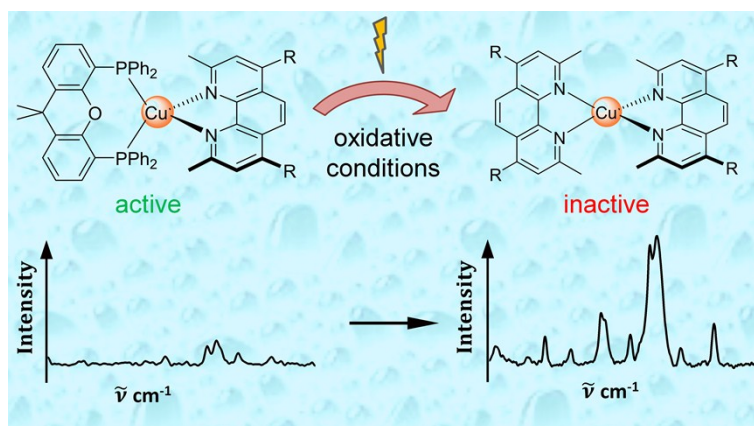


Determination of side products in the photocatalytic generation of hydrogen with copper photosensitizers by resonance Raman spectroelectrochemistry

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General Information

Complexes **1/1'** and **2/2'** were synthesised according to literature.¹ For electrochemical measurements all samples were dissolved in anhydrous and degassed acetonitrile (Sigma-Aldrich, spectroscopic grade), which was dried using calcium hydride (Sigma-Aldrich, 98%) and distilled under argon atmosphere prior to use. Tetrabutylammonium tetrafluoroborate (TBABF₄, Sigma-Aldrich, 99%) was dried at 80°C under vacuum and used as an electrolyte at a concentration of 0.1 M for the electrochemical and spectroelectrochemical experiments. Prior to each electrochemical measurement oxygen was removed by purging the respective solutions with argon. For UV-Vis and emission measurements acetonitrile was used without further purification. All studies were performed at room temperature.

Electrochemical measurements were carried out with a PC-controlled SP-150 potentiostat (BioLogic, France). A three-electrode system was employed, containing a Pt counter electrode, an Ag/AgCl pseudo-reference electrode and a glassy carbon working electrode. The scan rate for cyclic voltammetry (CV) was 100 mV/s unless otherwise noted, whereas differential pulse voltammetry was performed at a scan rate of 20 mV/s. Ferrocene was used as an external reference for calibration. The obtained potentials were finally converted into potentials versus NHE according to Ref 2.

UV-Vis spectra were recorded on a double-beam Cary 5000 UV-Vis spectrometer (Varian, USA), and **emission spectra** were recorded on a JASCO FP-6200 spectrofluorometer (USA). Raman peaks were removed from emission spectra by subtracting the background using a sample with the pure solvent. **Resonance Raman (RR) experiments** were performed through excitation by either an 473 nm blue diode pumped solid state laser (HB-Laser, Germany) or a TopMode-405-HP diode laser (Toptica, Germany), and detected by an IsoPlane 160 spectrometer (Princeton Instruments, USA) with an entrance slit width of 0.05 mm, a focal length of 750 mm, and grating 2400 grooves/mm. The Raman signals were recorded using a thermoelectric cooling PIXIS eXcelon camera (Princeton Instruments, USA).

Resonance Raman spectroelectrochemistry (RR-SEC) and UV-Vis spectroelectrochemistry (UV-Vis-SEC) measurements were performed in a three-electrode thin-layer spectroelectrochemical cell with a pathlength of 1 mm (Bioanalytical Systems, USA). As working electrode of the three-electrode system a Pt mesh was used. Firstly, spectrum was measured under open circuit potential, where no external potential is applied. Subsequently, a given positive oxidation potential was applied by chronoamperometry, and UV-Vis absorption- or RR spectra were recorded simultaneously. The spectra of the oxidised compounds were taken after a certain time until the spectra remain constant, allowing for saturation of the oxidation processes. As electrochemical reaction occurs at the surface of the electrode, even a Pt mesh working electrode is not able to oxidise all molecules in the cell. Therefore, the spectra obtained are from a majority of the oxidised species and a minority of neutral species.

The Raman spectra were initially baseline corrected and normalised with respect to an acetonitrile solvent band, i.e., to the signal at 1374 cm⁻¹. The acetonitrile spectrum was then subtracted from all RR spectra.

¹ a) S.-P. Luo, E. Mejía, A. Friedrich, A. Pazidis, H. Junge, A.-E. Surkus, R. Jackstell, S. Denurra, . Gladiali, S. Lochbrunner and M. Beller, *Angew. Chem.*, 2013, **125**, 437. b) E. Mejía, S.-P. Luo, M. Karnahl, A. Friedrich, S. Tschierlei, A.-E. Surkus, H. Junge, S. Gladiali, S. Lochbrunner and M. Beller, *Chem. Eur. J.*, 2013, **19**, 15972.

² V. V Pavlishchuk and A. W. Addison, *Inorg. Chim. Acta.*, 2000, **298**, 97.

Electrochemical Measurements

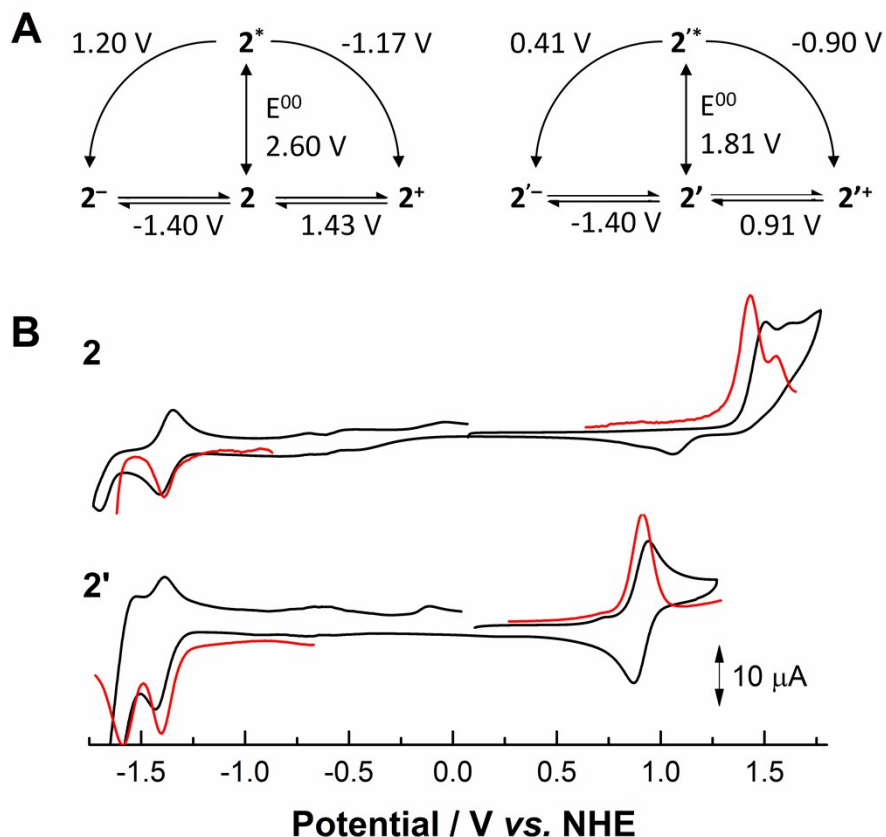


Figure S1: (A) Electrochemical potentials of the ground and excited state of complexes **2** and **2'** in acetonitrile, vs. NHE. Approximation of the zero-zero energy of the excited state is based on the intersection of the normalised absorption and emission spectra (for further description see main manuscript). (B) Cyclic voltammetry curves (black) of the complexes **2** and **2'** in 0.1 M TBABF₄/acetonitrile. Differential pulse voltammetry (red) were applied in addition for better analysis of the redox potentials.

UV-Vis Spectroscopy

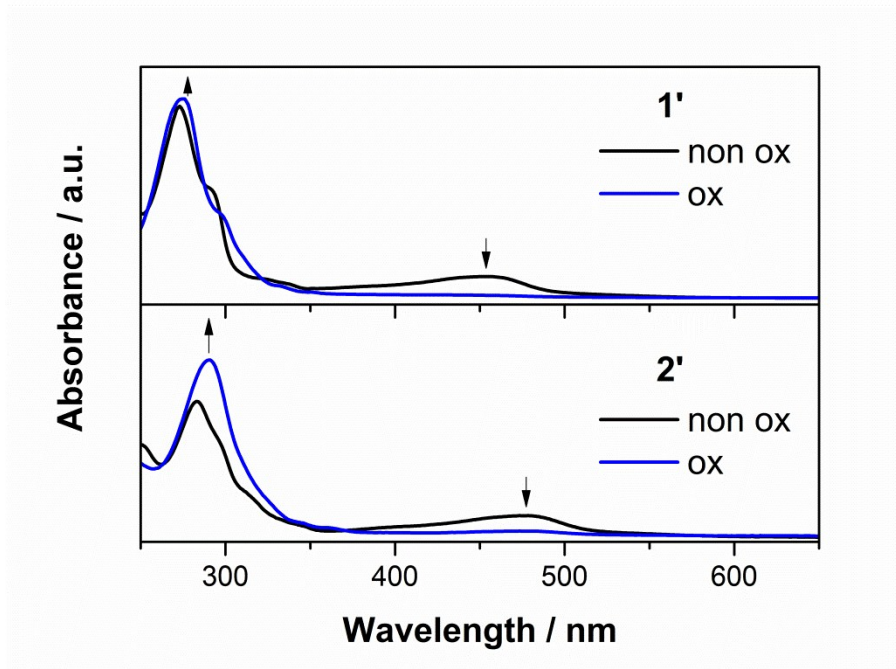


Figure S2: UV-Vis spectra of **1'** (upper panel) and **2'** (lower panel) under open circuit potential (black lines - non ox) and upon electrochemical oxidation (blue lines - ox) using chronoamperometry in 0.1 M TBABF₄/acetonitrile solution.

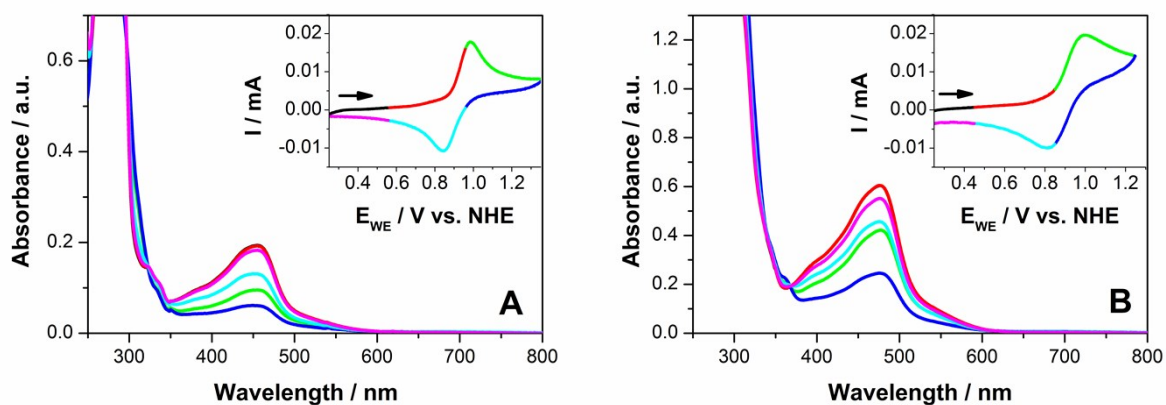


Figure S3: Absorption spectra of **1'** (A) and **2'** (B) in 0.1 M TBABF₄/acetonitrile solution during running cyclic voltammetry. The spectra correspond to respective applied potentials of the same colours.

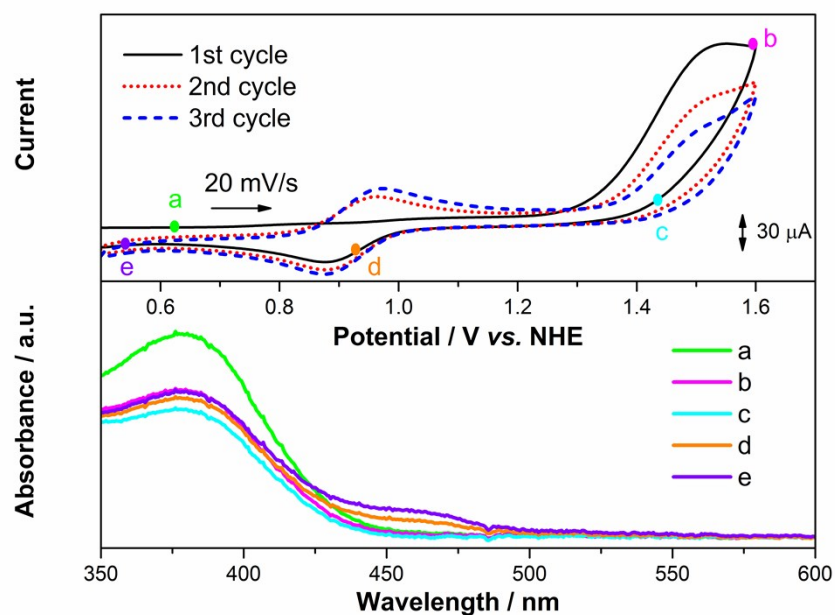


Figure S4: Absorption spectra of **1** in 0.1 M TBABF₄/acetonitrile solution during running a CV (black solid line) with a scan rate of 20 mV/s. The spectra in the lower panel correspond to the respective applied potentials of the same colours in the upper panel. The second- (red dot line) and third- (blue dashed line) CVs were followed, and the appearance of the new reversible bands indicates the formation of **1'**.

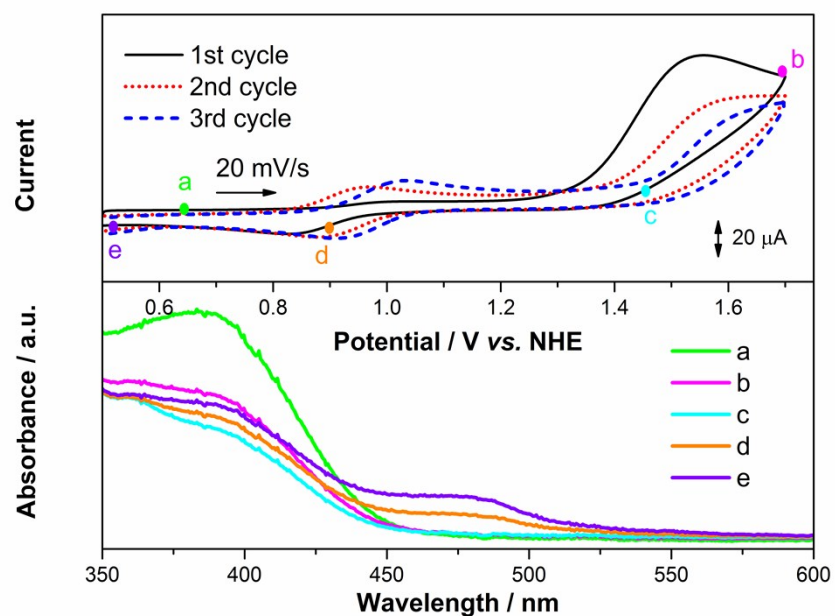


Figure S5: Absorption spectra of **2** in 0.1 M TBABF₄/acetonitrile solution during running a CV (black solid line) with a scan rate of 20 mV/s. The spectra in the lower panel correspond to the respective applied potentials of the same colours in the upper panel. The second- (red dot line) and third- (blue dashed line) CVs were followed, and the appearance of the new reversible bands indicates the formation of **2'**.

Resonance Raman Spectroscopy

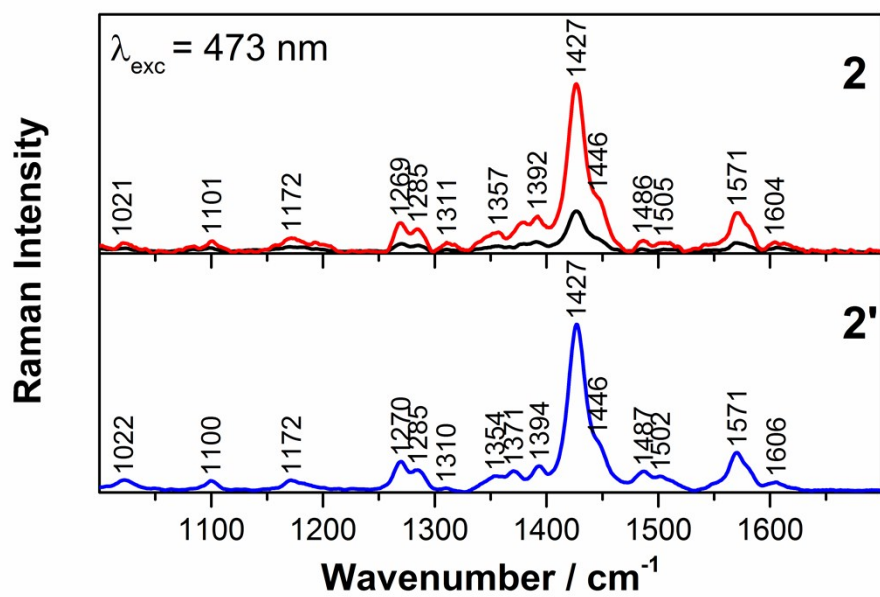


Figure S6: Resonance Raman spectra of **2** (upper panel) under open circuit potential (black line), after an oxidative cycle (red line) and **2'** (lower panel, blue line) in 0.1 M TBABF₄/acetonitrile, excited at 473 nm.

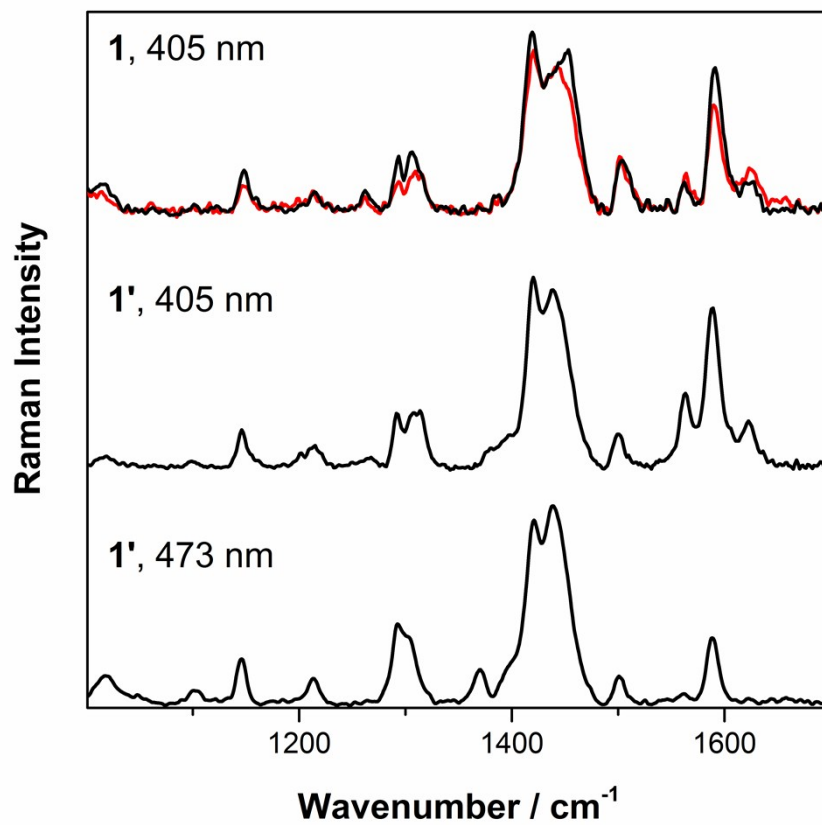


Figure S7: Resonance Raman spectra of **1** and **1'** dissolved in acetonitrile excited at different wavelengths (405 and 473 nm). The red curve in the upper panel refers to the spectrum of **1** after an oxidative cycle. The spectrum of acetonitrile has been subtracted.

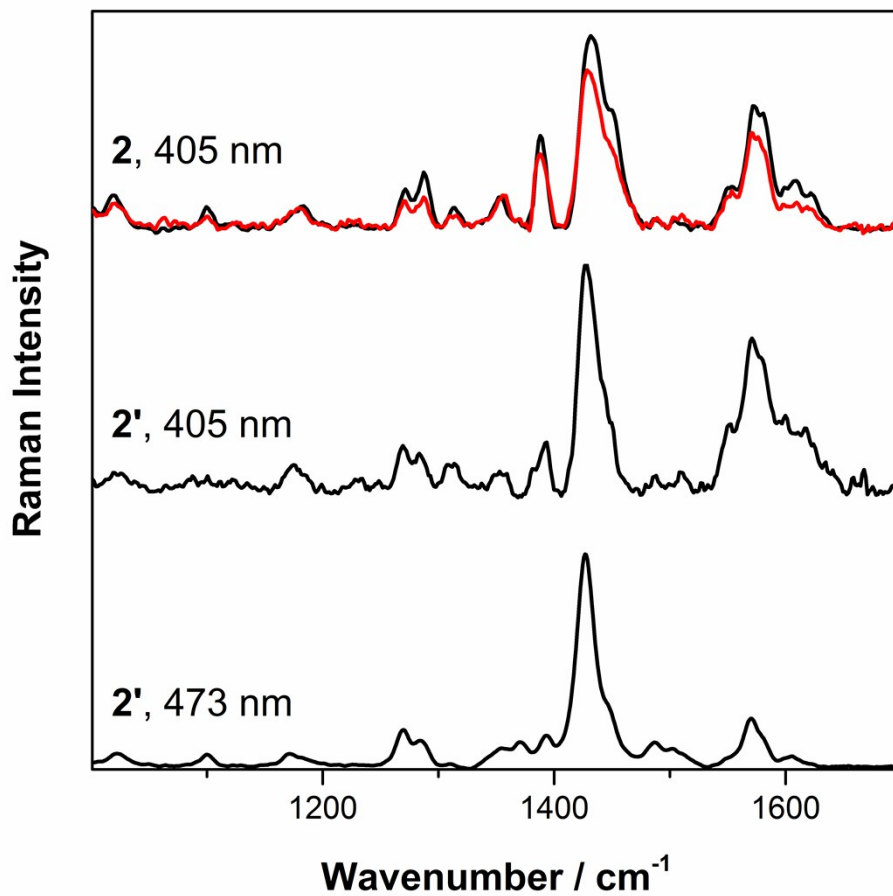


Figure S8: Resonance Raman spectra of **2** and **2'** dissolved in acetonitrile excited at different wavelengths (405 and 473 nm). The red curve in the upper panel refers to the spectrum of **2** after an oxidative cycle. The spectrum of acetonitrile has been subtracted.