

Supplementary Information for

Electron transfer in a covalent dye-cobalt catalyst assembly – a transient absorption spectroelectrochemistry perspective

Sebastian Bold,^{a,b,c,d} Linda Zedler,^b Ying Zhang,^{a,b}, Julien Massin, Vincent Artero,^d Murielle Charot-Kerlidou^d and Benjamin Dietzek^{a,b,c}

a - Institute of Physical Chemistry and Abbe Center of Photonics, Friedrich Schiller University Jena, Helmholtzweg 4, 07743 Jena, Germany.

b - Department Functional Interfaces, Leibniz Institute of Photonic Technology Jena (IPHT), Albert-Einstein-Straße 9, 07745 Jena, Germany.

c - Center for Energy and Environmental Chemistry, Friedrich Schiller University Jena, Philosophenweg 8, 07743 Jena, Germany.

d - Laboratoire de Chimie et Biologie des Métaux, Université Grenoble Alpes, CNRS, CEA, 17 rue des Martyrs, 38000 Grenoble, France.

Chemicals.

All solvents used were of spectroscopic grade. For the transient absorption spectroelectrochemistry (TA-SEC) measurements, dimethyl formamide (DMF) was dried over a 5 Å molecular sieve prior to use. For the UV-Vis SEC measurements, Acros organics extra dry DMF was used. The synthesis of compounds **1**¹ and **2**² was previously reported.

Procedure for immobilization on ZrO₂ films

For the immobilization on ZrO₂ films, the *tert*-butyl ester groups in **1** and **2** were deprotected according to our previous studies.^{1,2} ZrO₂ films were then soaked in a 0.2 mM solution of deprotected **1** or deprotected **2** in acetonitrile (ACN) for 24 hours. The films were then rinsed with ACN before measuring.

General characterization methods and equipment.

Steady-state UV-Vis absorption spectroscopy

Steady-state absorption spectra in solution were recorded on a Shimadzu UV-1800 spectrophotometer in 1 cm cuvettes. Absorption spectra on ZrO₂ films were recorded on an Agilent Cary 5000 equipped with a solid sample holder. Emission spectra were measured on a Horiba Fluorolog Spectrofluorometer in a 1 cm cuvette at 90° angle. Quantum yields were determined using an Edinburgh FLS980 emission spectrofluorometer equipped with an integrating sphere.

Spectroelectrochemistry

UV-Vis-SEC measurements were carried out in a three-electrode setup using a 1 mm cell equipped with a Pt mesh working electrode, a Pt wire counter electrode and a Ag/AgCl reference electrode (3M KCl). The potentiostat used was a BioLogic VSP-300. The spectra were recorded using an Agilent Cary 60 spectrometer. For the measurements, a cyclic voltammetry (CV) was run to establish the redox potentials, then potentials were applied in a Chronoamperometry and spectra recorded until equilibrium was reached before changing to the next potential. 0.1 M tetrabutylammonium tetrafluoroborate (TBABF₄) in DMF was used as electrolyte solution.

Time-resolved emission spectroscopy

The two-dimensional (time and wavelength) emission decay profiles were measured using a Hamamatsu streak scope C4334 in photon counting mode using a time-window of 10 or 20 ns. After excitation with the frequency-doubled output of a Ti-sapphire laser (Tsunami, Newport Spectra-Physics GmbH) at $\lambda_{\text{ex}} = 365$ nm at a pulse-to-pulse repetition rate of 400 kHz after passing a pulse selector (model 3980, Newport Spectra-Physics GmbH) the luminescence of the sample was collected

in a 90°-arrangement and spectrally dispersed using a Chromex 250IS 3 imaging spectrograph. Selected horizontal (spectral) and vertical (temporal) intervals were integrated using the HPDTA software delivered with the streak camera system. Measurements were carried out without a polarizer to decrease the acquisition time. The lifetime values were obtained from mono- or biexponential fits of the linear portion of the integrated decay profiles. The samples were prepared to yield an optical density of 0.1 at the excitation wavelength in a 1.0 cm quartz cuvette using air-equilibrated, spectroscopic grade solvents.

Transient absorption spectroscopy and spectroelectrochemistry

A custom-built setup was utilized to acquire fs-TA data. The TA setup is described in detail elsewhere.³ A white-light supercontinuum probe pulse at 1 kHz repetition rate was used to analyze the excited state dynamics. The supercontinuum was generated by focusing a minor part of the output of the Ti:Sapphire amplifier into a CaF₂ plate mounted on a rotating stage. After generation of the white light continuum, it is split into a probe and reference beam. Using a concave mirror with 500 nm focal length, the probe pulse was focused onto the sample by a concave mirror of 500 mm focal length. The spectra of probe and reference were detected by a Czerny-Turner spectrograph of 150 mm focal length (SP2150, Princeton Instruments) equipped with a diode array detector (Pascher Instruments AB, Sweden). The pump pulses used were of 403 nm wavelength and a pulse duration of approximately 100 fs. The repetition rate of the pump pulses was reduced to 0.5 kHz by a mechanical chopper and the polarization adjusted to the magic angle of 54.7° by a Berek compensator and a polarizer.

The data was analyzed using a customized data analysis software (Pascher Instruments AB, Sweden). First, the data was corrected for the chirp and subsequently, a sum of exponential functions was fitted to the data.

The pulse overlap region of ±200 fs was removed from the data to exclude the coherent artefacts present in this temporal region.

The TA measurements of **1** were carried out in ACN in a standard 1 mm cuvette ($OD_{400nm} = 0.3$). In the TA-SEC measurements, the pump and probe beam pass collinearly through a hole drilled into a 0.4 mm thick glassy carbon working electrode (hole diameter: 1 mm). This electrode design enables a high local concentration of reduced species at the focal point of the pump and probe beams, taking advantage of the highly resistant glassy carbon material while achieving optimal light transmission despite its opacity. The setup was completed by customized electronics and control software (Pascher Instruments AB, Sweden), allowing simultaneous control of the potentiostat unit and TA setup. This enabled simultaneous measurements of TA spectra, steady-state UV-Vis spectra, current, applied potential and ensured jitter-free timing of the datasets

Transient absorption spectra of the electrochemically reduced complex were recorded at set potentials and constant current response. Steady state UV-Vis spectra were simultaneously recorded with time-resolved TA-SEC in order to assess the concentration of the reduced species within the observation. To ensure good solubility of **2**, DMF was used as the electrolyte solvent with 0.1 M TBABF₄ as supporting electrolyte.

Procedure for the TA-SEC measurements.

TA-SEC measurements were carried out as follows: After assembly of the cell with all three electrodes, the cell was purged with Argon for ≈ 10 min. Afterwards, the sample solution was injected into the cell and purged with Argon for another ≈ 5 min. At the beginning of the day, a complete CV of the sample was measured to identify the reduction potentials versus the Ag wire pseudo-reference electrode. Before each TA measurement, a CV was measured with a vertex potential slightly negative of the desired reduction to check again for the correct reductive potential and account for a possible potential drift of the pseudo-reference electrode. After disconnecting the counter electrode (CE), a chronoamperometry (CA) measurement was started and the CE reconnected after about 5 data points to observe the initial current spike and subsequent levelling off to a plateau upon reaching equilibrium. This was done for one TA scan (about 6 minutes), so in total the system had about 10 min to approach equilibrium prior to the start of the TA-SEC measurement. The CA time prior to the TA-SEC measurement was not extended to avoid degradation of the sample since pump and probe beam were already irradiating it. Then, a TA measurement was started with the potential still applied (chronoamperometry).

During the CV, CA and the TA measurement the current as well as steady-state UV-Vis spectra were recorded. The UV-Vis spectra allow to control the reduction of the sample as well as to estimate the yield of reduced species in the sample chamber.

Table S1: Absorption and emission maxima and emission quantum yields of compounds **1** and **2** in acetonitrile, DMF and on ZrO₂ excited at 400 nm (emission quantum yields: excited at 435 nm).

Sample	Solvent/ Substrate	$\lambda_{\max} (\pi-\pi^*)$ /nm	$\lambda_{\max} (\text{ICT})$ /nm	$\epsilon_{\max} (\text{ICT})$ / $\text{M}^{-1}\text{cm}^{-1}$	$\lambda_{\max, \text{em}}$ /nm	Φ_{em} [%]
1	ACN	350	441	33811	653	19.3
	DMF	354	448	27666	646	23.6
	ZrO ₂	347	444		641	6.1
2	ACN	349	432	31752	630	3.9
	DMF	353	433	30884	608	0.7
	ZrO ₂	346	439		602	

Table S2: Emission lifetimes obtained by fitting the time-resolved emission data of **1** and **2** in ACN, DMF and on ZrO₂ with a mono- or biexponential fit in solution and a stretched exponential fit for **1** on ZrO₂. Also given are radiative (k_{R}) and non-radiative (k_{NR}) decay rates calculated from the emission quantum yield and emission lifetimes.

Sample	Solvent	τ_1 / ps	τ_2 / ps	τ_{ave} / ps	β dispersion parameter	α relative amplitude	$k_{\text{R}} / 10^8 \text{ s}^{-1}$	$k_{\text{NR}} / 10^8 \text{ s}^{-1}$
1	ACN		1745				1.11	4.62
	DMF		1874				1.26	4.08
	ZrO ₂			1006 ^a	0.542			
2	ACN	199	2056	366 ^b		0.91	1.07	26.3
	DMF	231	2127	439 ^b		0.89	0.16	22.6
	ZrO ₂		45					

a: obtained from the stretched exponential fit

b: amplitude-weighted average lifetimes calculated from the lifetimes and amplitudes obtained by the biexponential fit

In case of biexponential fits, the amplitude of the first component is given by α . For the calculation of the decay rates of **2**, the amplitude-weighted average lifetimes, calculated from the lifetimes and amplitudes obtained by the biexponential fit, were used. These are also given under τ_{ave} for completeness.

The stretched exponential fit was applied using the exponential function

$$I(t) = I_0 e^{-\left(\frac{t}{\tau_c}\right)^\beta}$$

convoluted with the instrumental response function. τ_c and β were used to calculate the average lifetime τ_{ave} :

$$\tau_{\text{ave}} = \frac{\tau_c}{\beta} \int_0^\infty x^{\frac{1}{\beta}-1} e^{-x} dx$$

β is the dispersion parameter, with $\beta = 1$ corresponding to a monoexponential decay. For **2** on ZrO_2 , the fit did not converge, and it was fitted with a monoexponential decay instead, probably due to the decay being very close to the IRF.

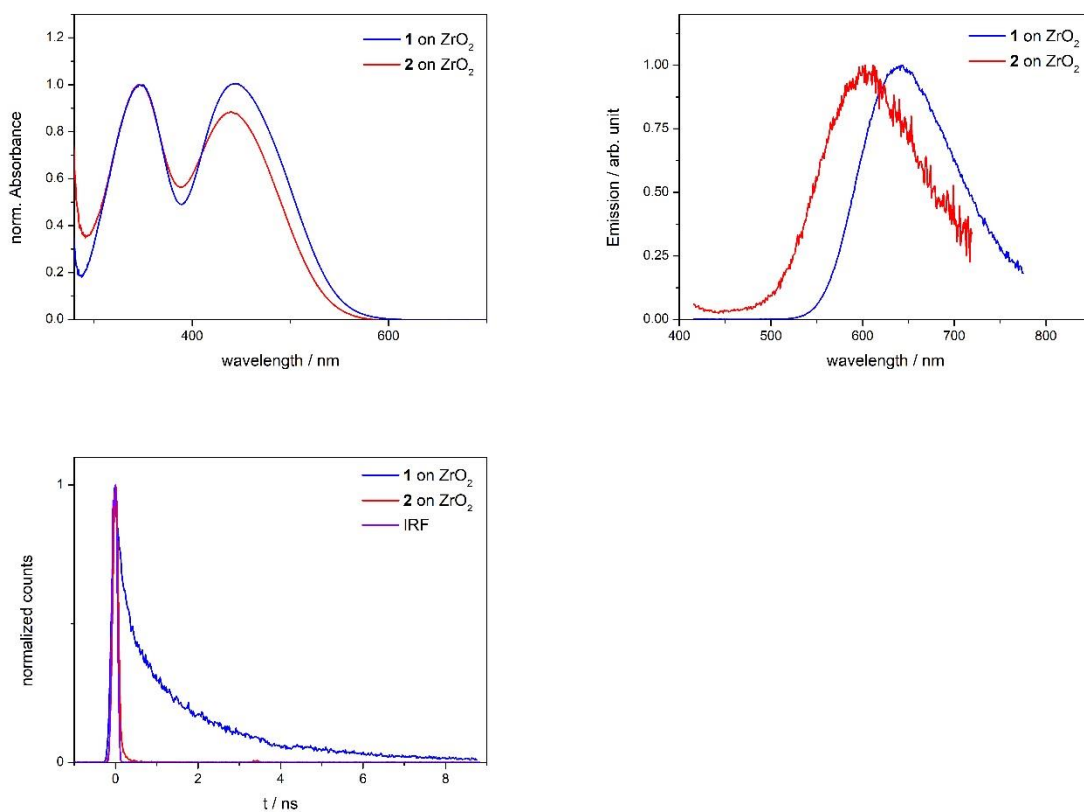


Figure S1: UV-Vis absorption spectra, normalized emission spectra and time-resolved emission of **1** and **2** immobilized on ZrO_2 films.

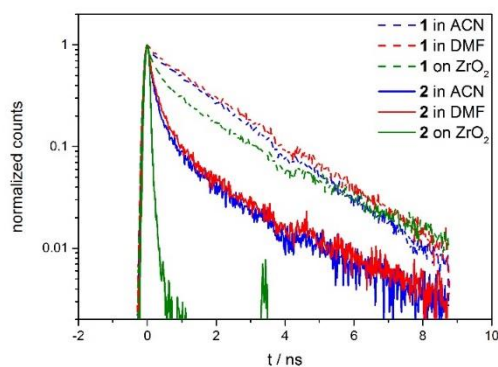


Figure S2: Semi-logarithmic plot of time-resolved emission data of **1** (dashed) and **2** (solid) in ACN (blue) and DMF (red) as well as on ZrO_2 (green).

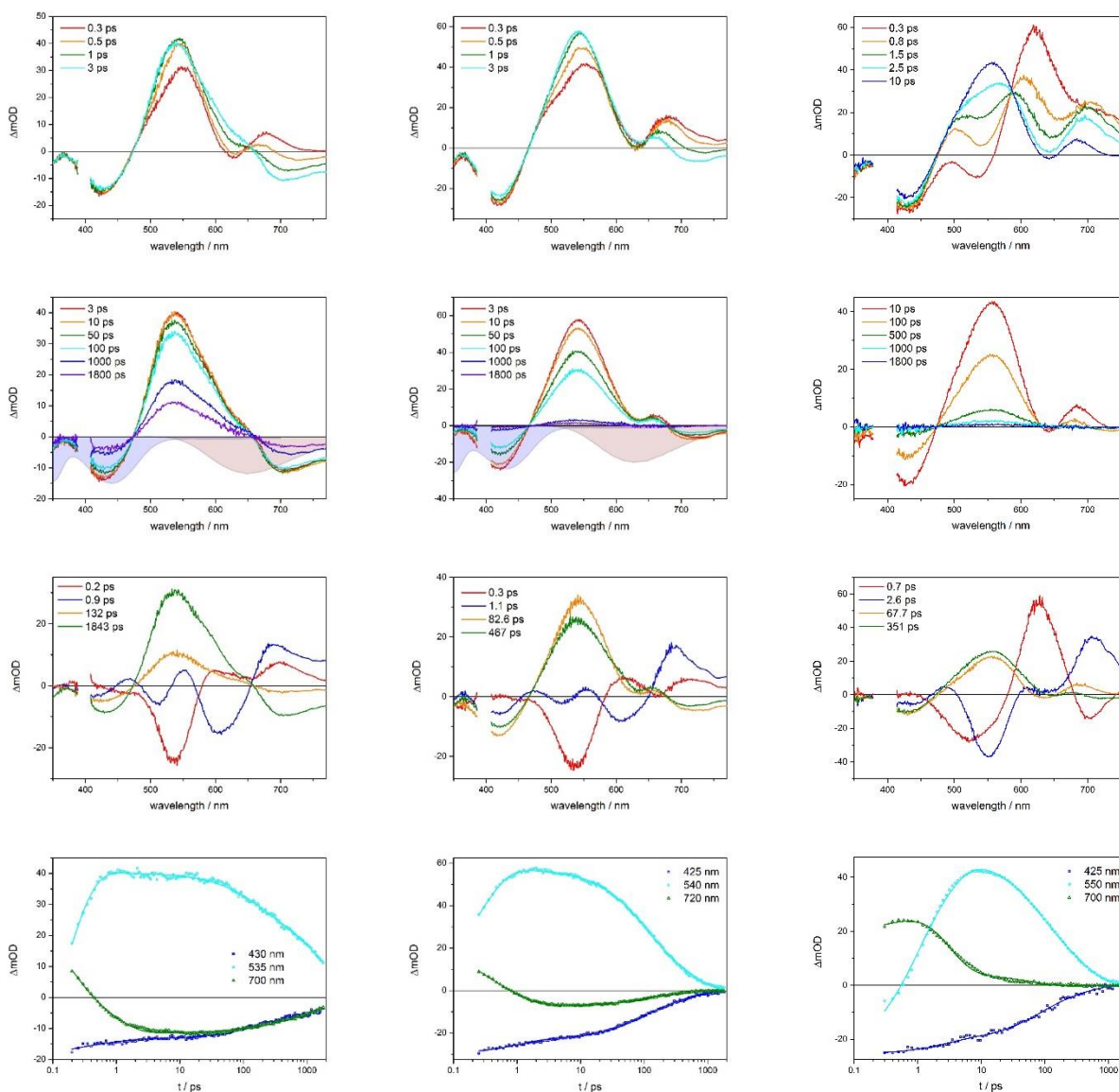


Figure S3: TA data of **1** (left) and **2** (middle) in ACN as well as of **2** in DMF (right). The top two graphs show the TA spectra at early (top) and late (bottom) delay times. The shaded areas depict the scaled and inverted steady-state absorption (blue) and emission (wine) spectra. The third row of graphs show the decay-associated spectra obtained with a four-component fit of the TA data. Bottom: Kinetics at the maxima of GSB (blue), ESA (cyan) and SE (green). The scatter plots show the recorded data while lines show the fit.

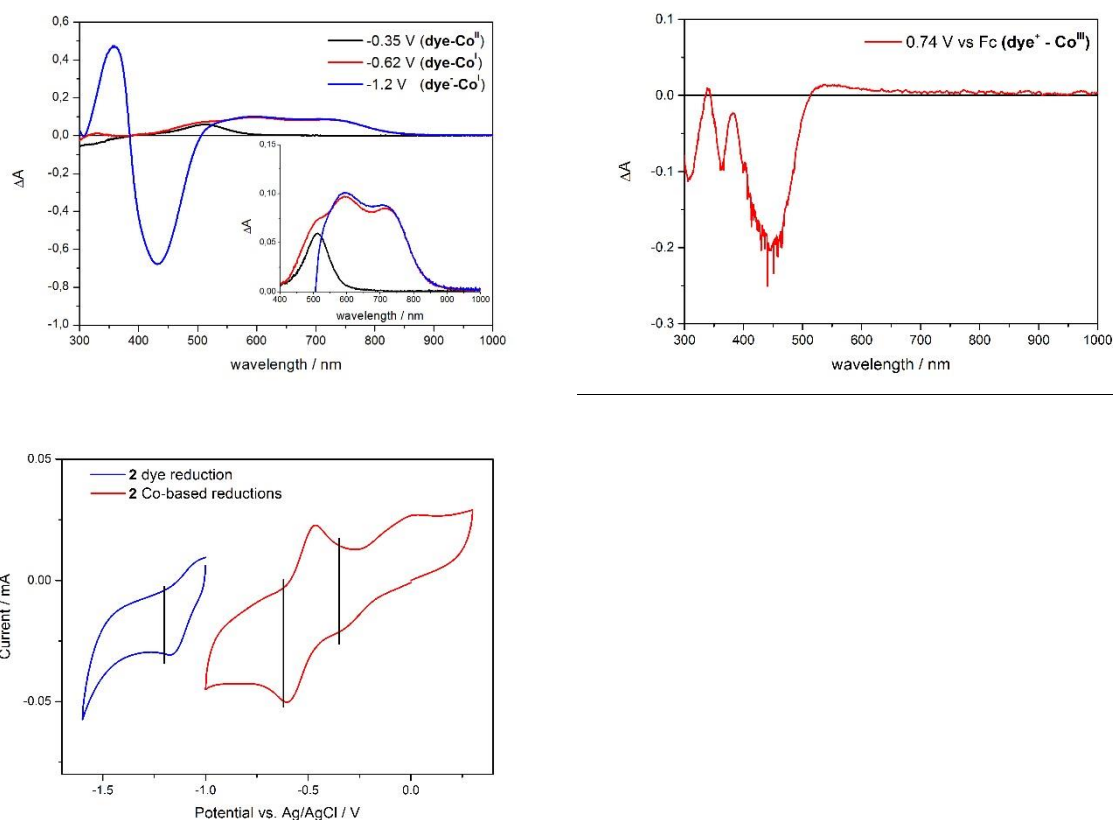


Figure S4: Differential steady-state UV-Vis-SEC spectra of a 0.2 mM solution of **2** in DMF (0.1 M TBABF₄) at different oxidation states of the catalyst and dye. On the bottom, the respective cyclic voltammograms are shown. All potentials were measured vs. Ag/AgCl with the exception of the oxidative measurements, measured against Fc⁺⁰. The potentials applied during chronoamperometry are shown by vertical black lines.

2 shows the rise of a positive band with a maximum at 512 nm upon reduction to the Co^{II} state. The Co^I state shows a double band at 595 and 717 nm, as previously observed in ACN.² It becomes apparent that upon reduction of the dye, the resulting bleach is much stronger than the Co^{II} absorption band, obscuring the latter. *This is a strong indication that, in a TA spectrum, the Co^{II} absorption band, which might be generated upon electron transfer, would be hidden beneath the GSB of the dye.*

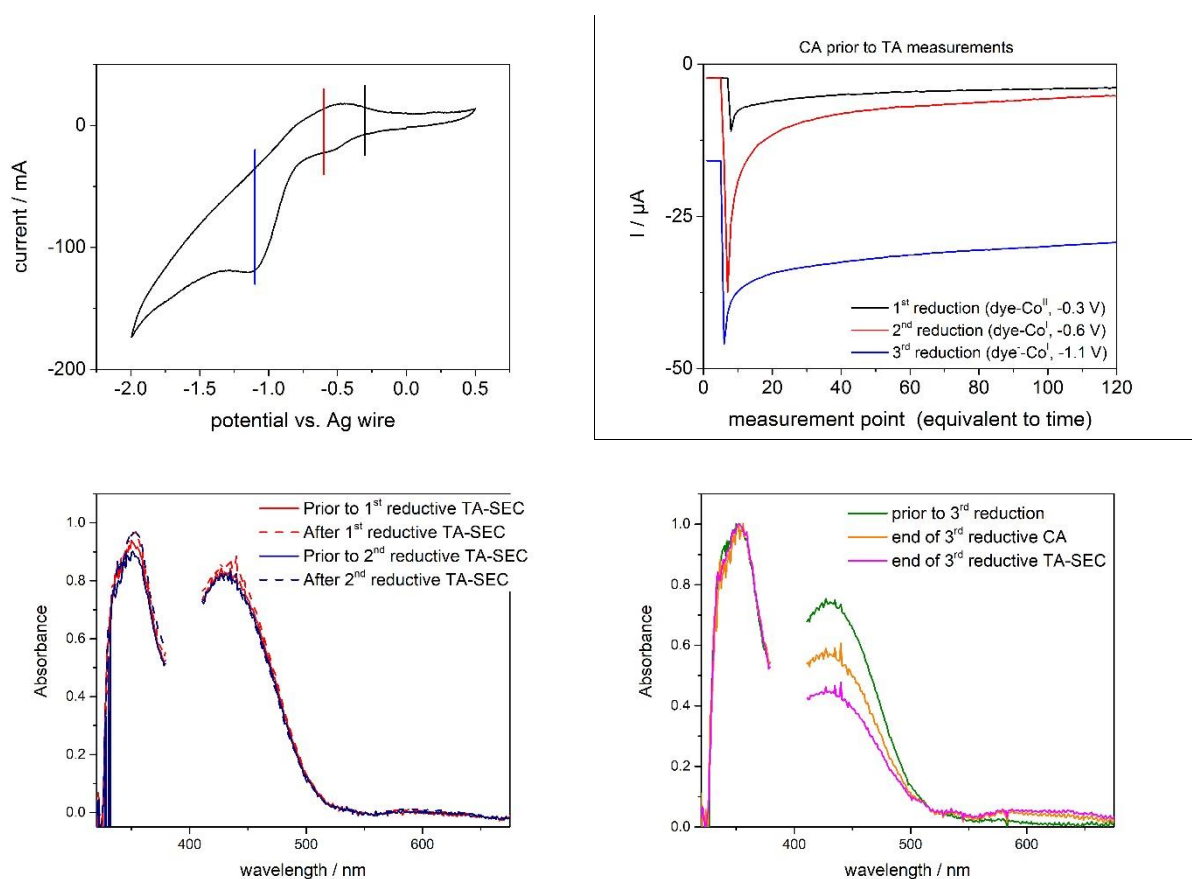


Figure S5: Electrochemical data (top) and steady-state UV-Vis spectra (bottom) recorded prior to and during the TA-SEC measurements. Top left: complete CV of **2** versus the pseudo-reference with the applied potentials applied for the TA measurements indicated by vertical bars. On the top right, the current vs. time of the CA run prior to the TA measurements is shown. The bottom left graph shows the steady state UV-Vis spectra of **2** prior to the CA (solid) and at the end of the TA measurement (dashed) for the first (red) and second (blue) reductive TA-SEC measurement. The reductive potentials applied for the TA measurements at these oxidation states were -0.3 (Co^{II}) and -0.6 (Co^{I}) V vs. Ag wire. No significant change in absorbance is observed in either case, proving the stability of the sample over the time range of the TA-SEC measurement. The failure to observe the expected Co^{I} double band after the second reduction (to the Co^{I} state) might be due to the low oscillator strength of this transition. To check if reduction of the sample was occurring, -1.1 V vs. Ag wire was applied to reduce the dye and obtain the $\text{dye}^{\ominus}\text{-Co}^{\text{I}}$ state. The steady-state UV-Vis spectra, normalized to the $\pi\text{-}\pi^*$ band to enable better comparison, of this measurement are shown in the bottom right graph. Indeed, during this reduction, a clear decrease in absorption of the ICT band is observed proving the reduction of the dye. From the change in absorbance and considering the positive ΔA for the $\pi\text{-}\pi^*$ band upon reduction (see UV/Vis SEC), the yield of reduced sample could be estimated to be $\approx 30\%$. Based on the relative differential absorbance of the dye bleach at 430 nm and the Co^{I} absorption band at 600 nm from UV-Vis SEC as well as the maximum GSB at OCP in the TA measurement, in case

of quantitative electron transfer a change in absorption of ≈ 3 mOD at 600 nm would be expected.

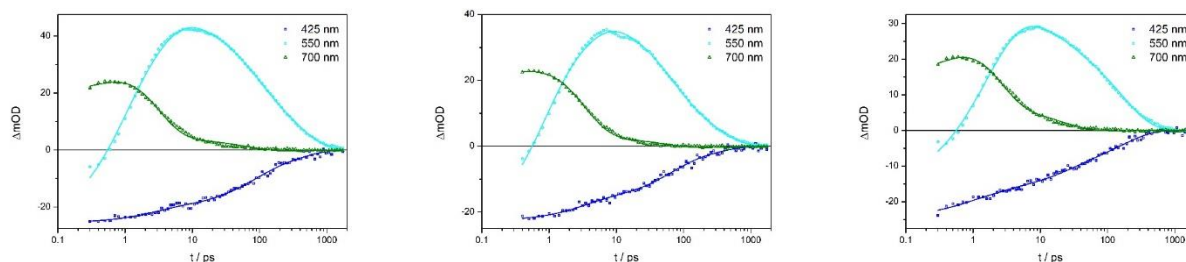


Figure S6: Kinetic traces of the TA measurements of **2** in DMF at OCP (left), Co^{II} (middle) and Co^I (right) at the maxima of GSB (blue), ESA (cyan) and SE (green). The scatter plots show the recorded data while lines show the fit.

1. J. Massin, M. Bräutigam, N. Kaefter, N. Queyriaux, M. Field, F. H. Schacher, J. Popp, M. Chavarot-Kerlidou, B. Dietzek, V. Artero *Interface Focus* 2015, **5**, 20140083.
2. N. Kaefter, J. Massin, C. Lebrun, O. Renault, M. Chavarot-Kerlidou and V. Artero, *J. Am. Chem. Soc.*, 2016, **138**, 12308–12311.
3. R. Siebert, D. Akimov, M. Schmitt, A. Winter, U. S. Schubert, B. Dietzek, J. Popp *ChemPhysChem*, 2009, **10**, 910–919.