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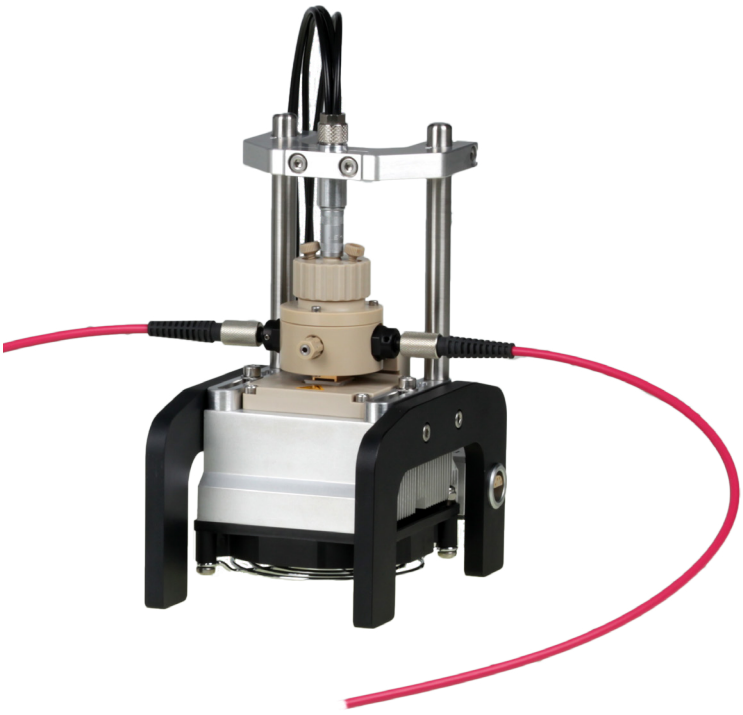
# Application note

## Spectroelectrochemical investigation of organic dyes

» 5-methyl-3-phenyl-1-*p*-tolyl-4,5-dihydro-1H-pyrazole-5-carboxylic acid methyl ester

» *N,N,N',N'*-tetramethyl-1,4-phenylenediamine



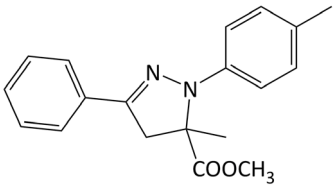

Mareike Falk

# Introduction

The study of charge transfer reactions does not only play a major role during investigation of energy conversion reactions in energy storage systems like fuel cells and batteries, but also in many other chemical or biological reactions as it holds for instance for the photosynthesis. By voltage application between two electrodes of opposite polarity separated by an electrolyte, charge transfer, resulting in oxidation and reduction reactions within the system, is forced. Thereby, the electron transfer reactions occur at the electrode/electrolyte interface. The electrodes might be either inert or could also be oxidized/reduced during the charge transfer reactions. Often, firstly reactive transition products like radicals are formed, which further react to the final products of the electrochemical system under investigation [1].

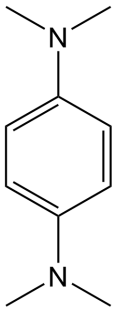
By application of a constantly increasing voltage with time as it is performed during cyclic voltammetry (CV) experiments, the reaction potentials of the species in the system under investigation are scanned. This delivers manifold information like for instance activation energies and stability windows as well as information about the kinetic behaviour of the system, kinetic inhibitions or diffusion coefficients [2], [3]. For determination of these values sometimes serial experiments with varying measurement parameters like scan speed or temperature have to be performed.

However, in many cases reaction potentials cannot be assigned unambiguous to a certain charge transfer reaction, i.e. the formation of a particular species. Here, the application of other analytical tools is needed for unequivocal identification of the detailed reaction mechanism. If for example the charge transfer reaction goes along with varying optical properties of the system, employment of UV/Vis spectroscopy, in which the formation and disappearance of different species can be monitored by in- or decrease of absorption bands that are characteristic for a certain species, would be suitable. Thus, the so called UV/Vis spectroelectrochemistry is a powerful tool for identification and study of manifold charge transfer reactions to get further insight in detailed reaction mechanisms as well as for determination of stability bounds of complete redox systems.




**Scheme 1:** 5-methyl-3-phenyl-1-p-tolyl-4,5-dihydro-1H-pyrazole-5-carboxylic acid methyl ester.

In this application note the redox behaviour of two different organic dyes is investigated by means of spectroelectrochemistry. The first substance we focus on is 5-methyl-3-phenyl-1-p-tolyl-4,5-dihydro-1H-pyrazole-5-carboxylic acid methyl ester, CAS No. 118794-97-1, see Scheme 1. It undergoes one step oxidation to the radical cation at approximately 0.6 V vs. $Ag/Ag^+$ (0.01 mol/l $AgNO_3$ in 0.1 mol/l tetrabutylammonium hexafluorophosphate in acetonitrile) and associated therewith a change in colour from yellow to light orange [4]. In the second step we study the redox behaviour of *N,N,N′,N′*-tetramethyl-1,4-phenylenediamine (TMPD), CAS No. 100-22-1, see Scheme 2. In organic solvents like acetonitrile its electrochemistry should follow a simple two-step mechanism, thereby changing its colour from transparent to blue [2].




**Scheme 2:** TMPD.

[1] B. Speiser, Chemie in unserer Zeit **1981**, *15*, I, 21-26

[2] L. A. Clare et al., J. Phys. Chem. C **2010**, *114*, 8938–8949

[3] R. G. Compton, C. E. Banks, *Understanding Voltammetry*, World Scientific Publishing Company, 2007

[4] Deutsche Metrohm GmbH & Co. KG, EC Application Work AW DE9-015-012011, *Spektroelektrochemische Untersuchung von 5-Methyl-3-phenyl-1-p-tolyl-4,5-dihydro-1H-pyrazol-5-carbonsäuremethylester*

# Experimental

For combined spectroscopic and electrochemical measurements of the dyes, a TSC spectro measuring cell, see Figure 1, in combination with a Microcell HC setup has been used. This measuring cell enables the simultaneous spectroscopic and electrochemical investigation of liquid moisture-, air- or photosensitive samples under temperature control. The PEEK casing guarantees hermetic sealing of the cell interior from the outside. As working and counter electrode a platinum mesh and a stainless steel disc electrode, 6 mm in diameter, were used. A $Ag/Ag^+$ pseudo reference electrode was employed and positioned as close as possible to the platinum mesh for resistance minimization between these two electrodes. Since the position of the optical windows inside the casing is variable to a certain extent, the length of the optical path can be easily varied in the range between 1.4 and less than 0.5 mm until the windows nearly contact the platinum mesh to meet the best conditions for the sample under investigation regarding its concentration and absorption strength.

Besides measuring cell TSC spectro mounted onto the Microcell HC setup, a Metrohm Autolab PGSTAT204 equipped with a FRA32-module was used for the electrochemical analysis. For data acquisition, the NOVA 1.11 software (Metrohm Autolab B.V.) has been employed. In the Microcell HC setup, temperature is controlled via a Peltier element which enables adjusting sample temperatures ranging from -40 °C up to +100 °C, depending on dew point and sample amount. It can be controlled either by the software from many measurement bridge manufacturers like Novocontrol, Biologic, Zahner or Solartron, as well as by a dll embedded into a NOVA specific procedure (hcDLL SE, developed by rhd instruments GmbH & Co. KG). In combination with a Microcell HC setup the temperature accuracy is 0.1 °C in the thermo block.

An Avantes AvaSpec-2048 spectrometer equipped with AvaLight-DHc light source and software Avasoft 7.7 was used for recording the UV/Vis spectra in the range of 220 to 1000 nm. The spectrometer was used in the external trigger mode and coupled to NOVA software, so that each second voltage step a spectrum was recorded.


**Figure 1:** Exploded view of measuring cell TSC spectro. The measurement solution is filled from above into the PEEK casing. If needed, a membrane can be placed between the upper and lower part of the casing, being connected to each other by three screws and sealed by a gasket ring to separate the electrolyte compartments of counter and working electrode.

For the experiments an electrolyte composed of 0.1 to 0.25 mol/l tetrabutylammonium hexafluorophosphate (Fluka, $< 99.9$ %) in acetonitrile (ROTIDRY®, min. 99.9 %, by Carl Roth) was used. Concentrations of the dyes in the electrolyte solution were 0.25 mmol/l in case of the pyrazole derivative and 0.125 to 2.5 mmol/l for TMPD (Sigma-Aldrich, 99 %). The different concentrations result from optimization to obtain a good spectrum with maximum contrast as well as sufficient signals in the cyclic voltammogram. All chemicals were used as received without further purification. Preparation of the pure electrolyte and the TMPD solution occurred in an argon filled glovebox. For the pyrazole derivative, mixing with the electrolyte was performed at ambient air. Approximately 2 ml of the electrolyte-dye solutions were used for each of the experiments. All measurements were performed at 20.0 °C.

To reduce the diffusion of species formed at the counter electrode during the electrochemical experiment towards the working electrode, the compartments of counter and working/reference electrode can be separated by means of a membrane that acts as barrier especially for large molecules, but enables transfer of electrolyte salt molecules needed for charge balance during redox reactions at counter and working electrodes.

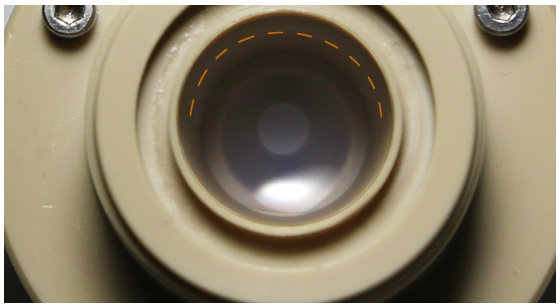


**Figure 2:** Top view of TSC spectro after spectroelectrochemical experiment using TMPD as analyte. The lower compartment, in which the working electrode is located, is blue coloured due to formation of the radical cation, while the upper part above the membrane (see the white bubble that formed under it for its exact location) is still transparent. The dotted orange line is displayed as guide for the eye to locate the upper filling level of the transparent part of the solution.

For spectroelectrochemical study of TMPD partially a Celgard® C480 membrane with a pore size of 21.5 µm was placed between working and counter electrode. Its blocking effect on the diffusion of the blue coloured radical cation is apparent from Figure 2, showing the top view of TSC spectro after a spectroelectrochemical experiment using TMPD as analyte. While the solution in its lower part, where the working electrode is located, and thus the formation of the radical cation took place, appears in blue colour, the upper part above the membrane is still transparent. However, the membrane does not completely hinders diffusion of the radical cation. Thus, after several hours the upper compartment also becomes blue, but for lifetime of a typical experiment the blocking effect of the Celgard® membrane is sufficient. By application of tighter woven membranes with smaller pores the diffusion hindrance would be even enhanced. Thus, by proper selection of a membrane suitable for the system under investigation, an effective separation of the cell compartments containing the electrolytes of counter and working electrode can be reached. This could distinctly limit the influence of side products on the sensibility of the spectroscopic experiment.

Scan speed of the cyclic voltammogram of TMPD was set to 10 mV/s, while the CV of the pyrazole derivative was recorded with 25 mV/s. Different values again are caused by optimization of each measurement. For instance, a faster scan speed results in reduced diffusion effects during the experiment and thus in a more complete reverse reaction, as the products formed during prior reactions have less time to leave the region close to the working electrode.

In both cases step size in the CV was set to 5 mV. For each of the two substances under investigation the respective voltage range was adjusted in a way to completely cover the whole redox reaction of the respective substance. Thus, for the pyrazole derivative a range from -0.2 V to 1.2 V was studied, while in case of TMPD a voltage range from -0.9 to 0.4 V was investigated to study only the first redox step, whereas for monitoring the complete reaction the range was selected to -0.5 to 1.5 V. While for the single step reactions, i.e. the spectroelectrochemical study of the pyrazole derivative and the first redox step of the TMPD, a relatively broad optical path length of 1.4 mm could be used, for investigation of the two step behaviour of the TMPD a smaller path length of less than 0.5 mm was needed to reduce diffusion of the intermediate away from the electrode so that it could react to the final product.

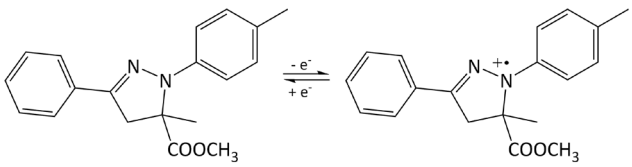
Prior to investigation of the dye containing solutions, pure electrolyte was filled into the measuring cell to record the dark and reference spectrum needed for background correction and calculation of the absorbance of the analyte dissolved in the electrolyte.

After filling the TSC spectro with the dye solution, firstly the contact between counter and working as well as between working and reference electrode was checked by means of impedance spectroscopy. Problems may arise due to air bubbles especially by usage of a membrane between the upper and lower compartment of the cell. If both high frequency impedance values are below a certain value depending on the sample properties, especially its conductivity, - in the present case of approximately 250 to 500 Ω in dependence on the concentration of the supporting electrolyte - sufficient contact exists and spectroelectrochemical studies could be started.

# Results

a) *5-methyl-3-phenyl-1-p-tolyl-4,5-dihydro-1H-pyrazole-5-carboxylic acid methyl ester*

In the applied potential range from -0.2 to 1.2 V the pyrazole derivative undergoes one step oxidation to the radical cation according to the following reaction [5]:




**Scheme 3:** Oxidation reaction of 5-methyl-3-phenyl-1-p-tolyl-4,5-dihydro-1H-pyrazole-5-carboxylic acid methyl ester.

The corresponding CV and UV/Vis spectrum is displayed in Figure 3 and Figure 4, respectively. Three cycles were recorded. However, for facility of inspection only the third cycle is displayed. Oxidation occurs with 0.7 – 0.8 V at a slightly higher potential value than the value reported by [4]. One reason for this difference might be the usage of different Ag/$Ag^+$ reference electrodes, thus resulting in a bit varying reference potential. While in the present study a silver wire was employed as pseudo reference, the experiments presented in [4] were performed using a solution of 0.01 mol/l $AgNO_3$ in 0.1 mol/l tetrabutylammonium hexafluorophosphate in acetonitrile.

In the UV/Vis spectrum the formation of the radical cation can be monitored by increase of an absorption band at approximately 650 nm and a second broad one below 500 nm. During reverse reaction both features distinctly reduce, before they reform during the subsequent oxidation reaction. A closer look reveals that the maximum of both bands is not reached directly after traverse of the oxidation peak, but the radical cation formation proceeds even in the beginning of the reverse scan until the potential is lowered to the reduction potential of the radical cation. The reduction reaction also proceeds further than the potential reversal and stops shortly before the oxidation potential is reached.

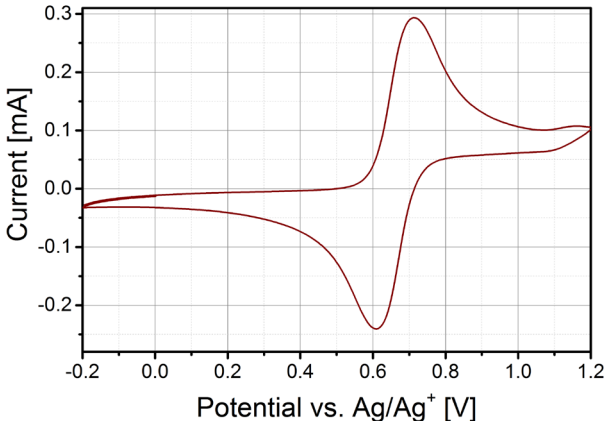



**Figure 3:** CV recorded during spectroelectrochemical investigation of 5-methyl-3-phenyl-1-p-tolyl-4,5-dihydro-1H-pyrazole-5-carboxylic acid methyl ester dissolved in 0.1 mol/l $Bu_4NPF_6$ in acetonitrile. The cyclic voltammogram was recorded with a scan speed of 25 mV/s between -0.2 and 1.2 V vs. Ag/$Ag^+$ starting at -0.2 V vs. Ag/$Ag^+$.

In the first cycle the band at 650 nm nearly completely diminishes, thus showing an almost completely rereduction of the radical cation. However, in further cycles the increasingly incomplete decrease of this band surely can be attributed to diffusion of the radical cation species away from the working electrode, so that not all of them are reduced in the consecutive reduction step. This aspect

[5] M. Kubicsko, L. Grubert, and S. Haug, Metrohm USA & Germany, Humboldt University of Berlin, *Spectroelectrochemical analysis of a N-aryl-Δ2-pyrazoline derivative*

is also reflected in the increasing height of the absorption band at 650 nm with increasing cycle number as subsequently more radical anions are formed and thus accumulate in the solution, see Figure 5. This effect can be nearly completely suppressed by application of a smaller optical path length than the 1.4 mm used in this experiment, as can be seen in the next section during study of the two step mechanism of the TMPD molecule.

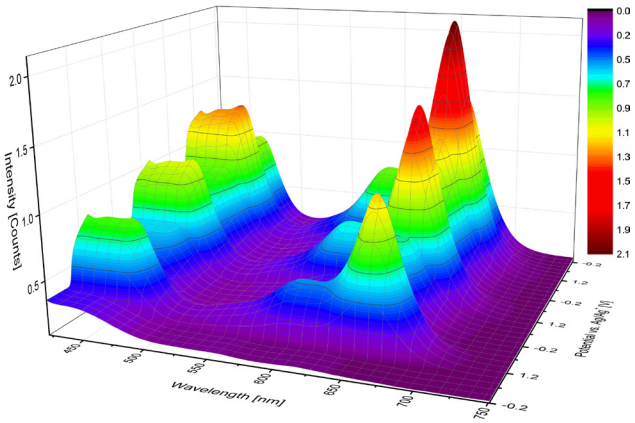



**Figure 4:** UV/Vis spectra recorded during spectroelectrochemical investigation of 5-methyl-3-phenyl-1-p-tolyl-4,5-dihydro-1H-pyrazole-5-carboxylic acid methyl ester dissolved in 0.1 mol/l $Bu_4NPF_6$ in acetonitrile. The corresponding CV is shown in Figure 3. The potentials depicted on the y-axis mark the vertex potentials in the CV.

To emphasize the spectral changes during repeated oxidation and subsequent reduction of the pyrazole derivative and the accumulation of the radical cation with cycle number the spectra recorded at the vertex points of the CV are depicted in Figure 5.

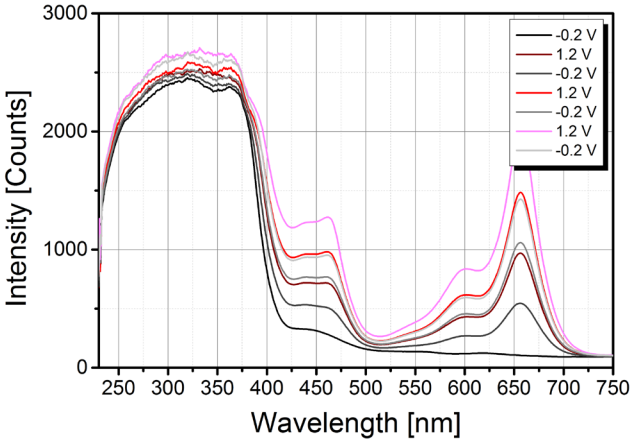
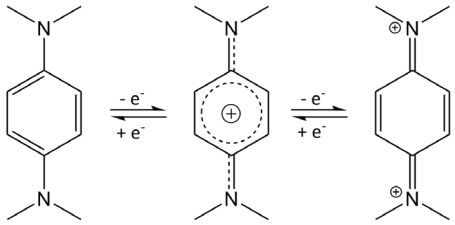



**Figure 5:** UV/Vis spectra recorded at the vertex points of the CV during spectroelectrochemical investigation of 5-methyl-3-phenyl-1-p-tolyl-4,5-dihydro-1H-pyrazole-5-carboxylic acid methyl ester dissolved in 0.1 mol/l $Bu_4NPF_6$ in acetonitrile. The corresponding CV is shown in Figure 3.

b) *N,N,N',N'-tetramethylphenylenediamine*

In organic solvents like acetonitrile the redox behaviour of the second species, TMPD, should follow a simple two-step mechanism as sketched in the following reaction scheme [2]:




**Scheme 4:** Two-step oxidation reaction of TMPD.

In the first of the two separate 1 electron oxidations a radical cation is generated, which is further oxidized to a quinonediimine dication in the second step. The cyclic voltammogram of such a two-step reaction should show two waves of approximately the same size, each corresponding to one 1 electron reaction, as it holds for the CV depicted in Figure 6 [2].

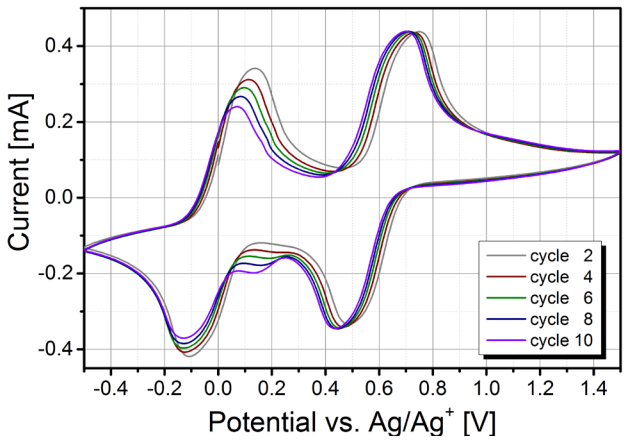



**Figure 6:** CV of TMPD dissolved in 0.25 mol/l $Bu_4NPF_6$ in acetonitrile. The cyclic voltammogram was recorded with a scan speed of 10 mV/s between -0.5 and 1.5 V vs. $Ag/Ag^+$ starting at -0.4 V vs. $Ag/Ag^+$. For better overview only every second scan is depicted.

Formation of the radical cation occurs in accordance with literature at approximately 0.1 V vs. $Ag/Ag^+$ during the anodic scan and its further oxidation to the quinonediimine dication proceeds at approximately 0.7 V [2],

[6]. Potentials of the reverse reactions are shifted of about 0.2 V in cathodic direction. There is a slight shift of the peaks in the anodic as well as in the cathodic scan over time.

For detailed study of the formation of the radical cation and its reduction to the neutral TMPD firstly only the first oxidation step and the corresponding reduction is studied by limiting the upper vertex potential in the CV to 0.4 V, see Figure 7. Three cycles were recorded, but for facility of inspection only the third cycle is displayed.

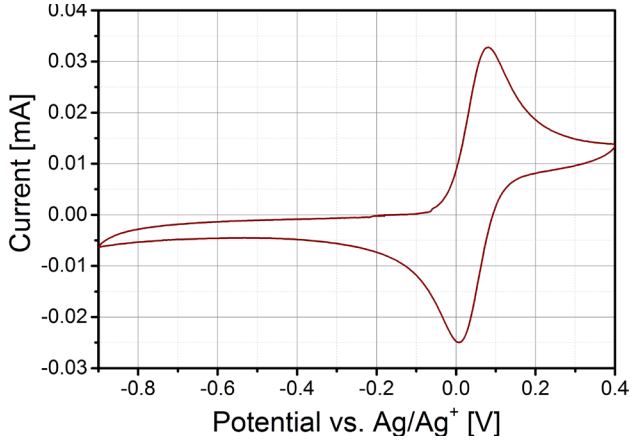



**Figure 7:** CV of TMPD dissolved in 0.1 mol/l $Bu_4NPF_6$ in acetonitrile, thereby only focussing on the formation of the radical cation and its reduction to the neutral TMPD. The cyclic voltammogram was recorded with a scan speed of 10 mV/s between -0.9 and 0.4 V vs. $Ag/Ag^+$ starting at -0.4 V vs. $Ag/Ag^+$.

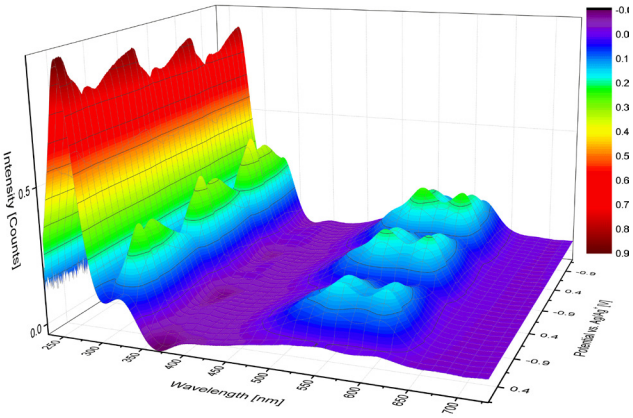



**Figure 8:** UV/Vis spectra recorded during spectroelectrochemical investigation of TMPD dissolved in 0.1 mol/l $Bu_4NPF_6$ in acetonitrile, thereby only focussing on the formation of the radical cation and its reduction to the neutral TMPD. The corresponding CV is shown in Figure 7. The potentials depicted on the y-axis mark the vertex potentials in the CV.

The corresponding UV/Vis spectrum is depicted in Figure 8. Formation of the radical cation can be monitored by a double band at 525 – 620 nm and an additional absorption band at approximately 325 nm. The bands significant for the radical cation rise during anodic scan at potentials above 0.1 V and decrease at potentials lower than its reduction potential of approximately 0.0 V vs. $Ag/Ag^+$. As discussed for the pyrazole derivative, the absorption bands of the radical cation diminish almost completely only in the beginning of the experiment, but later on increasing intensities residue, showing incomplete reduction due to diffusion of the radical cation away from the working electrode caused by usage of a rather broad optical path length of 1.4 mm.

In Figure 9 the UV/Vis spectrum of the complete two step redox behaviour of TMPD corresponding to the CV depicted in Figure 6 is displayed. In this experiment, a distinctly smaller optical path length of 0.35 mm was used to reduce diffusion of the radical cation away from the working electrode. Otherwise, its oxidation to the dication could not be monitored in the UV/Vis spectrum. Due to the lower amount of the redox active species in the optical path, its concentration had to be increased for sufficient contrast in the spectrum. Thus, with 2.5 mmol/l a 20 times higher concentration was used in comparison to study of only the formation of the radical cation using a wider optical path.

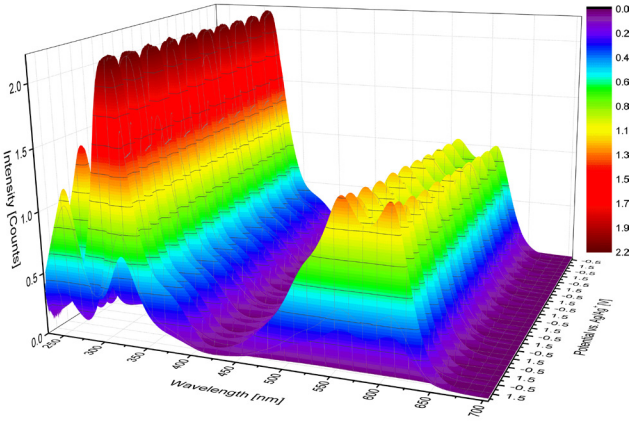



**Figure 9:** UV/Vis spectra recorded during spectroelectrochemical investigation of TMPD dissolved in

[6] B. Kerstin, D. Siebert, Inorg. Chem. **1998**, 37, 3820-3828

0.25 mol/l $Bu_4NPF_6$ in acetonitrile. The corresponding CV is shown in Figure 6. The potentials depicted on the y-axis mark the vertex potentials in the CV.

Again the repeated rising and decreasing of the absorption bands significant for the radical cation (a double band at 525 – 620 nm and an absorption band at approximately 325 nm) as well as for the dication showing a characteristic band at 295 nm and the neutral form of the TMPD molecule are clearly visible [[2]. The latter one shows an absorption band around 265 nm, which is present in the beginning of the experiment and rises when the radical cation is reduced to the neutral form of TMPD, i.e. when the band of both the radical cation and the dication diminish. By usage of the small optical path length the reaction is almost completely reversible so that even for prolonged cycling over 10 cycles the variation in the respective absorption bands is still clearly visible and the height of the bands characteristic for the dication and the neutral form of TMPD remains constant over the whole experiment.

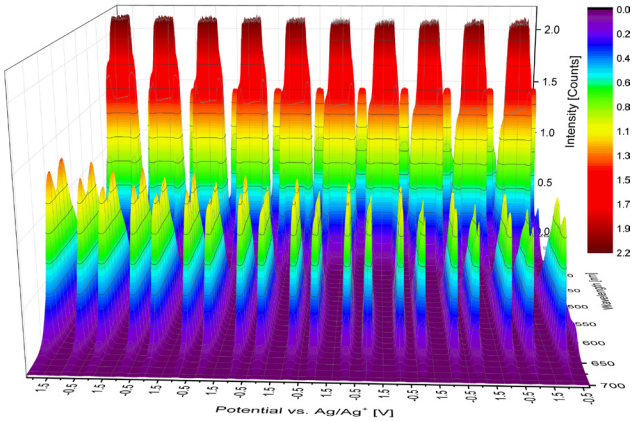



**Figure 10:** Tilted version of the UV/Vis spectra recorded during spectroelectrochemical investigation of TMPD dissolved in 0.25 mol/l $Bu_4NPF_6$ in acetonitrile to emphasize the alternating rising and decreasing of the bands significant for the three different forms of TMPD. The corresponding CV is shown in Figure 6. The potentials depicted on the y-axis mark the vertex potentials in the CV.

This is even more obvious in Figure 10 and Figure 11. The first one represents a tilted version of Figure 9 to emphasize the alternating rising and decreasing of the bands significant for the three different forms of TMPD, while the second one shows a plot of wavelengths 295 nm and 560 nm, selected as significant wavelengths for the dication and the radical cation, respectively, in dependence of scan number. They show the reverse behaviour, i.e. the wavelength at 295 nm decreases, if the one at 560 nm increases and vice versa. The third wavelength depicted in this figure is significant for the neutral TMPD molecule

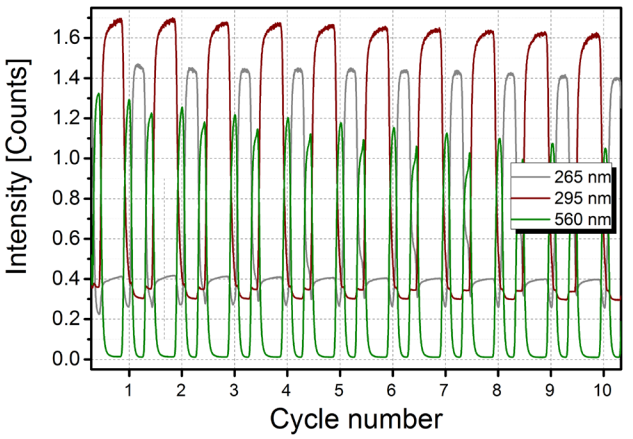



**Figure 11:** Evolution of three selected wavelengths during spectroelectrochemical investigation of TMPD dissolved in 0.25 mol/l $Bu_4NPF_6$ in acetonitrile: 265 nm symbols the neutral form of the TMPD molecule, 295 nm the dication and 560 nm the radical cation. The corresponding CV is shown in Figure 6.

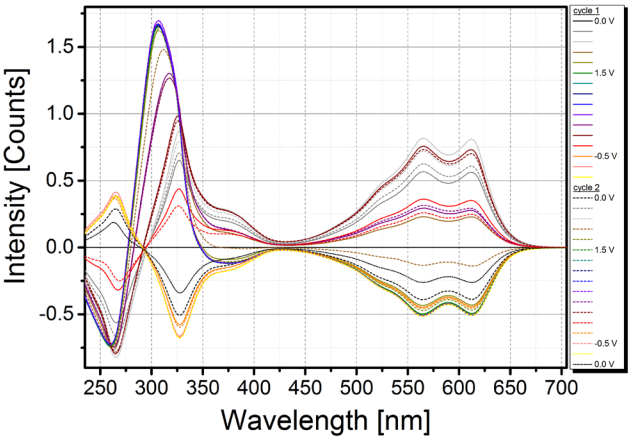



**Figure 12:** Differential plot of the UV/Vis spectra during spectroelectrochemical investigation of TMPD dissolved in 0.25 mol/l $Bu_4NPF_6$ in acetonitrile. The corresponding CV is shown in Figure 6. Differential spectra were calculated by substraction of the first spectrum from the subsequent ones. For better overview only every 25. spectrum for the first two cycles is displayed.

However, while the height of the bands characteristic for the dication and the neutral form

of TMPD remain constant over the whole experiment, the radical cation bands steadily decrease with increasing cycle number. During cathodic scan in the CV, see Figure 6, at about 0.1 V an additional peak rises over time, while the peak corresponding to the formation of the radical cation both during the cathodic and the anodic scan reduces in height, thus pointing to a side reaction at the expense of the radical cation.

This becomes even clearer in a differential plot of the spectra, see Figure 12, in which the first spectrum was subtracted from the following to highlight even small changes.

In conclusion, this application note intended to show that the combination of electrochemistry and spectroelectrochemistry is a very powerful tool. However, often compromises are needed to fulfil the requirements of both methods in one experiment. This is also shown in this application note by variation of several parameters like concentration of both the analyte as well as of the electrolyte salt, scan speed and length of the optical path to optimize the measurement for the present task. If not required, due to e.g. study of consecutive reactions, a broader optical path is easier to handle, but could limit the "reversibility" of the reaction concerning the evaluation of the spectroscopic response.

## Acknowledgement

Thanks to Dr. Lutz Grubert from Humboldt University of Berlin and Sandro Haug from Deutsche Metrohm for fruitful discussions and helpful tips regarding spectroelectrochemical measurement setups and parameters.