# Spectroelectrochemistry of Electrochromic and Electroluminescent Substances with Screen-Printed Electrodes and with an Optically Transparent Platinum Mesh Electrode
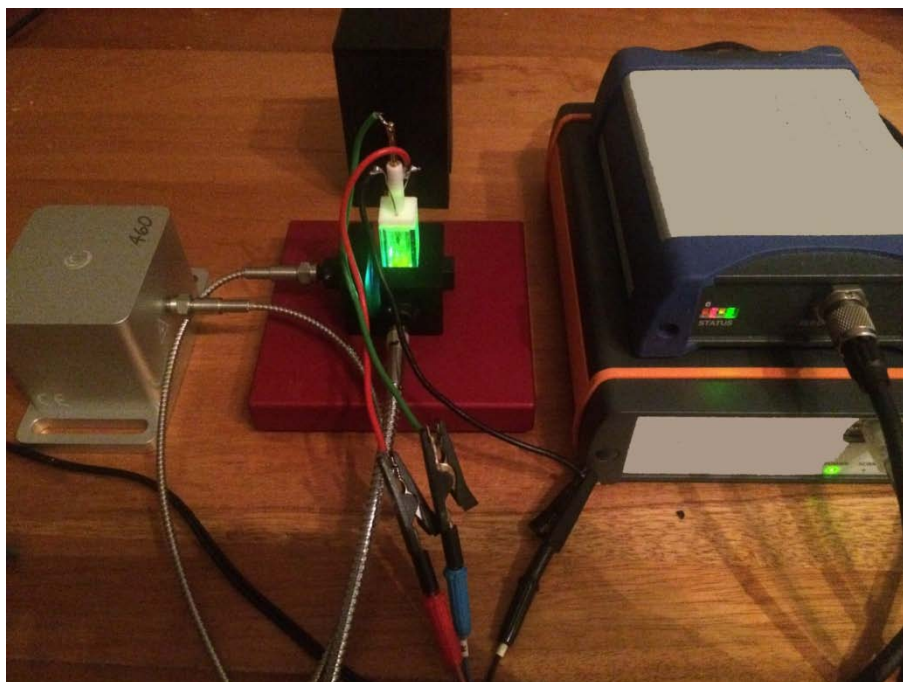
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**Abstract**  Spectroelectrochemistry of Electrochromic and electroluminescent substances shows a strong correlation between electrochemical reactions on electrodes and changes in absorbance or luminescence adjacent to the electrode. This was demonstrated by the well-known substances methylviologen and tris (2,2'-bipyridyl) dichloro-ruthenium [Ru (bpy)$_3$]$^{2+}$. The experimental setup used a conventional potent iostat connected to a fiber spectrometer. Different commercial spectroelectrochemical cells were used: A thin-film absorption cell with a platinum mesh working electrode and as pecular reflection/transmission cell with different screen-printed electrodes. For luminescence measurements, a conventional quartz cuvette with the platinum mesh electrode was used. All cells were inserted into commercial cell holders with connectors for optical fibers. Spectroelectrochemistry becomes increasingly important as an analytical method. In addition, the empirically observed didactical problems of misunderstanding electrochemical electrode reactions can be overcome by visualizing the electrode processes in spectroelectrochemical measurements. The procedures followed in these experiments were designed for typical undergraduate students in electrochemistry.

Graphical Abstract

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# 1. Introduction

Two different techniques, electrochemistry and (optical) spectroscopy, can be combined for studying redox reactions in detail. By applying an appropriate voltage to an electrode, the substance under investigation can be oxidized or reduced. Spectral measurements were simultaneously made adjacent to the electrode. This bidimensional spectroelectrochemical technique is a convenient means for simultaneously obtaining spectra and redox potentials and for observing subsequent chemical reactions of the electrogenerated species [1]. This will be shown with the electrochromic methylviologen ($MV^{2+}$) and the electroluminescent tris (2,2'-bipyridyl) dichlororuthenium ($[Ru(bpy)_3]^{2+}$).

Electrochromic or electroluminescent substances are redox indicators that change color or luminescence depending on their redox state [2,3]. Electrochromic materials have different applications: electrically conductive windows ("smart windows" or "chemical blinds"), heat insulation glazing, and rear-view mirrors in cars that can be darkened when high-beams would blind the driver [2].

A desired characteristic of electrochromic and electroluminescent materials is their cyclic stability. This means that a huge number of color changes are possible without affecting the color. Some examples of electrochromic materials are tungsten oxide ($WO_3$) [4,5,6,7], polyaniline (PANI) [8,9,10,11], and different viologens [12,13,14,15,16,17,18,19]. $[Ru(bpy)_3]^{2+}$ is one of the most widely studied electroluminescent systems. After oxidation, $[Ru(bpy)_3]^{3+}$ reacts with an appropriate co-reactant [20] and an excited state ($[Ru(bpy)_3]^{2+})^*$ is produced that decays under the emission of radiation. The intensity is a means of the concentration of the co-reactants [20,21,22,23].

The investigation of electrochromic and electroluminescent materials is not only interesting for their technical applications but also under didactical aspects, because the combination of electrochemical and optical information may promote the understanding of electrochemical processes [24,25,26]. Empirical research has shown that students do not understand the relationship between electrode reactions and current. Students also mix up ions and electrons. In addition, electron transfer processes and diffusion to and from the electrode are often misunderstood, and diffusion and migration in an electric field are mixed up [27,28,29,30,31].

We think that some of these problems of misunderstanding electrochemical reactions could be overcome by visualization of the electrode processes. Therefore, some of the investigated difficulties in understanding electrochemistry can be reduced by combining electrochemistry and optical spectroscopy. This means that voltage-induced redox reactions are correlated with color changes or luminescence. Because our survey was just qualitative, we did no investigations with empirical rigor. The results are explorative, a first step in reducing some misconceptions in electrochemistry for a better understanding of electrode processes.

More reliable empirical investigations have to be done to see whether the combination of electrochemical and spectroscopic measurements result in a deeper understanding of these processes.

The combination of electrochemistry and optical spectroscopy comprises electrogenerated chemiluminescence [32,33,34,35] and voltabsorpto- and voltluminograms [21]. Here, we focus on the last two. It is convenient to present the derivation of the absorbance or luminescence versus voltage because, in this presentation, the beginning of the optical change can be much better highlighted.

# 2. Laboratory Work and Didactical Objectives

The experiments are part of an experimental physical chemistry course at the University of Education Ludwigsburg, Germany, and can be completed by pairs of students in one semester (total laboratory work in four hours a day, 4 weeks in total. The described experiments here are only a part of the total laboratory work).As mentioned in the keywords, the described experiments were conducted in a second-year undergraduate-level university course in the analytical electrochemistry part of the physical chemistry course.

Until now, sixty students (in three lab periods 2017-2019, in six courses) carried out the described experiments at the end of a practical electrochemistry course. This electrochemistry part comprises the following four experiments: silver-zinc and lithium-ion battery, cyclic voltammetry and square wave voltammetry of different pharmaceutics, electrogenerated chemiluminescence of $[Ru(bpy)_3]^{2+}$ with tripropylamine and proline as co-reactants and at least the described experiments. We would like to summarize the didactic reasons for spectroelectrochemistry to an audience of chemistry students. From a lecture in physical chemistry first-year undergraduates already know the theoretical background of cyclic voltammetry. In the practical electrochemistry course, students measured cyclic voltammograms for the first time, followed by the investigation of electrogenerated chemiluminescence (ECL) of $[Ru(bpy)_3]^{2+}$ with different co-reagents. This means that the experiments described here, link both cyclic voltammetry and spectroscopic measurements. This includes not only the theoretical background, but also the practical investigation of the combination of electrochemical instruments (potentiostat with working, reference and counter electrode), and light sources (LED and Xe-lamp) and light detection (photodiode, photomultiplier and CCD-detector). The pedagogical effectiveness comprises the understanding of two different analytical methods that are combined in spectroelectrochemistry. This expands the knowledge about electrode processes, because changes of the current are connected with an optical phenomenon. Indicating by the negative current peak in the cyclic voltammogram the color change must be the result of a reduction.

Students showed a deep understanding of the main topics of cyclic voltammetry (three-electrode setup, diffusion, electrode kinetics, i.e. reversible, quasi-reversible, irreversible reactions, relation between current peak and scan rate). As spectroscopic measurements were already part of several courses in organic and inorganic chemistry and cyclic voltammetry and ECL measurements were done just

before, most of the students were able to perform the spectroelectrochemical experiments successfully. The electrode processes of the ECL of $[Ru(bpy)_3]^{2+}$, however, are quite complex and must be specified by the literature.

We suggest that high-achieving students enjoyed especially the spectroelectrochemical experiments, because the combination of two disparate subjects-electrochemistry, and light detection-were quite unusual.

The limitation of the described experiments is the narrow spectral range that excludes both UV and IR (and Raman) measurements. In addition, changes on a microscopic scale cannot be detected.

In ongoing experiments fourth-year undergraduates have to estimate the analytical strength of spectroelectrochemistry and compare it with cyclic voltammetry, square wave voltammetry and gas chromatography mass spectrometry. In addition, students have to investigate the influence of the electrode surface on electrode kinetics that can be done by electrochemical impedance spectroscopy.

# 3. Hazards

Methylviologen dichloride hydrate or 1,1′-Dimethyl-4,4′-bipyridinium dichloride (Paraquat dichloride), CAS number 75365-73-0, purchased from Sigma-Aldrich, No. 856177,has acute oral toxicity and is toxic by inhalation and irritation to the skin.

Tris (2,2'-bipyridyl) ruthenium (II) chloride hexahydrate $([Ru(bpy)_3]^{2+}$ $Cl_2*10H_2O)$, CAS number 50525-27-4, purchased from TCI, No. T1655, has no known toxicity.

Sulfuric acid (2 N), 99,999%, purchased from Sigma-Aldrich, No. 339741, is toxic by irradiation to the skin.

Sodium dihydrogenphosphate dihydrate, purchased from Roth (Germany), No. T 879.1, is non-toxic; specific cautions are not necessary.

# 4. Experimental Procedure

## 4.1. Reagents

We used $10^{-3}$mol/L methyl viologen ($MV^{2+}$)in sulfuric acid (2 N) and $10^{-4}$mol/L $[Ru(bpy)_3]^{2+}$in $NaH_2PO_4*2H_2O$ (0.01 mol/L). Ultrapure water was obtained from tap water with additional cleaning in a reversed osmosis system, leading to an electric conductivity of about 0.2 μS/cm.

## 4.2. Apparatus and Instrumentation

Cyclic voltammetry measurements [36-44] were carried out with μStat 400 potentiostat from Drop Sens that was controlled by Drop View software.

We used commercial screen-printed electrodes (SPE) [45] from DropSens: DRP-110 with carbon, DRP-220 AT with gold as the working electrode for specular reflectance measurements, and DRP-ITO with indium tinoxide as the working electrode for transmission measurements. SPEs from other firms (Orion High Technologies, Pine Instruments, BVT Technologies, BST Bio Sensor Technologies, or Gwent) could also be used. SPEs are low cost and easy to use electrodes, and the volume of the investigated solution requires only 60μL. However, they

have the disadvantage that they cannot be cleaned by polishing or in an ultrasonic bath because the coating would be damaged. While other experiments with SPEs focus on the analytical determination of an analyte [46], the SPEs used here provide a fast and easy indication of an electrochemical reaction by simultaneously recording a color or luminescence change.

Thanks to the spectroelectrochemical thin-film quartz cell [47] "OTE"(we used DRP-PTGRID-TRANSCELL from DropSens), bulk electrolysis could be easily carried out while optical transmission measurements (optical path of 1 mm) are acquired in the solution close to the electrode. The platinum mesh working electrode, the silver chloride reference electrode, and the platinum counter electrode are connected on top in a Teflon cap and have a transmission of light of about 90%. This electrode system could also be used in conventional cuvettes for luminescence measurements. In this case, the electrode cap with the mounted platinum mesh would be placed in a 45° position in the cuvette. Stray light could be eliminated by the spectrometer software as reference.

The electrochemical cell "E-cell" (DropSens, DRP-Trans-/Reflecell) is made of Teflon® and is suitable for performing reflection and transmission experiments with opaque and transparent SPEs. The SPE was put into a milled groove. Above the SPEs, the excitation/reflection fiber was inserted into a hole directly above the working electrode (4 mm diameter). The fiber consists of six illumination fibers around one read fiber. The first was connected with the light source, the last with the spectrometer. Below the SPE, a lens (DropSens, DRP-CLENS, focal length about 10 mm, wavelength 190-1250 nm) focusses the light that passes through the transparent ITO-SPE into the transmission fiber. The transmission fiber (DropSens RPROBE-VIS-UV and TFIBER-VIS-UV, wavelength 190-1250 nm)guided the transmitted light into the spectrometer.

We used two different light sources, a broadband Xe-lamp for absorption and reflection measurements (HID Xenon-Kit H11 55 W Slim - 4300K from Led Perf (https://www.ledperf.de) and a 365 nm LED for luminescence measurements (Lasertack, Kassel, Germany, PD-01237).

The spectrometer used was the fiber spectrometer AvaSpec ULS 4096 CL, 350-800 nm, from Avantes, controlled by the software AvaSoft (distributer: Mountain Photonics, Augsburg, Germany).

Some commercial spectroelectrochemical two-in-one systems exist: Spelec from DropSens/ Metrohm and Spectro-115U UV/Vis from Gamry. These systems are new and relatively expensive.

Here, we used a combination of a potentiostat with a conventional spectrometer because it is much cheaper and still fulfills all the requirements of a spectroelectrochemical measurement. This combination has the educational advantage that because the electrochemical and spectroscopic parts are separated and transparent, students can easily understand the experimental setup in detail.

However, the disadvantage is that potentiostat and spectrometer are controlled by different software, and because the potentiostat does not generate a trigger pulse to start the spectrometer, temporal correlation of the two systems must be done manually. However, after only minimal training, the jitter between the potentiostat and

spectrometer could be reduced to a fraction of a second, which is low enough for accurate measurements.

## 4.3. Procedure

The following experiments comprise a combination of cyclic voltammetry and absorption/transmission and luminescence measurements.

The correlation between the electrochemical processes and the optical response becomes significant when the derivative absorption or luminescence is represented, which can easily be done using Excel.

Figure 1 shows the thin-film absorption cell used with the cuvette holder and the reflection/absorption cell. Luminescence was measured in a conventional cuvette. All cuvette holders have fiber connections.
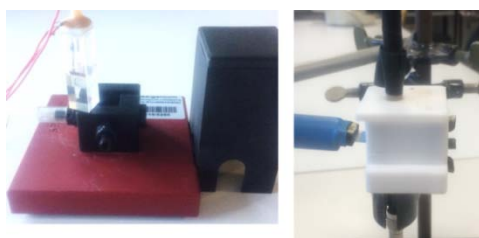


**Figure 1.** Left: Thin-film absorption cell (DropSens) with cuvette holder and coverage for preventing stray light (Avantes): "OTE". Right: Reflection/transmission cell with two types of fibers: specular reflectance fiber (above, black) and transmission fiber (bottom, bright). The electrode holder for the screen-printed electrodes is on the left side: "E-cell".

## 5. Results and Discussion

### 5.1. Cyclic Voltammogram of $MV^{2+}$

Figure 2 shows the cyclicvoltammogram of $MV^{2+}$ with ITO-SPE. The reduction peaks (negative current) and oxidation peaks (positive current) are characterized in Table 1.

As the reduction peaks are clearly determinable, the anodic peaks 1 and 2 are vague. In this paper, however, we do not want to elucidate the complete reaction mechanism [13].

### 5.2. Spectra of $MV^{2+}$ and $MV^+$

$MV^{2+}$ is colorless and absorbes around 255 nm. In order to get information about the absorption spectrum of $MV^+$, we reduced $MV^{2+}$electrochemically at -0.85 V in the thin-film cell. Figure 3 shows two spectra, one at -0.5 V (no reduction, only $MV^{2+}$) and another at -0.85 V (partial reduction to $MV^+$ after 30 s). The spectra were conducted with a conventional UVVIS spectrometer with the thin-film cuvette and the optically transparent platinum mesh electrode. It is obvious that the $MV^{2+}$ concentration decreases (solid line) while the $MV^+$ concentration increases (dotted line). Because the reduction is only adjacent to the electrode, the bulk solution still contains unreduced $MV^{2+}$ and the absorbance around 255 nm does not completely vanish.
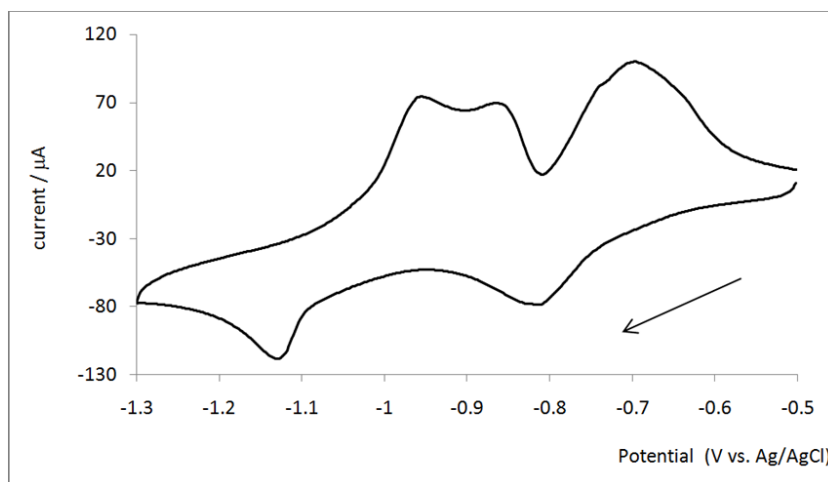


**Figure 2.** Cyclic voltammogram of methylviologen in sulfuric acid. Scanrate 10 mV/s. SPE DRP-ITO with ITO as the working electrode. The arrow indicates the scan direction.

**Table 1. Methylviologen redox reaction and dimerization / dissociation (assignments from Ref. 13).**

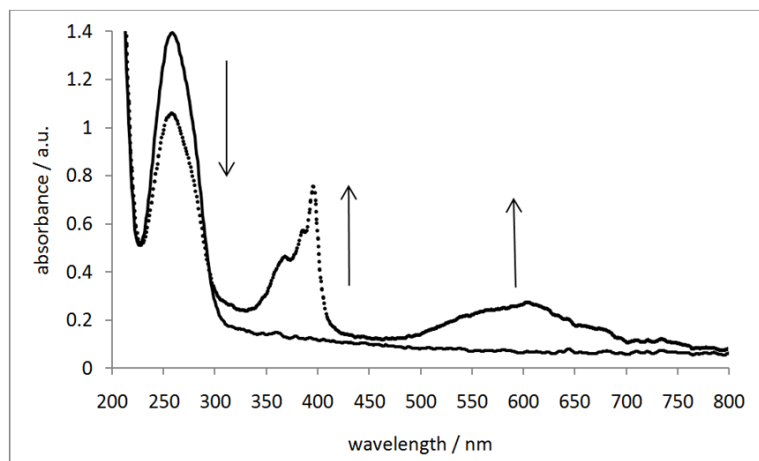| Cathodicpeak | Voltage(V)(at a platinum electrode) | Reaction | Color change |
|---|---|---|---|
| 1 | -0.8 | $MV^{2+} + e^- \rightarrow MV^+$ | colorless → blue |
| 2 | -1.115 | $MV^+ + e^- \rightarrow MV$ and $MV + MV^{2+} \rightarrow 2\,MV^+$ (comproportionation) | blue → yellow |
| Anodic peak | | | |
| 1 | -0.95 | $2\,MV \rightarrow (MV)_2$ (dimerization) | no color change in the visible region |
| 2 | -0.85 | $(MV)_2 \rightarrow 2\,MV^+ + 2e^-$ | colorless → blue |
| 3 | -0.7 | $MV^+ \rightarrow MV^{2+} + e^-$ | blue → colorless |

**Figure 3.** Absorption spectra of $MV^{2+}$ at two different potentials: Solid line: -0.2 V (pure $MV^{2+}$); dotted line: -0.7 V ($MV^+$ and $MV^{2+}$). The arrows indicate the change in absorption at -0.7 V.

Because MV is unstable in water [13], we could not record its spectrum. For technical applications, however, only the redox couple $MV^{2+}$ / $MV^+$ is more interesting, because, as Table 1 shows, MV dimerizes and may reduce the efficiency of a technical MV system by an incomplete formation and decay of the dimer.

## 5.3. Derivated Voltabsorptogram of $MV^{2+}$

Figure 3 indicates that the change of the spectrum around 350-400 nm and around 600 nm can be suitable for measuring the change in the absorption of $MV^+$ as a function of the applied voltage. Figure 4 shows the derivated voltabsorptogram, as a result of the specular reflection measurements with the opaque DRP-110 SPE inserted into the E-cell.

The non-derivative voltabsorptogram (supporting information, S5) shows that it is difficult to precisely determine the change in the absorbance and correlate them with the CV. The derivative absorbance, however, which could easily be calculated using Excel, gives more details (Figure 4). In this presentation, the variation in the absorbance is highlighted much better and the correlation between CV and absorbance change is more obvious [48,49].

The absorbance increases at about -0.7 V, the beginning of the first reduction of $MV^{2+}$ to $MV^+$. At about -0.85 V, the absorbance reaches a second maximum at about -1.06 V (see the star in Figure 4). The current peak results in the comproportionation reaction $MV^0 + MV^{2+} \rightarrow 2\ MV^+$, the absorbance of $MV^+$ increases a second time. [13] At lower potentials, $MV^{2+}$ is consumed and only MV results, followed by a decrease in the absorbance. In the reversed scan beginning at -1.25 V, the absorbance increases continuously: $MV \rightarrow MV^+$. At about -0.7 V, the blue $MV^+$ oxidizes to the colorless $MV^{2+}$ and the absorbance decreases. The reaction cycle is closed.

The derivative voltabsorptogram with ITO-SPE is presented in the supporting information (S5).

## 5.4. Three-Dimensional Representation

On measuring the accumulation effect at the electrode, several scans must be done in a row. Here, we used gold as the working electrode. $MV^+$ accumulated on the electrode, as can be seen in both the cyclic voltammogram and the spectra (Figure 5). Here, the voltage range includes only the redox reaction $MV^{2+} + e^- \leftrightarrow MV^+$. It can be noticed that each scan increases the $MV^+$ concentration through absorption effects.
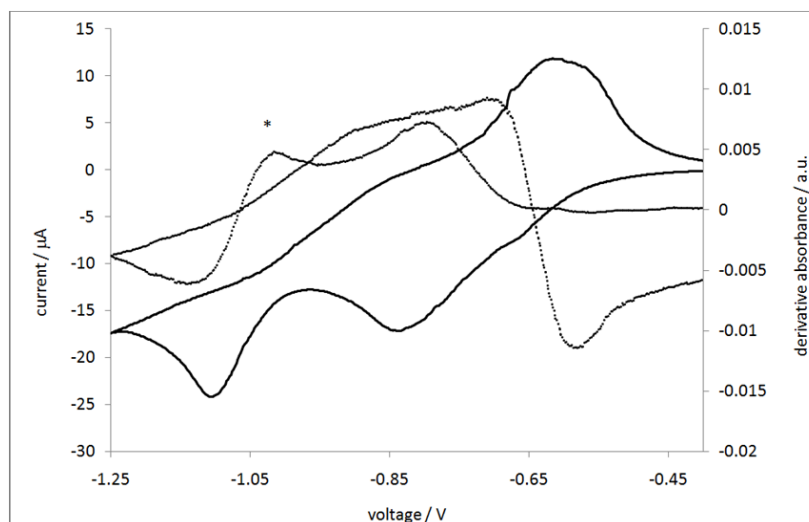


**Figure 4.** Voltabsorptogram with derivative absorbance at 600 nm (dotted line). Solid line: CV. The arrow indicates the scan direction. Scan rate: 10 mV/s.
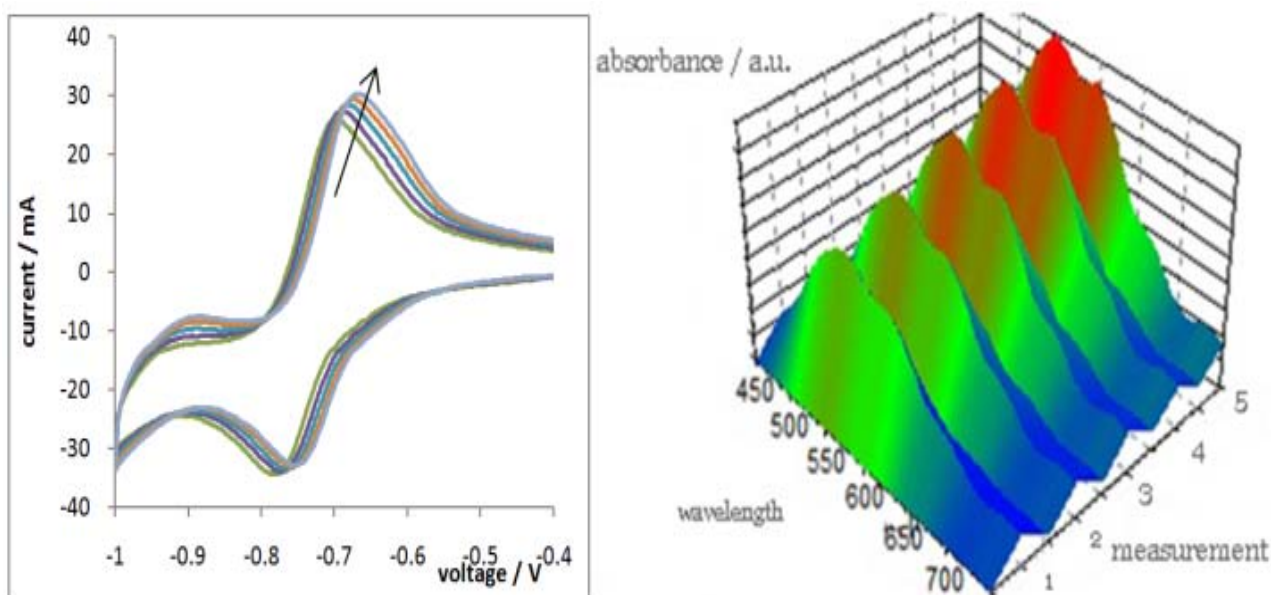
**Figure 5.** Accumulation effect of MV$^+$ on a gold electrode. Left: Cyclic voltammogram; right: spectra. Five times in a row. The arrow indicates the increase of the scan.
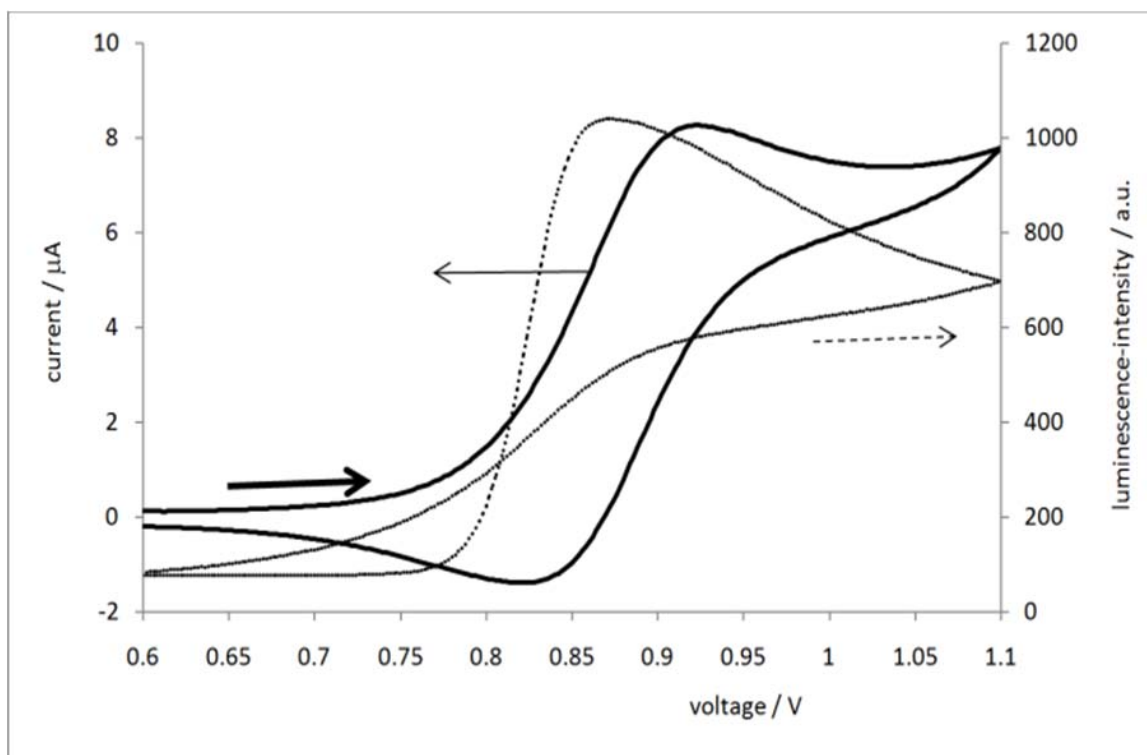


**Figure 6.** Left: Cyclic voltammogram (solid line) and luminescence-intensity (dotted line) of [Ru(bpy)$_3$]$^{2+}$ (1 mmol) vs. potential. Scan rate: 10 mV/s. The broad arrow indicates the direction of the scan.

## 5.5. Voltluminogram of [Ru(bpy)$_3$]$^{2+}$

A literature search of the database SciFinder resulted in 410 references containing both keywords "electrochemistry" and "luminescence". Most of these publications are concerned with the mechanism of the formation of electrochemiluminescence, and the application as a detection method in HPLC and capillary electrophoresis. In a review article [50], Kalyanasundaram refers to the salient features of the photochemical, photophysical, and electrochemical properties of [Ru(bpy)$_3$]$^{2+}$. Here, we will focus only on some aspects that are associated with our voltluminogram measurements. The cyclic voltammogram and luminescence intensity are shown in Figure 6. Here, the luminescence was recorded via a photomultiplier (Hamamatsu 1 P28A) and is not spectrally resolved.

The absorption and luminescence are shown in Figure 7.

Figure 8 shows the voltluminogram of [Ru(bpy)$_3$]$^{2+}$. Both the cyclic voltammogram and voltluminogram show distinct correlations. At 0.83 V, the oxidation of [Ru(bpy)$_3$]$^{2+}$ → [Ru(bpy)$_3$]$^{3+}$+ e$^-$ occurs and the luminescence decreases (note that the negative luminescence is plotted).

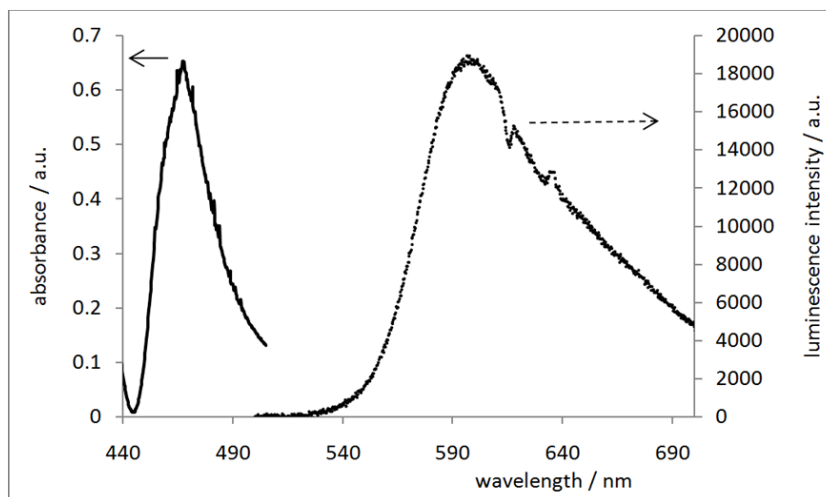**Figure 7.** Left: Absorption- (solid line) and luminescence spectrum (dotted line) of $[Ru(bpy)3]^{2+*}$ (Note that the two features in the luminescence spectrum is due to a failure in the CCD of the spectrometer used).
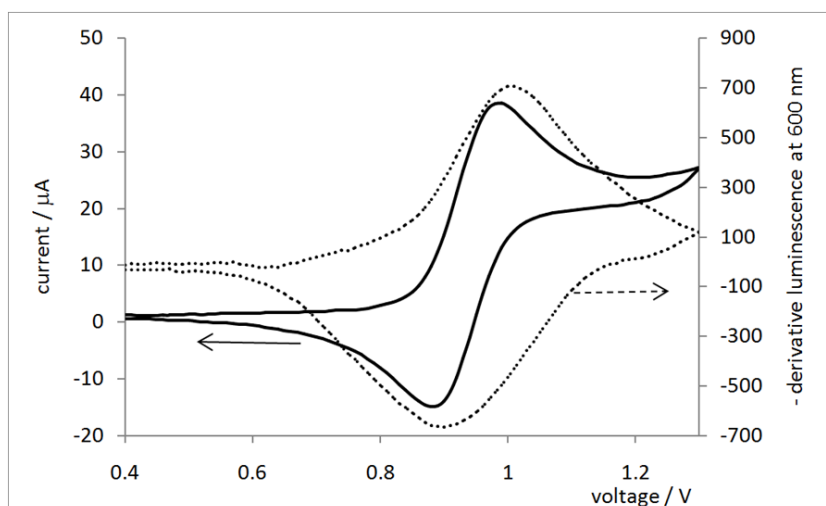


**Figure 8.** Voltluminogram of the luminescence variation of $[Ru(bpy)3]^{2+}$ at 600 nm. Cyclic voltammogram (solid line) and negative derivated luminescence spectrum (dotted line). The broad arrow indicates the direction of the scan.

# 6. Conclusion

Spectroelectrochemistry is a very powerful technique to observe electrochemical and optical changes at the electrode. Using low-cost disposable opaque and transparent screen-printed electrodes and a thin-film electrochemical cuvette, changes in electrochemical and optical properties could be easily measured. The combination of a potentiostat with a fiber spectrometer offered a new tool in studying the redox chemistry of substances that change their color when oxidized or reduced. The electrochromic methylviologen and the electroluminescent $[Ru(bpy)_3]^{2+}$ are model substances for demonstrating the spectroelectrochemical principle.

Our explorative qualitative study suggests, that in a didactical sense spectroelectrochemical information offers a new way for understanding electrode processes, because they become more clearly by combining electrochemistry with spectroscopic measurements.

# Accociated Content

In the supporting information the procedure of the experiments is listed. This includes the detailed description of the user interface of the measuring programs and the measuring procedure, especially the correlation between potentiostat and spectrometer.

# Notes

The author declares no competing financial interest.

# Acknowledgments

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# Supporting Information

### S1: Procedure of the experiments

The lab is opened during the days, and the participants have to register in advance. Students had to determine the oxidation and reduction potentials of the substance (methyl viologen and $[Ru(bpy)_3]^{2+}$) from internet research before laboratory work: $MV^{2+} / MV^{+}$: -0.73 V, $MV^{+} / MV^{0}$: -1.03 V and $Ru^2 / Ru^{3+}$: 0.88 V (all against Ag/AgCl, depending on the solvent)

All chemicals are putted on the lab bench.

Students had to prepare the different solutions with given concentrations:

- $10^{-3}$mol/L methyl viologen dichloride hydrate (purchased from Sigma-Aldrich, No. 856177) in sulfuric acid (2 N), 99,999% (purchased from Sigma-Aldrich, No. 339741).
- $10^{-4}$mol/L tris(2,2'-bipyridyl)ruthenium(II) chloride hexahydrate ($[Ru(bpy)_3]^{2+}Cl_2*10H_2O$) (purchased from TCI, No. T1655) in $NaH_2PO_4*2H_2O$ (0.01 mol/L).

Then students had to identify the main experimental devices for measuring voltabsorptogram and voltluminogram: Potentiostat (DropSens µStat 400), light sources (broadband Xe lamp for absorption and reflection measurements (HID Xenon- Kit H11 55 W Slim - 4300K from Led Perf (https://www.ledperf.de), a 5500 K white light LED for absorption measurements and a 470 nm LED for luminescence measurements (Lasertack, Kassel, Germany, PD-01237)). Afiber - spectrometer (AvaSpec ULS 4096 CL, 350-800 nm, from Avantes, controlled by the software AvaSoft,version 8.9.10 (distributer: Mountain Photonics, Augsburg, Germany),a thin-film cell in the cell holder(DRP-PTGRID-TRANSCELL from DropSens)and different opaque and transparent screen-printed electrodes (all from DropSens) (Figure S1).
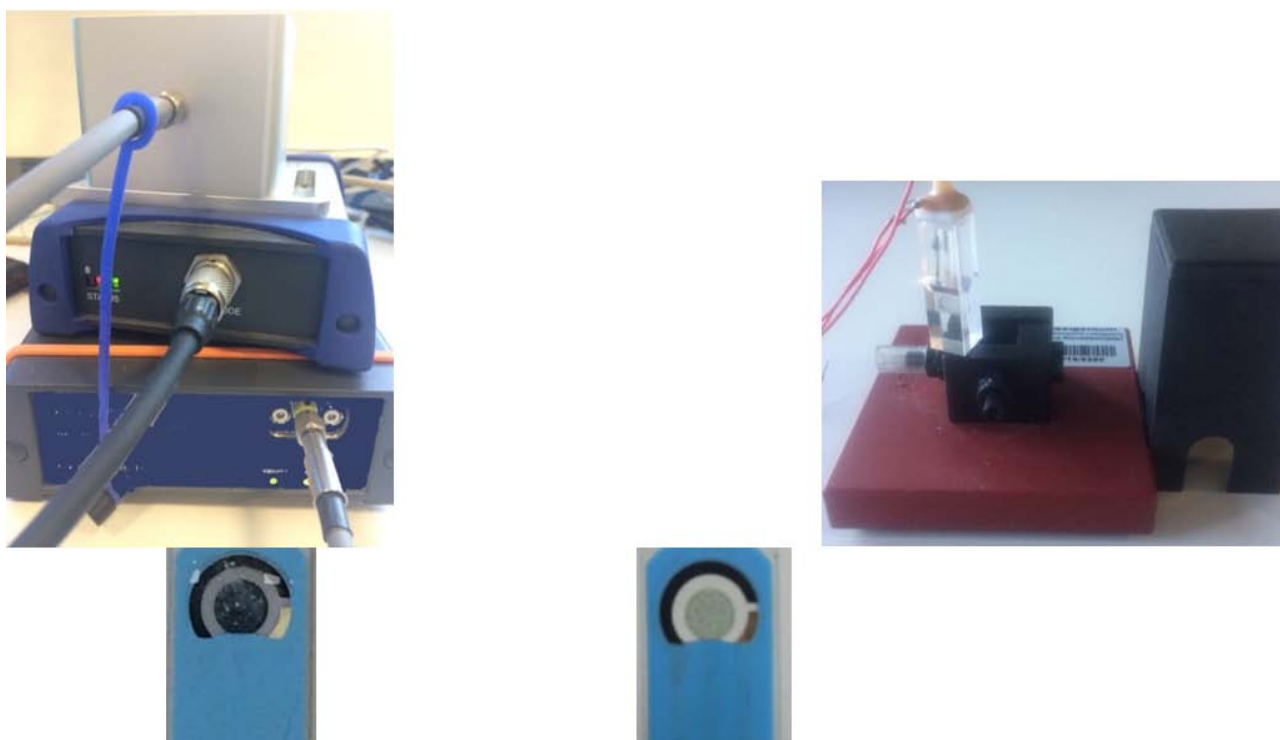


**Figure S1.** Left: LED, potentiostat, and fiber-spectrometer. Top, right: thin-film cell with cell holder and coverage. Bottom: opaque (left) and transparent SPE (right).

#### a) Voltabsorptogram

First, the appropriate light source must be chosen, either the Xe-lampor the LED. Therefore, the absorption spectrum of methyl viologen ($MV^{+}$) must be compared with the emissions spectra of the light sources (Figure S2). Note, that the spectrometer used has a limited spectral range from 350 nm to 800 nm. Therefore, the change of the absorption of $MV^{+}$, the reduced species of $MV^{2+}$, is measured in the visible region and not the absorption of $MV^{2+}$ in the UV.

Obviously, the emission of the LED has the best overlap with the absorption spectrum of $MV^{+}$.

By means of Figure S3 students are able to connect the different parts of the experiment. In detail, they connect the potentiostat with the three electrodes in the thin-film absorption cell (DropSens, DRP-PTGRID-TRANSCELL) via alligator clips. The cell is placed inside the cuvette holder (Avantes). Stray light can be prevented by coverage (this is especially important in luminescence experiments). Lamp and spectrometer were connected with the cell holder via two fibers (diameter: 1mm, 1 m long, wavelength range 200-800 nm, SMA jack, Avantes).

Figure S4 shows the user interface of the measuring programs. After starting the programs, students have to set the scan rate and the current range of the potentiostat. The spectrometer software proposes integration time and averaging number of the spectra. With these proposed values no saturation is measured.
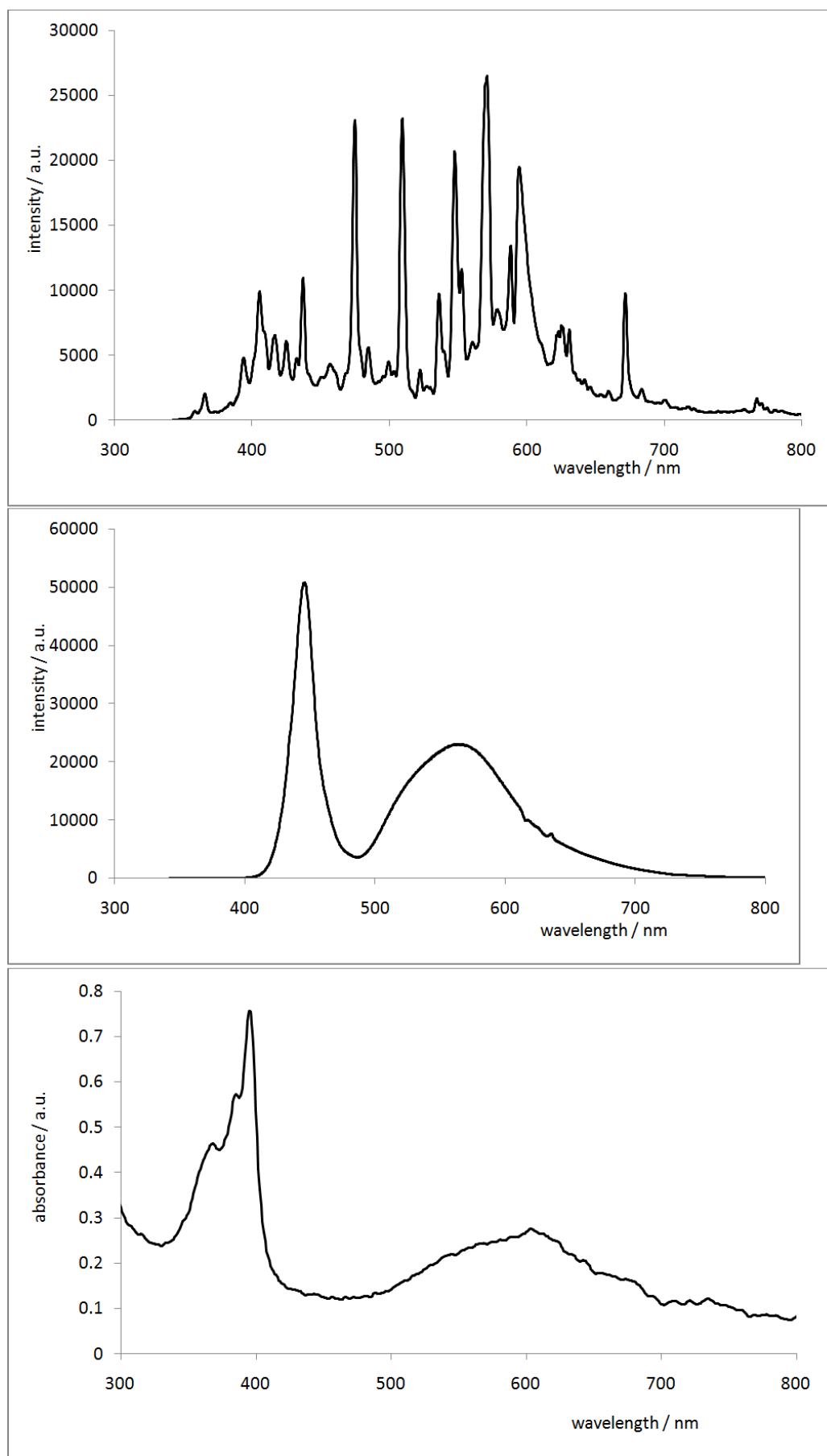
**Figure S2.** Emission spectra of the Xe-lamp (top), of the 5500K LED(middle) and absorption spectrum of MV$^+$ (bottom). All spectra were measured with the Avantes spectrometer.
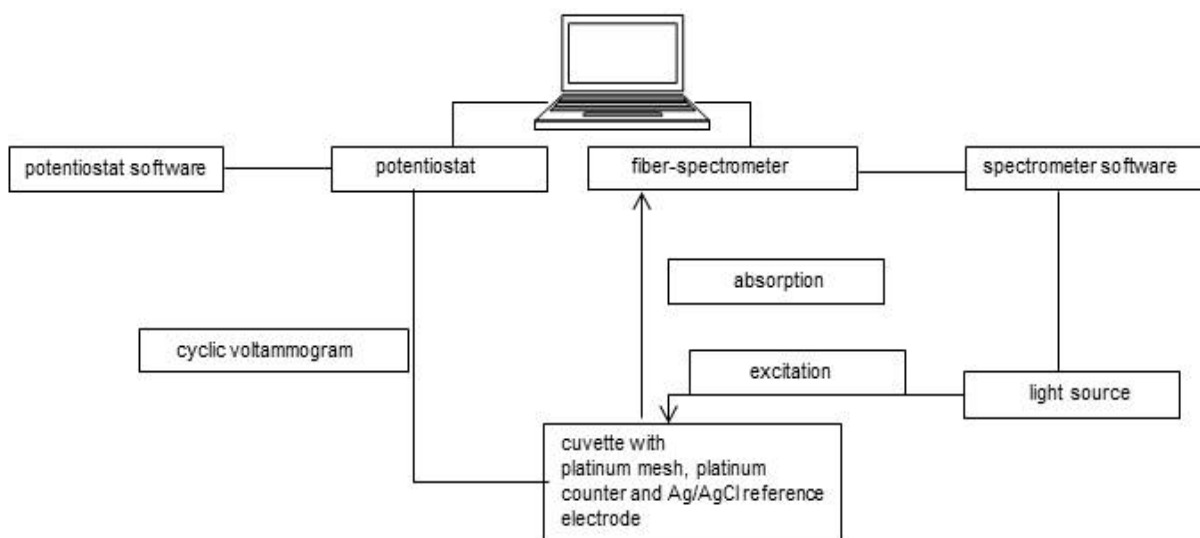
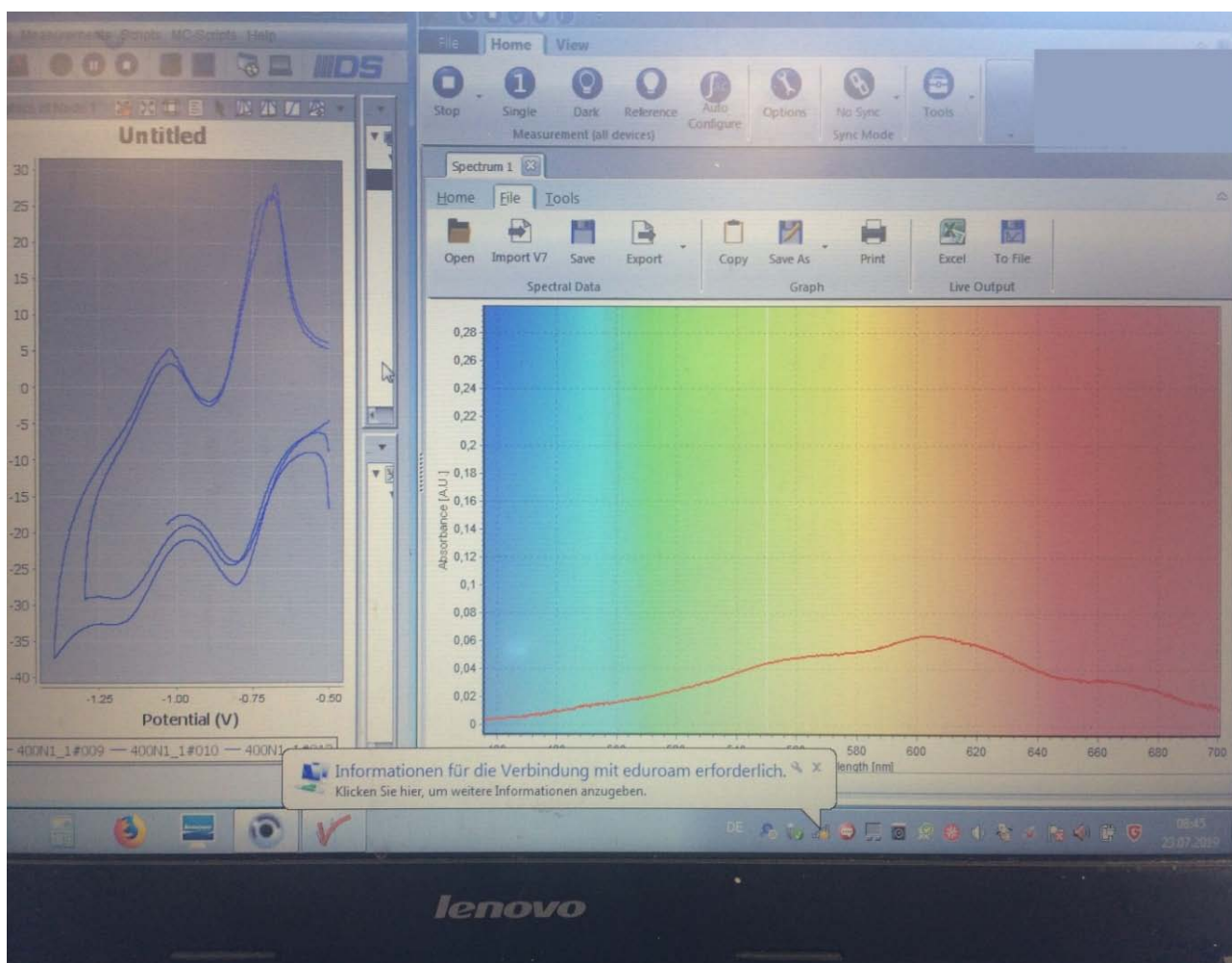**Figure S3.** Scheme of the voltabsorptogram.



**Figure S4.** The measuring programs used. Left: Cyclic voltammogram, right: UV-VIS spectra (350 nm-700 nm).

The absorbance mode is set by the absorbance button, luminescence by the scope mode. Every new integration time needs a new dark and reference zero adjustment. After clicking the button the absorbance or scope intensity become zero.

After fixing the values of the cyclic voltammogram (scanrate and scan range, i.e. start, reversal and end values), the potentiostat can best arted. After sending the set values to the potentiostat the software sends an equilibration command for about 3 seconds, and the potentiostat begins to run. Immediately, the spectrometer must be started manually.

The CV and spectrometer data must be synchronized. This means that if the potentiostat takes 200 current / voltage couples (+0.5 V -> -0.5 V -> +0.5V, scan rate 0.01 V/s) the spectrometer also must record 200 spectra - one per second. The spectrometer used has two options: single and continuous measurement. Here the last must be activated.

After the end of a measurement cycle, all data can be transferred into Excel and displayed separately: voltage against current and absorbance against wavelength. One can separate those absorbance data at a given wavelength that show a maximum change as a function of the applied voltage (600 nm in Figure S5). Another option may be plotting the whole spectrum against fixed voltages (i.e. the voltage where no reduction or oxidation occurs and the voltage of a current peak). Therefore, one can easily show the difference between the spectra with and without an electrochemical reaction. Figure S5 shows an extract of the data and the voltabsorptogram. In addition, three spectra with and without an electrochemical reaction are shown.
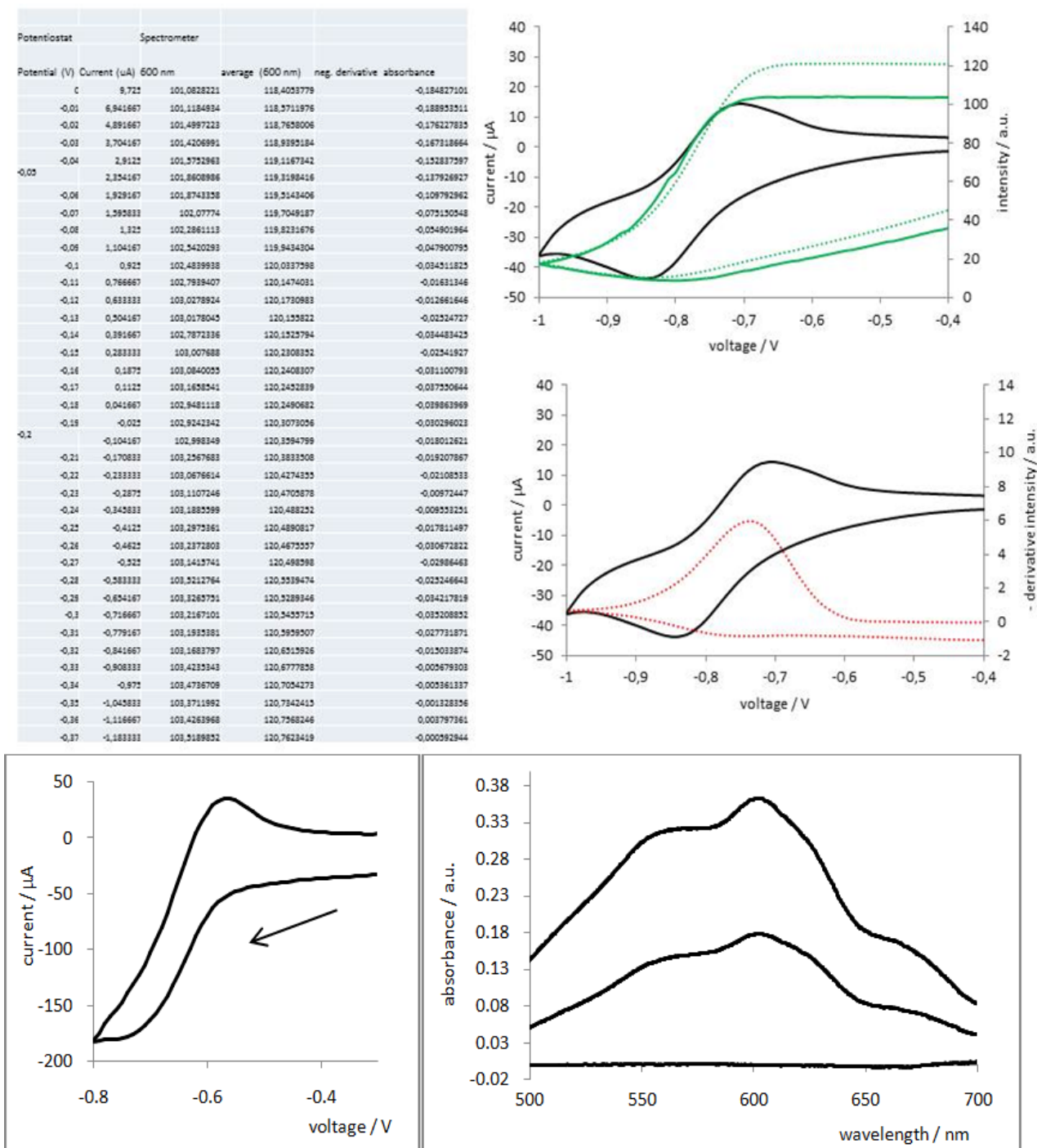


**Figure S5.** Extract of the CV and spectra data. Top left: data. Top right: Black line: CV. Greenline: absorbance intensity. green dotted line: average of the absorbance intensity. Middle right: negative derived absorbance (red, dotted line). Bottom: left: CV, right: spectra at different voltages. Curve 1: -0.5 V (start potential), curve 2: -0.8 V (forward scan), curve 3: -0.5 V (reversed scan)
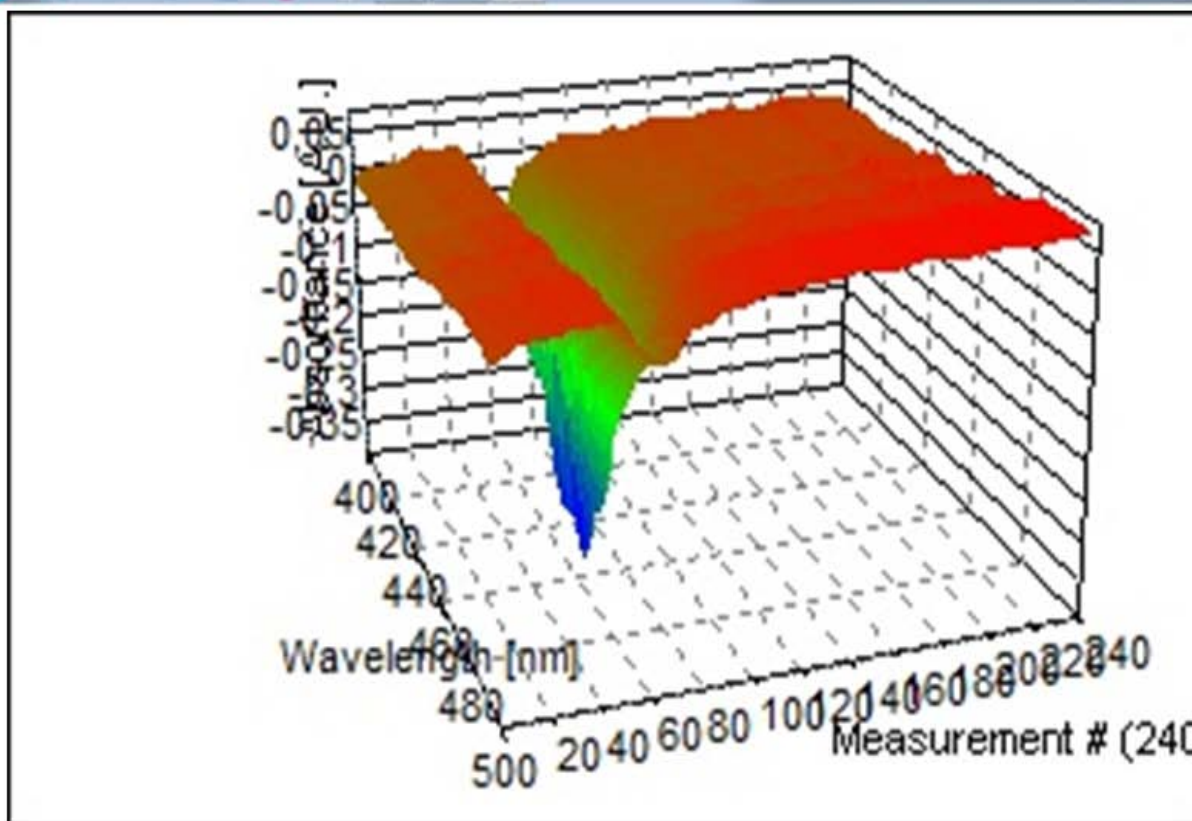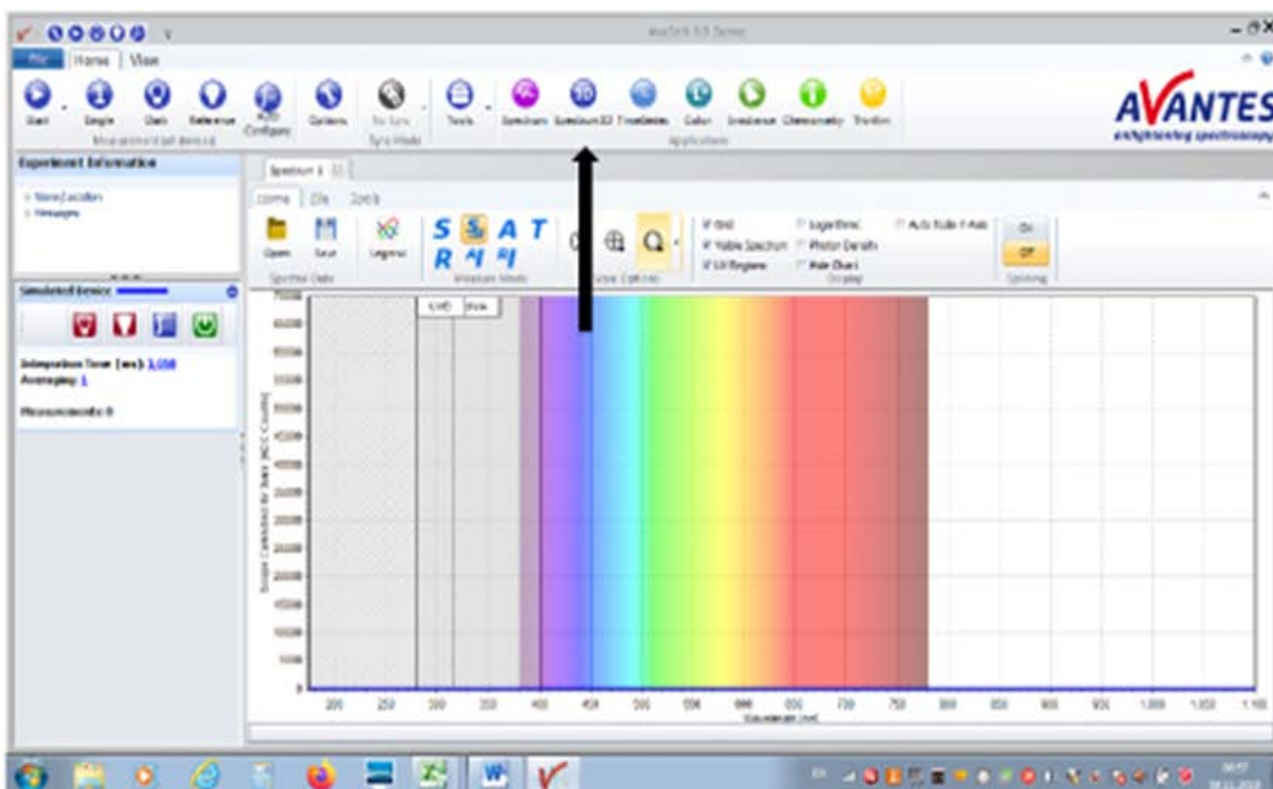
**Figure S6.** Top: Measuring program (circle and arrows: absorbance, transmission and 3d button). Bottom: 3d-absorption spectrum (note the shortcoming of the software used by turning of the 3d representation: axis labels overlap with numbers).

The spectra can be plotted in a three-dimensional diagram as well (Figure S6: absorbance vs. wavelength vs. number of measuring spectra. The last can easily be correlated to the potential).

b)  Specular reflection and transmission

The SPEs (opaque or transparent) were putted into the electrochemical cell (DropSens, DRP-Trans-/Reflecell). Above the SPEs the excitation/reflection fiber was inserted into a hole directly above the working electrode (4 mm diameter, DropSens: DRP-PROBE). The bifurcated fiber consists of six illumination fibers around one read fiber(Figure S7).
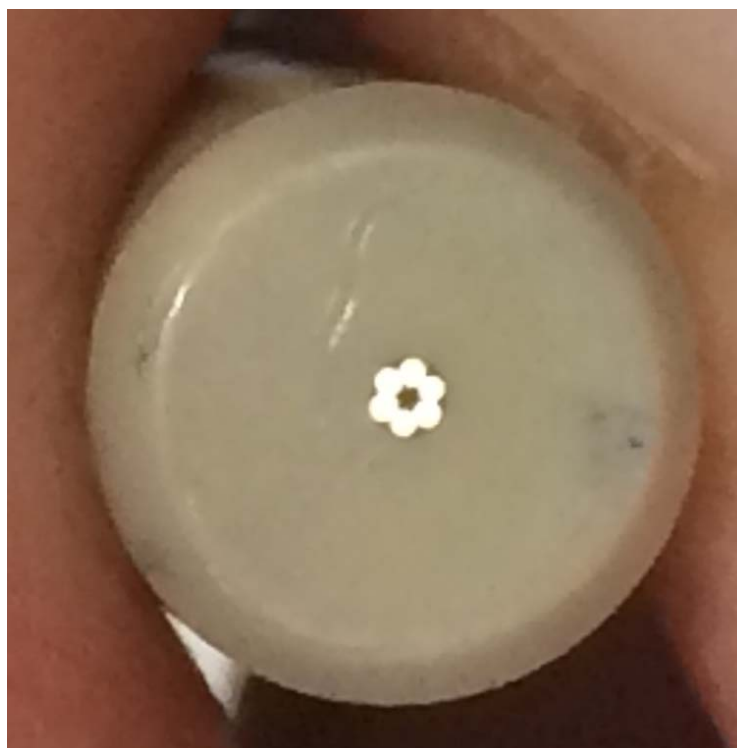
**Figure S7.** Bifurcated excitation - read fiber. Middle: read fiber (dark), surrounded by six excitation fibers (illuminated).

In case of absorbance measurements, the first was connected with the light source, the last with the spectrometer. The light passed through the solution (60 μL), was reflected from the surface of the opaque SPE and collected via the read fiber. In the transmission configuration a lens (DropSens, DRP-CLENS, focal length about 10 mm, wavelength 190-1250 nm) below a transparent SPE focused the light that passes through this SPE into the transmission fiber. The transmission fiber (RPROBE-VIS-UV and TFIBER-VIS-UV, wavelength 190-1250 nm from DropSens) guided the transmitted light into the spectrometer (Figure S8). In case of transmission measurements a transparent ITO-SPE was used (DRP-ITO from DropSens).



**Figure S8.** Electrochemical cell (white). Top: Excitation fiber (connected with the light source), read fiber (connected with the spectrometer). Bottom: Transmission fiber (connected with the spectrometer). Left: SPE with electrode holder (blue).

c)  Voltluminogram

There exist two different methods to measure voltluminograms: spectral resolved and unresolved luminescence.

**Unresolved luminescence**

As light detector a photomultiplier (Hamamatsu 1 P28A) was used (Figure S9). The photomultiplier tube was fixed directly above the opaque SPE. The light beam excites the substance under grazing incidence (not shown). The whole set-up must be light-proofed (black cardboard must be used).
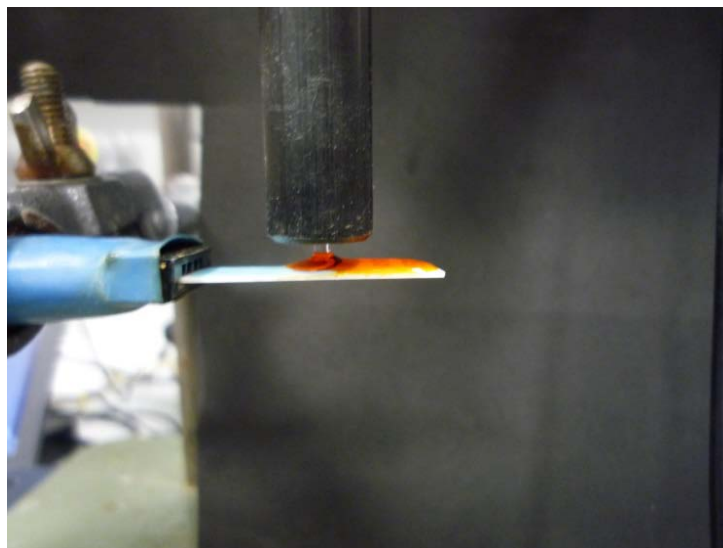
**Figure S9.** Luminescence measurement (total emission spectral, not spectral resolved): Opaque SPE, photomultiplier tube above the SPE. Light source is not shown.

### Spectral resolved luminescence

In case of spectral resolved voltluminogram measurements a conventional cuvette was used. The electrode cap with the mounted platinum mesh was placed in a 45° position in the cuvette. Excitation light source was the 470 nm LED ($\lambda_{max}$ ($[Ru(bpy)_3]^{2+}$) = 465 nm). In the cuvette holder used a mirror is placed in opposite to the detected luminescence to increase the emission signal.

Before starting the potentiostat, the emission intensity must be corrected to zero to better detect the change in luminescence intensity.

### ECL measurement

The used $[Ru(bpy)_3]^{2+}$ has a rel. strong luminescence; it is readily soluble in water and in non-aqueous media at room temperature and undergoes a one-electron oxidation reaction at about +1.0 V. $[Ru(bpy)_3]^{3+}$ can react with a co-reactant forming $([Ru(bpy)_3]^{2+})^*$ which can subsequently luminescent around 600 - 650 nm (Figure S10).
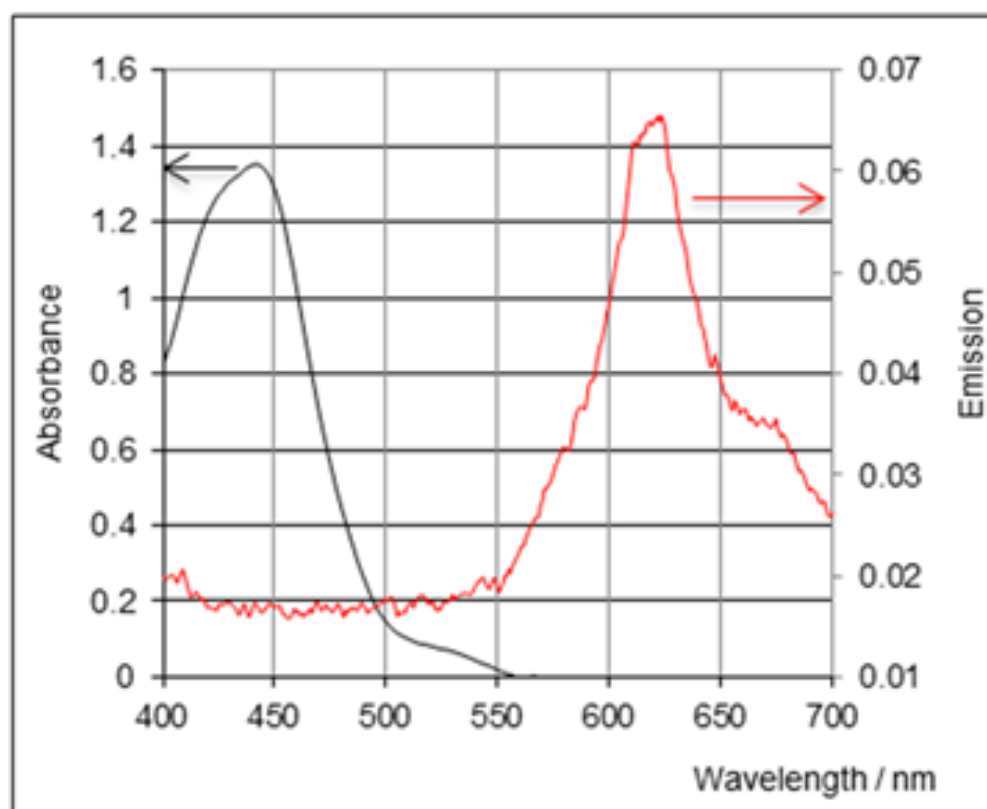


**Figure S10.** Absorption (black) and emission spectra (red) of $[Ru(bpy)_3]^{2+}$

DropSens offers an ECL-measuring system (ECL-Stat) comprising a potentiostat and a photodiode (Figure S11).

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**Figure S11.** ECL-Stat from DropSens. Left: Chamber with SPE, above: photodiode. Right: potentiostat.

The probe was 30 µL of 1 mmol/L $[Ru(bpy)_3]^{2+}$ in 0.1 mol/L $NaH_2PO_4$ and 30 µL 1 mmol/L DL-proline in 0.1 mol/L $NaH_2PO_4$. The solution was dropped onto the SPE, and the photodiode in the housing was folded onto the electrode.

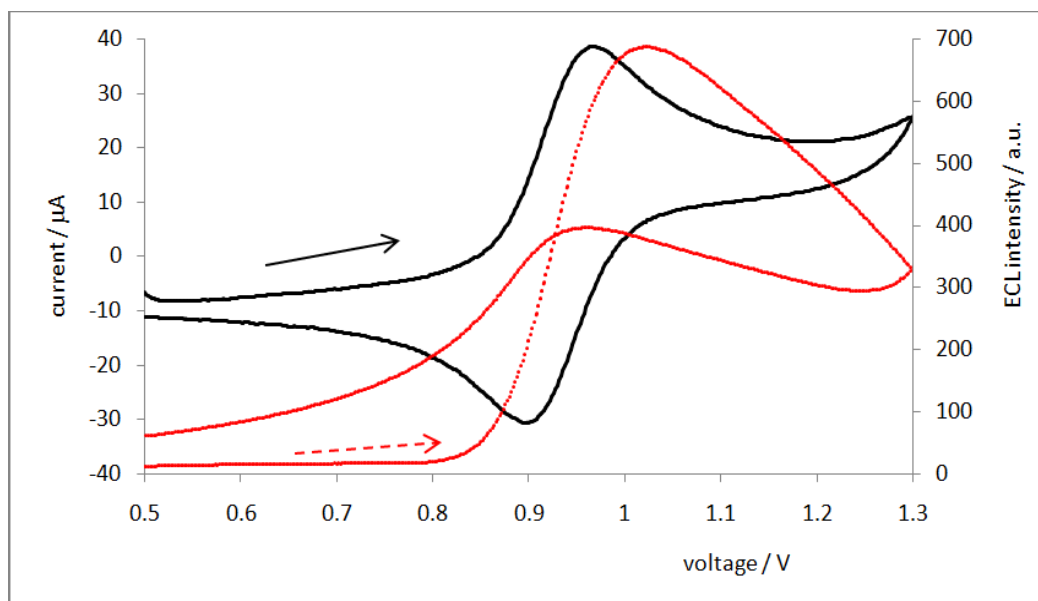Figure S12 shows the results (CV and ECL-intensity vs. voltage).



**Figure S12.** CV (black line) and ECL-intensity (red, dotted line) of $[Ru(bpy)_3]^{2+}$ / proline. The arrow indicates the scan direction. Scan rate: 0.01 V/s.

## S2: Questionaire

At the end of the experiments students had to complete a questionnaire ("Explain what happens at the first reduction potential of methyl viologen". "Explain the difference between absorption and luminescence measurements". "Interpret the measured voltabsorptogram and voltluminogram". "Why are the derivative spectra meaningful"? "What, do you think, is the advantage of the bidimensional spectroscopy")?