DOH]Br.