Electronic Supplementary Information

Not that innocent – ammonium ions boost homogeneous light-driven hydrogen evolution

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1. Methods and Materials

Materials: All chemicals were purchased from Sigma Aldrich, Fisher Scientific or ACROS and were of reagent grade. The chemicals were used without further purification unless stated otherwise.

Gas chromatography: Gas-chromatography was performed on a Bruker Scion GC/MS, with a thermal conductivity detector 15 (column: molecular sieve 5Å 75 m x 0.53 mm. oven temperature 70 °C, flow rate 30 mL min⁻¹, detector temperature 200 °C) with Argon as carrier gas. The calibration was done by direct injection of know H₂ amounts.

2. Synthesis

Synthesis of (NH₄)₂[Mo₃S₁₃] x 2 H₂O: The thiomolybdate (NH₄)₂[Mo₃S₁₃] x 2 H₂O was prepared as previously reported¹: (NH₄)₆[Mo₇O₂₄] x 4 H₂O (4.0 g, 3.2 mmol) were dissolved in water (20 mL) in a round bottom flask. An ammonium polysulfide ((NH₄)₂S_x) solution (120 mL, 25 wt.-%) was added and the flask covered with a condenser. The solution was kept at 96 °C for five days without stirring. Dark-red crystals of (NH₄)₂[Mo₃S₁₃] x 2 H₂O formed and were removed by filtration, washed with water, isopropanol, carbon disulfide, THF and ether. The product was air-dried. Yield: 5.6 g (7.16 mmol, 97.9 % based on Mo).

Synthesis of Na₂[Mo₃S₁₃] x 5 H₂O: Na₂[Mo₃S₁₃] x 2 H₂O was synthesized as follows. $(NH_4)_2[Mo_3S_{13}] \times 2 H_2O$ (3.0 g, 3.86 mmol) was suspended in an aqueous NaOH solution (1 wt.-%, 40 mL) and stirred under reduced pressure for 2 h, in order to remove ammonium as NH₃ gas. The resulting dark red solution was filtered into an aqueous NaCl solution (10 wt.-%, 100 mL). After 12 h, the precipitated product was isolated by filtration, washed with isopropanol and ether, and air-dried to give orange powder of Na₂[Mo₃S₁₃] x 5 H₂O. Yield: 3.20 g (3.78 mmol, 95.9% based on Mo).

Synthesis of [Co(dmgH)₂PyCI]: Co(dmgH)₂PyCI was synthesized according to literature.²

Synthesis of [lr(ppy)₂(bpy)](PF₆): lr(ppy)₂(bpy)(PF₆) was synthesized according to Literature.³

3. Light-driven Catalysis

Solvents: All solvents were purged with high-purity Argon before each measurement to remove traces of oxygen.

Standard reaction setup: 21 mL Schlenk tubes were filled with 8 mL of the reaction mixture under inert conditions, containing solvent, catalyst (Cat), photosensitiser (PS) and sacrificial electron donor (SED) at the concentrations specified. The Schlenk tubes were sealed with a rubber septum. The samples were irradiated with a LED light source (λ_{max} = 470 nm, P ~ 40 mW cm²⁻) in a custom-built, air-cooled photoreactor. Hydrogen evolution was quantified by gas-chromatography with an external calibration. Each measurement was carried out in triplicate, the values reported are the resulting average.

Standard conditions: solvent: MeOH or acetone : water 9:1 (v:v), [CAT] = 0.3 μ M (for {Mo₃}) or 4 μ M (for cobaloxime), [PS] = 20 μ M, [SED] = 10 mM with pH adjusted to 4.0 or 6.0.

Definitions: $TON = n(H_2) / n(catalyst)$



Figure S1: Turnover numbers over time in acetone at pH 4 adjusted with different bases. Conditions: $[[Ru(bpy)_3]^{2+}] = 20 \ \mu\text{M}, [\{Mo_3\}] = 0.3 \ \mu\text{M}, [ascorbic acid] = 10 \ \text{mM}, acetone:H_2O 9:1 (v:v).$



Figure S2: Turnover numbers over time in methanol at pH 4 adjusted with different bases. Conditions: $[[Ru(bpy)_3]^{2+}] = 20 \ \mu\text{M}, [\{Mo_3\}] = 0.3 \ \mu\text{M}, [ascorbic acid] = 10 \ \text{mM}, MeOH:H_2O 9:1 (v:v).$



Figure S3: Turnover numbers over time in acetone at pH 6 adjusted with different bases. Conditions: $[[Ru(bpy)_3]^{2+}] = 20 \ \mu\text{M}, [\{Mo_3\}] = 0.3 \ \mu\text{M}, [ascorbic acid] = 10 \ \text{mM}, acetone:H_2O 9:1 (v:v).$



Figure S4: Turnover numbers over time in methanol at pH 6 adjusted with different bases. Conditions: $[[Ru(bpy)_3]^{2+}] = 20 \ \mu\text{M}, [\{Mo_3\}] = 0.3 \ \mu\text{M}, [ascorbic acid] = 10 \ \text{mM}, MeOH:H_2O 9:1 (v:v).$

4. Emission Quenching Studies

The influence of ammonium ions on the quenching behaviour of ascorbic acid on $[Ru(bpy)_3]^{2+}$ was investigated. The experimental conditions for the quenching experiments were chosen to be similar to the catalytic studies reported in the manuscript: solvent: MeOH:H₂O 9:1 (v:v), [PS]=20 µM, [SED]=10 mM, [NH₄]⁺]=[Et₄N⁺]=10 mM, pH=6.



Figure S5: Emission quenching of $[Ru(bpy)_3]^{2+}$ by ascorbic acid in presence of NH₄⁺ (black) and the presence of the reference Et₄N⁺ (red). Conditions: [PS] = 20 μ M, [SED] = 10 mM, [NH₄⁺] = [Et₄N⁺] = 10 mM MeOH:H₂O 9:1 (v:v).

5. Time-resolved Spectroscopy

5.1 fs-TA measurements

A detailed description of the experimental set-up used for fs-TA measurements has been reported in ⁴.For the experiments reported here, the measurements were performed within a delay-time window of 10 ns upon excitation at 400 nm (temporal resolution 120 fs). Excited molecules were probed by white light super continuum, generated by focusing a residual of the fundamental laser pulses into a CaF₂ plate. The mutual polarization between pump and probe beam were set to magic angle. Experimental conditions were identical with the catalytic reactions as described in the main paper. Firstly, the fs-TA measurements were performed with photosensitizer [Ru(bpy)₃]²⁺) without any ascorbic acid/ascorbate as sacrificial electron donor. Upon excitation of the MLCT transitions at 400 nm, fs-TA spectra of the [Ru(bpy)₃]²⁺ photosensitizer are characterized by a ground-state bleach (GSB) between 385 and 490 nm and excited-state absorption (ESA) below 375 nm and broad featureless absorption in the visible region. The spectral features summarized in Figure S5 are characteristic for ³MLCT states of [Ru(bpy)₃]²⁺-derived chromophores.^{5,6} Upon addition of the sacrificial electron donor, MLCT excitation caused

the increase of an additional ESA at around 510 nm (Figure S6). This feature is associated with the formation of the reduced photosensitizer $[Ru(bpy)_3]^+$. Similar measurements were conducted in both ammonium and tetraethyl ammonium-containing solution (which also contained the SED), however no difference in the evolution of ESA at 510 nm was noted upon addition of the ammonium species (Figure S7).



Figure S6: Transient absorption spectrum of $[Ru(bpy)_3]^{2+}$. Conditions: $[[Ru(bpy)_3]^{2+}] = 20 \ \mu\text{M}$, in MeOH:H₂O 9:1 (v:v).



Figure S7: Transient absorption spectrum of $[Ru(bpy)_3]^{2+}$. Conditions: $[[Ru(bpy)_3]^{2+}] = 20 \ \mu\text{M}$, [ascorbic acid/ascorbate] = 10 mM, $[NH_4^+] = 10 \ \text{mM}$; MeOH:H₂O 9:1 (v:v).



Figure S8: Kinetic evolution of reduced $[Ru(bpy)_3]^+at 510 \text{ nm. Conditions: } [[Ru(bpy)_3]^{2+}] = 20 \ \mu\text{M}$, [ascorbic acid/ascorbate] = 10 mM, [ammonium-ion] = 10 mM in MeOH:H₂O 9:1 (v:v).

5.2 ns-TA measurements

In order the probe the decay of the reductively quenched ($[Ru(bpy)_3]^{2+}$) photosensitizer, ns-TA spectroscopy was implemented. For this we have used a commercially available detection system from Pascher Instruments AB, running on a 10 Hz Nd:YAG laser combined with an OPO. Temporal evolution of the system was 10 ns and further details about the set up can be found in reference.⁷ All measurements were conducted with degassed solvent under inert condition and with pump wavelength of 450 nm.

6. Literature

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