SUPPLEMENTARY INFORMATION FOR

Carbon dioxide reduction via light activation of a ruthenium-Ni(Cyclam) complex

Christian Herrero,*[a] Annamaria Quaranta,[b] Sanae El Ghachtouli,[b] Boris Vauzeilles,[c,d] Winfried Leibl,[b] and Ally Aukauloo*[a,b]

Experimental

Electrochemical measurements

Cyclic voltammetry was performed with a CH Instruments electrochemical workstation. Acetonitrile was distilled prior to each experiment and the solution (1 mM for the complexes, 0.1 M of tetrabutylammonium perchlorate) was introduced in an argon-purged electrochemical cell. The experiments were performed using a glassy carbon electrode as the working electrode, a platinum wire as the counter electrode, and an Ag/$AgClO_4$ (0.01 M) electrode in acetonitrile as the reference electrode (0.29 V vs. SCE).

Steady-state absorption and emission

Ground state absorption spectra were measured in a Specord spectrophotometer (Analytic Jena) with 1 cm quartz cells. Steady state emission spectra were recorded in a Varian Eclipse Spectrofluorimeter. Samples were excited at 460 nm with absorbances optically matched at 0.1. $[Ru(bpy)_3]^{2+}$ was used as reference for emission quantum yield (Φ_{em}) calculation in acetonitrile with a $\Phi_{em} = 0.059$.[1] Samples were purged for 20 min with argon prior to each experiment.

Nanosecond laser flash photolysis

For transient absorption kinetic and spectral measurements in the time range 10 ns to 100 ms we used an Edinburgh Instruments LP920 Flash Photolysis Spectrometer system that incorporated a Continuum Surelite OPO for sample excitation (~7 ns pulse duration). The OPO was pumped by a Continuum Q-switched Nd:YAG laser operating at 355 nm. The LP920 system uses a 450 W Xenon arc lamp as the probe for the transient absorption kinetic measurements. Detection of the signal was performed either by a PMT or a water-cooled ICCD camera. The presented transient absorption spectra were typically the average of 20-50 measurements.

Photocatalysis and Gas Chromatography

In photocatalysis experiments, a 20 mL aqueous solution containing ~30 μM Ru-Cyclam-Ni **(9)** and 100 mM ascorbate (pH 6.5) was irradiated with a 800W CW halogen lamp, after being purged with CO_2 for 1 hour. In order to excite only the chromophore's MLCT band and to prevent the sample from excessive heating a 435 nm cut-off filter and a water bath were set between the sample and the light source. For gas analysis 50 μL gas aliquots were withdrawn from the head space with a gas-tight syringe and injected into a GC (Trace GC Ultra, Thermo Scientific) equipped with a TCD detector. The GC was equipped with a 30 m molecular sieve column having a diameter of 0.53mm and helium was employed as carrier gas. Under these experimental conditions, CO was detected with a retention time of ~2 minutes, and H_2 at ~0.90 minutes.

EPR spectroscopy and Sample Illuminations

For X-band EPR measurements, we used a Bruker Elexsys E 500 EPR spectrometer with an Oxford ESR9 liquid helium flow cryostat using a gold-chromel thermocouple directly below the sample position. A dual mode cavity ER 4116DM was used with resonance frequency 9.6 GHz (perpendicular mode). Ru^{II}-Cyclam-Ni **(9)** was dissolved in a 1:1 (v/v) mixture of acetonitrile/100 mM triethylamine aqueous solution, transferred to an EPR tube and frozen in a liquid nitrogen:ethanol solution. The EPR tube was then pumped to vacuum 4-5 times to purge oxygen from the sample, and finally transferred into liquid nitrogen for cooling to 77 K before being entered into the EPR spectrometer. Sample concentrations were typically 1 mM. For illuminations experiments the sample in the EPR tube (prepared as described above) was thawed and illuminated using a 450 nm diode at room temperature for 5 minutes. After illumination, the sample was rapidly transferred to a ~ -100°C ethanol bath for ~1-2 minutes, and then into liquid nitrogen before being transferred to the EPR spectrometer.

Spectroscopic properties

Steady state absorption

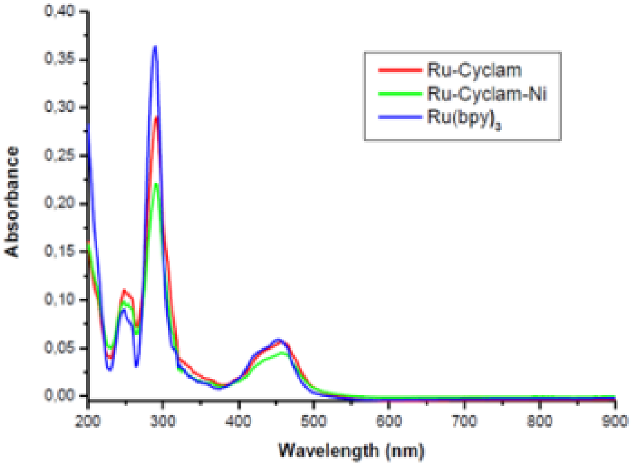


Figure S1. Ground-state absorption of $[Ru(bpy)_3]^{2+}$ (blue), Ru-Cyclam **(8)** (red), Ru-Cyclam-Ni **(9)** (green).

Emission

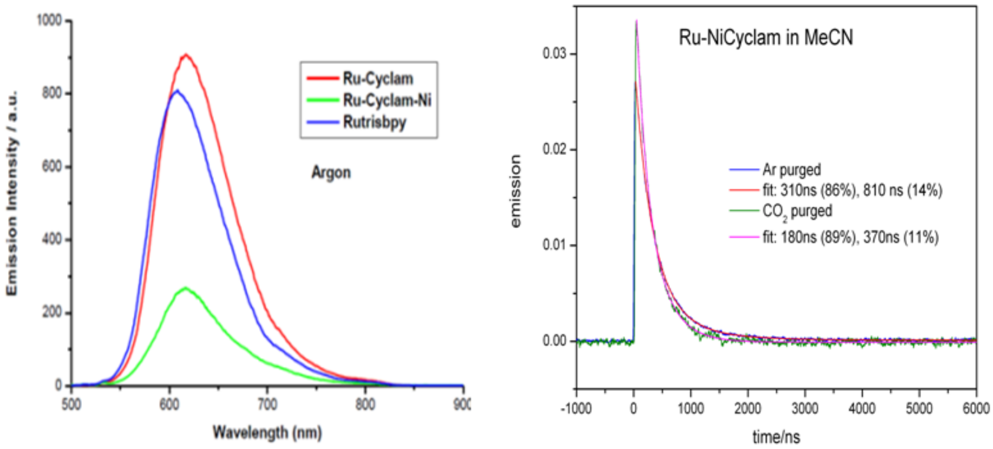


Figure S2. (Left): Emission spectra of Ru-Cyclam **(8)** (red), Ru-Cyclam-Ni **(9)** (green), and $[Ru(bpy)_3]^{2+}$ (blue). Right: Kinetics of Ru-Cyclam-Ni **(9)** in acetonitrile solutions purged with Ar (blue) or CO_2 (green). λ_{exc} = 450 nm, λ_{det} = 610 nm.

Photoinduced electron transfer

To investigate photo-induced electron transfer reactions, ascorbate was used as reversible electron donor. On the timescale of our laser flash photolysis experiments, degradation of oxidized ascorbate may be safely neglected since, as shown in Figure S3 for complex 9, at long time delays after the laser flash (1 ms) the transient absorption spectrum does not indicate any significant absorption features.

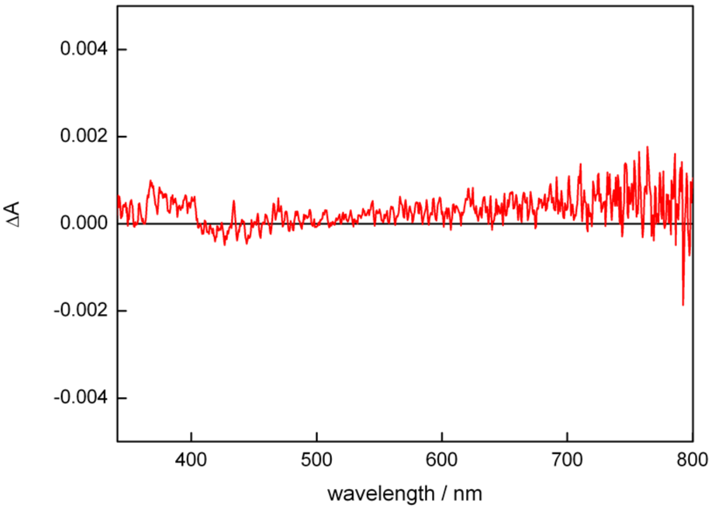
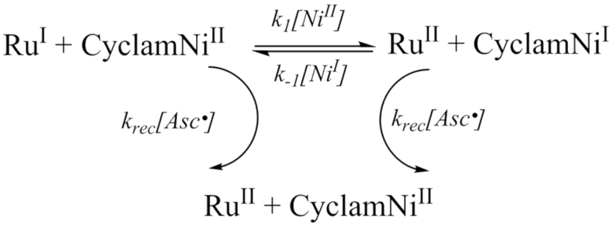


Figure S3. Transient absorption spectrum recorded for complex **9** in H_2O/CH_3CN (50:50) at 1 ms after laser flash (gate: 1 µs). λ_{exc}= 460 nm, A_{460} = 0.4. Laser energy 6 mJ.

In our experiments, we have observed that the recombination reaction of $[Ru(bpy)_3]^+$ and oxidized ascorbate follows a pseudo-first order kinetics rather than, as expected, a pure second order one. This is explained by the presence of traces of some oxidized ascorbate, even in a newly opened ascorbate bottle (purity ≥ 98%, Aldrich). Due to the high concentrations of ascorbate employed (100 mM), even the presence of 0.1% oxidized ascorbate (100 µM) yields a background concentration of oxidized ascorbate significantly higher than the concentration of flash-generated Ru^I (~1 µM) thus justifying a pseudo-first order approximation.

Inter-molecular electron transfer

In the presence of Cyclam-Ni^{II}, reaction Scheme 1, given below, was considered:



Scheme S1: Possible reaction pathways after photo-activation of $[Ru(bpy)_3]^{2+}$ in presence of Cyclam-Ni and an electron donor.

And the associated equations were obtained

$$\frac{dRu^I}{dt} = -k_1[Ru^I][Ni^{II}] - k_{rec}[Ru^I][Asc^\bullet] + k_{-1}[Ru^{II}][Ni^I] \tag{1}$$

$$\frac{dNi^I}{dt} = +k_1[Ru^I][Ni^{II}] - k_{rec}[Ru^I][Asc^\bullet] - k_{-1}[Ru^{II}][Ni^I] \tag{2}$$

However, the scheme becomes simplified by few considerations

(i) Taking into account that $[Ni^I] \leq [Ru^I] \sim 1$ µM and that $k_{-1} \leq k_d \sim 10^9$ M^{-1} s^{-1}, it results that $k_{-1}[Ni^I] \leq 10^3$ s^{-1}, that is charge recombination between Ru^{II} and Ni^I is slower than charge recombination with $Asc^\bullet$ (2.5×10^4 s^{-1}), and it can be neglected;

(ii) As previously discussed, charge recombination with oxidized ascorbate is a pseudo-first order reaction with a decay rate constant $k_{rec}[Asc^\bullet]_0$;

(iii) Also, reduction of Cyclam-Ni^{II} can be considered as a pseudo-first order reaction since Cyclam-Ni^{II} is in large excess thus [Cyclam-Ni^{II}] ~ [Cyclam-Ni^{II}]$_0$.

Finally, Ru^I decay becomes a simple pseudo-first order reaction:

$$\frac{dRu^I}{dt} = -k_1[Ru^I][Ni^{II}]_0 - k_{rec}[Ru^I][Asc^\bullet]_0 \tag{3}$$

With an apparent rate constant

$$k_{app} = k_1[Ni^{II}]_0 + k_{rec}[Asc^\bullet]_0 \tag{4}$$

Ru^I decay traces at 510 nm were well fitted by a monoexponential decay. Form the linear fit of k_{app} *vs* [CyclamNi^{II}]$_0$ concentration (Figure S4), k_1 is given by the slope, while the intercept corresponds to $k_{rec}[Asc^\bullet]_0$.

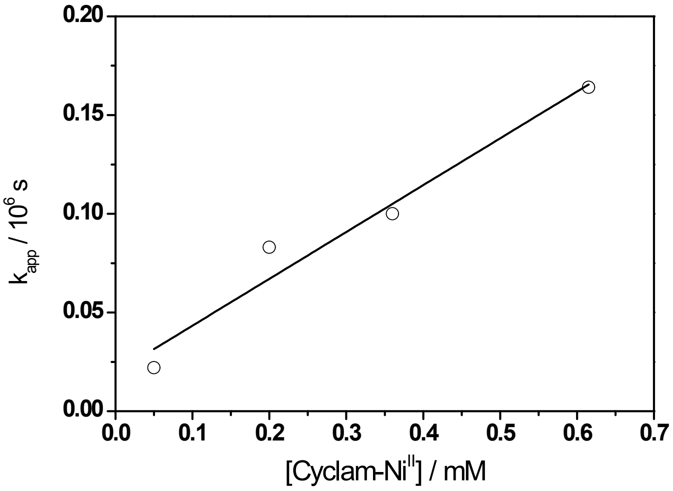


Figure S4. Linear fit of k_{app} *vs* Cyclam-Ni^{II} concentration.

Intra-molecular electron transfer

Photo-induced electron transfer between Ru-Cyclam-Ni **(9)** and ascorbate was examined using Scheme 2 given in the article. In such scheme, the two rate constants for recombination with oxidized ascorbate have been approximated to be described by the same parameter k_3. This is a reasonable assumption since the two rate constants are close to diffusion controlled in the solvent. With equations (5) and (6) below

$$\frac{d[Ru]^I}{dt} =- (k_{et} + k_3)[Ru^I] + k_{bet}[Ni^I] \tag{5}$$

$$\frac{d[Ni^I]}{dt} =- (k_{bet} + k_3)[Ni^I] + k_{et}[Ru^I] \tag{6}$$

we obtain

$$Ru^I(t) = Ru^I_0 \frac{k_{bet}}{k_{et} + k_{bet}} e^{-k_3 t}\left(1 + \frac{k_{et}}{k_{bet}} e^{-(k_{et} + k_{bet})t}\right) \tag{7}$$

$$Ni^I = Ru^I_0 \frac{k_{et}}{k_{et} + k_{bet}} e^{-k_3 t}\left(1 - e^{-(k_{et} + k_{bet})t}\right) \tag{8}$$

The Ru^I decay at 510 nm was fitted with a biexponential decay according to eq. (7) and from averaging different measurements, $k_{et} = 3.2 \times 10^4$ s^{-1} and $k_{bet} =$ 2.4×10^4 s^{-1} were obtained as reported in the article. For the recombination rate constant approximated with the single rate k_3 a value of $k_3 = 7 \times 10^3$ s^{-1} has been found, which is similar to the value of $k_{rec}[Asc^\bullet]_0$ obtained for the $[Ru(bpy)]_3^{2+}$ /ascorbate system (2.5×10^4 s^{-1}),further supporting our assumption.

Photocatalysis

The TDC detector was calibrated by injecting known amounts of pure CO and H_2.

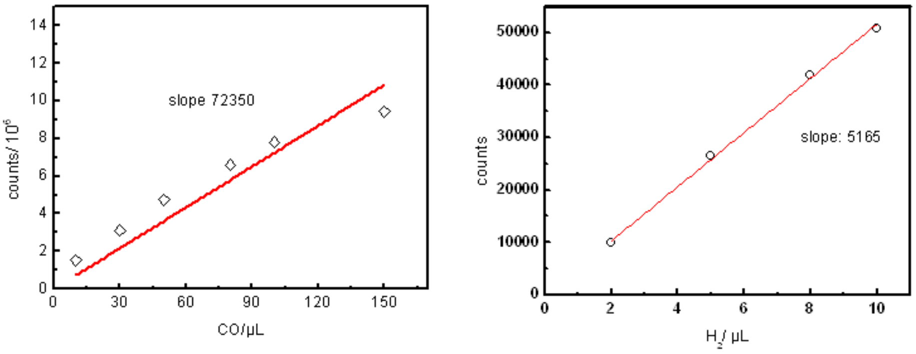


Figure S5. Calibration of the GC/TCD detector

Under our experimental conditions 1 μL of CO corresponds to (72000±4000) counts (Fig. S5 left), and 1 μL of H_2 to 5200 counts (Fig. S5 right).

The maximum amount of CO detected was 11000 counts, after 60 hours irradiation, corresponding to 0.15 μL of CO in 50 μL injection (Fig. S6) and 3.1 μmol of CO in the headspace volume used in the experiment (25 mL). With the quantity of Ru-Ni complex employed of N_{cat} ~0.6 μmol, this yields a turn over number TON = 5.2.

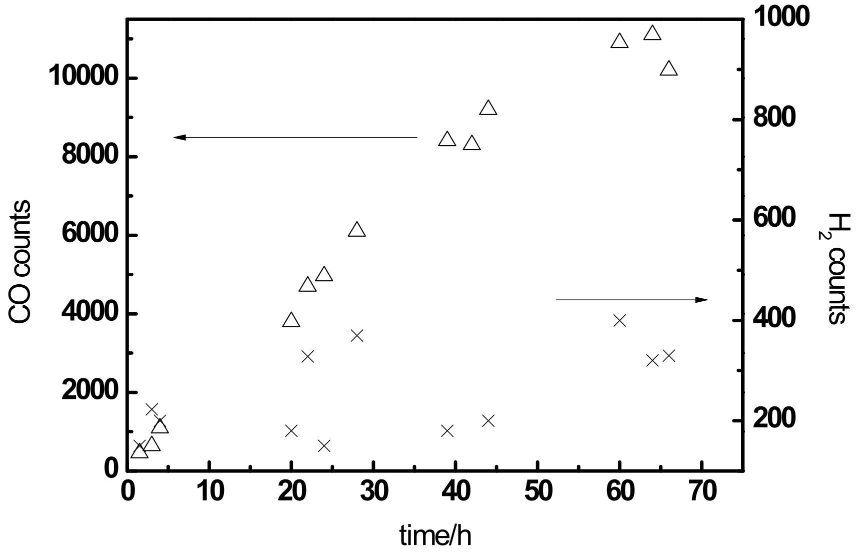


Figure S6. Quantity of produced CO and H_2 as a function of irradiation time.

For the H_2 peak the maximum counts was 330 corresponding to 0.06 μL of H_2. This results into 1.25 μmol in gaseous phase. Thus for H_2 generation TON is 2.

References

1. V. Balzani and A. Juris, *Coordination Chemistry Reviews*, 2001, **211**, 97-115.