

# Journal of Visualized Experiments

## Using Cyclic Voltammetry, UV-Vis-NIR, and EPR spectroelectrochemistry to analyze organic compounds --Manuscript Draft--

Article Type:	Methods Article - JoVE Produced Video
Manuscript Number:	JoVE56656R3
Full Title:	Using Cyclic Voltammetry, UV-Vis-NIR, and EPR spectroelectrochemistry to analyze organic compounds
Keywords:	Cyclic voltammetry; EPR; UV-Vis-NIR; organic electronics; OLED; OPV; conjugated polymers; Electron Affinity; Ionization Potential; Charge Carriers; Spectroelectrochemistry.
Corresponding Author:	Przemyslaw Data Durham University Durham, Durham UNITED KINGDOM
Corresponding Author's Institution:	Durham University
Corresponding Author E-Mail:	przemyslaw.data@durham.ac.uk
Order of Authors:	Sandra Pluczyk Marharyta Vasylieva Przemyslaw Data
Additional Information:	
Question	Response
Please indicate whether this article will be Standard Access or Open Access.	Open Access (US\$4,200)
Please indicate the <b>full address</b> at which this article will be <b>filmed</b> .	Politechnika Slaska, Strzody 9, 44-100 Gliwice, Poland

**TITLE:**

Using Cyclic Voltammetry, UV-Vis-NIR, and EPR spectroelectrochemistry to analyze organic compounds

**AUTHORS & AFFILIATIONS:**

Sandra Pluczyk<sup>1</sup>, Marharyta Vasylieva<sup>1</sup>, Przemyslaw Data<sup>1,2,3</sup>

<sup>1</sup>Faculty of Chemistry, Department of Physical Chemistry and Technology of Polymers, Silesian University of Technology, Poland

<sup>2</sup>Durham University, Department of Physics, South Road, Durham, United Kingdom

<sup>3</sup>Center of Polymer and Carbon Materials of the Polish Academy of Sciences, Zabrze, Poland

Corresponding Author:

Przemyslaw Data ([przemyslaw.data@polsl.pl](mailto:przemyslaw.data@polsl.pl))

Email Addresses of Co-authors:

Marharyta Vasylieva ([marharyta.vasylieva@polsl.pl](mailto:marharyta.vasylieva@polsl.pl))

Sandra Pluczyk ([sandra.pluczyk@polsl.pl](mailto:sandra.pluczyk@polsl.pl))

**KEYWORDS:**

Cyclic Voltammetry, Electron Paramagnetic Resonance, Ultraviolet-Visible and Infra-Red spectroscopy, Organic Electronics, Organic Light Emitting Diodes, Organic photovoltaics, Conjugated Polymers, Electron Affinity, Ionization Potential, Charge Carriers, Spectroelectrochemistry.

**SHORT ABSTRACT:**

In this article, we describe electrochemical, electron paramagnetic resonance, and ultraviolet-visible and near-infrared spectroelectrochemical methods to analyze organic compounds for application in organic electronics.

**LONG ABSTRACT:**

Cyclic voltammetry (CV) is a technique used in the analysis of organic compounds. When this technique is combined with electron paramagnetic resonance (EPR) or ultraviolet-visible and near-infrared (UV-Vis-NIR) spectroscopies, we obtain useful information such as electron affinity, ionization potential, band-gap energies, the type of charge carriers, and degradation information that can be used to synthesize stable organic electronic devices. In this study, we present electrochemical and spectroelectrochemical methods to analyze the processes occurring in active layers of an organic device as well as the generated charge carriers.

**INTRODUCTION:**

Worldwide, researchers are continually searching for new organic materials that can be used in organic electronics with desirable performance or stability, which drops due to extended use. In the case of organic devices, it is important to understand the behavior of the charge carrier to fully know the rules driving the device behavior. Analysis of the effect of the molecular structure

on the generation of the charge carrier and the dynamics and maintenance of the balance of injected charge carriers, both positive (holes) and negative (electrons), is crucial to improve the efficiency and stability of the organic devices. This ensures the effective recombination of these individual charges and consequently significantly improves the photoluminescence efficiency of the organic light emitting diodes (OLEDs)<sup>1,2</sup>. For organic photovoltaics (OPVs)<sup>3,4</sup> as well as organic field effect transistors (OFETs)<sup>5,6</sup>, it is necessary to have materials with high charge carrier mobility. In addition to the analysis of charge carriers, several important parameters of organic electroactive materials help in predicting where the material could be used: ionization potential (IP), electron affinity (EA) energy levels, and band-gap between them<sup>7-10</sup>.

In this work, we present a method for the efficient measurement of cyclic voltammetry (CV) that can be used in the analysis of all types of electroactive materials. This technique provides information about redox properties, the doping/dedoping mechanism, the stability, the conversion and storage of energy, *etc.* It also allows for the estimation of electron affinity and ionization energy of the test compounds in a much cheaper and faster way compared to other high vacuum methods. The aforementioned parameters correlate with the energy levels of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO).

The method presented in this article can be used to analyze all types of conjugated compounds such as those with delocalized  $\pi$ -electrons in their structures. Conjugated compounds may be small molecules with large polymeric chains. Small molecules can also be monomers; during the initial reaction (photochemical, electrochemical, or chemical) monomers can form polymers. In OLED application, the energy level values are necessary to enable the use of the correct host for the emitter in a thermally activated delayed fluorescence (TADF) guest-host system or to decide with which compounds the exciplex donor-acceptor layer could be formed and what additional layers (electron transporting layer (ETL), hole transporting layer (HTL), electron blocking layer (EBL), and hole blocking layer (HBL)) will be necessary to synthesize stable efficiently charged balanced OLED devices<sup>11-17</sup>. Additional electrochemical measurements allow the investigation of possible side reactions during the process of degradation of the active layer and the formation of low mobile charge carriers (bipolarons)<sup>18-22</sup>.

Coupling electrochemical and spectroelectrochemical methods allows for easy, accurate, and reliable determination of the degree of oxidation or reduction of conjugated compounds and their degradation potential, which is crucial for stability<sup>23-28</sup>. Ultraviolet-visible and near-infrared (UV-Vis-NIR) spectroscopy coupled with electrochemistry can characterize the fundamental chromatic properties of all new conjugated compounds, such as the changing of the absorption band during doping<sup>18-30</sup>.

In a study related to the doping mechanism, it is important to define the type of charge carriers. In this process, two classes of charged quasiparticles take part, one with uncompensated spin (polarons) and the second being diamagnetic (bipolarons); electron paramagnetic resonance (EPR) spectroscopy provides invaluable assistance, which directly allows one to observe and track changes in populations of paramagnetic polarons<sup>29-32</sup>. In small molecules, it is difficult to form bipolarons, but these molecules can be quite conjugated and have bipolaron-inducing properties;

it is important to check if and at which potential polarons and bipolarons are formed in the structure. Bipolarons are at least one order lower in mobility than that of polarons; therefore, if bipolarons are formed in working devices, then it could lead to an unbalanced ratio of the charge carriers, which would result in high current and overheating of the OLED device or may well be the centers of degradation<sup>33</sup>.

The method of measurement proposed in this study is cheap and faster and allows for the determination of the most valuable operative parameters for a large number of electroactive materials without the need for special devices that are based on newly synthesized materials to check its performance. By applying electrochemistry and spectroelectrochemistry, it is possible to select one material that is really promising from hundreds of new materials. In addition, it is possible to obtain detailed information regarding the processes of doping and their effects on the chemical structure of the test conjugated systems using electrochemical and spectroelectrochemical methods, which allows constructing more efficient organic electronics devices.

## **PROTOCOL:**

### **1. Preparation of the Experiment**

1.1. Prepare 25 mL of 0.1 M electrolyte solution.

Note: Depending on the compounds under investigation, use different electrolytes as the mixture of organic salt and solvent: the most common salts used in the analysis of organic molecules are tetrabutylammonium hexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ ) or tetrabutylammonium tetrafluoroborate ( $\text{Bu}_4\text{NBF}_4$ ); the most common solvent used in the analysis are dichloromethane, acetonitrile, or tetrahydrofuran.

1.1.1. Choose the electrolyte solvent based on the solubility of the test compounds. It should be a solution during investigation but be in a solid state when the material is used in the making of the device, as a thin film deposited on the working electrode surface.

1.2. Clean the electrodes to be used in the experiment<sup>29</sup>.

1.2.1. For electrochemical measurements, use a 1 mm diameter platinum disk electrode as the working electrode (WE), a platinum coil or wire as the auxiliary electrode (AE), and a silver/silver chloride ( $\text{Ag}/\text{AgCl}$ ) electrode as the reference electrode (RE).

1.2.2. For EPR spectroelectrochemical measurements, use platinum wire as the WE, a platinum coil or wire as the AE, and  $\text{Ag}/\text{AgCl}$  as the RE.

1.2.3. For UV-Vis-NIR spectroelectrochemical measurements, use a quartz indium tin oxide (ITO) or fluorine-doped tin oxide (FTO) as the WE, a platinum wire as the AE, and an  $\text{Ag}/\text{AgCl}$  electrode as the RE.

1.2.4. Polish the platinum disk electrode by rubbing the downside of the electrode (the platinum electrode working area) on a polishing pad covered with 1  $\mu\text{m}$  alumina slurry for 3 min.

1.2.4.1. Rinse the electrode with deionized water to remove all of the slurries from the electrode and clean in an ultrasound bath (320 W, 37 kHz) with deionized water for 15 min.

1.2.4.2. Rinse the electrode using a 1 mL syringe with isopropanol (3 x 1 mL) and then with acetone (3 x 1 mL).

1.2.4.3. Use a paper towel to remove all solid residues and dry in the air for 3 min.

1.2.5. Clean the ITO and FTO electrodes with deionized water. Place them in an ultrasound bath (320 W, 37 kHz) in acetone for 15 min and then in isopropanol for the next 15 min.

1.2.6. Burn the platinum electrodes, wires, and coils using a high-temperature gas torch (>1000  $^{\circ}\text{C}$ ) for 1 min. Be careful! Use tweezers to hold the electrodes. Wait for 5 min after burning and before using the electrodes.

1.3. Clean the electrochemical and spectroelectrochemical cells (**Figure 1**) with water and then with acetone. Use a paper towel to remove all the solid residues. Clean all other elements (ca. PTFE parts) with acetone and dry in the air before use.

## 2. CV Analysis

2.1. Turn on the potentiostat and computer.

2.2. Fill an electrochemical cell with 1.5 mL of the electrolyte solution to be analyzed.

2.3. Put all the three electrodes (WE, AE, and RE) in a cell (the cell's cap is equipped with the PTFE electrode holder, so put electrodes through the holes in this holder) and connect it to a potentiostat. Keep the WE and RE as close to each other as possible (**Figure 1**). Follow the information regarding the connection of each wire of the potentiostat to its respective electrode.

2.4. If needed (for example during reduction analysis), put the argon (or nitrogen) pipe (through an additional hole in the electrode holder) and start bubbling the solution for at least 5 min. After this, move the argon (or nitrogen) pipe above the solution's level and keep the gas flow running for the measurement.

Note: The cell looks closed but cannot be completely leak-proof; therefore, a method to remove the redundant amount of gas from the cell must be available (*e.g.*, by an additional small hole in the electrode holder). The pressure depends on the pipe used; set the pressure to high as it is required to set the slow gas flow. If a highly volatile solvent is used in the experiment (*e.g.*, dichloromethane) or the experiment is taking a long time (more than 30 min), then use the

Drechsel bottle to saturate argon (or nitrogen) gas with the solvent used in the measurement.

2.5. Run the potentiostat software, choose the CV procedure and use the following settings: start potential of 0.00 V, upper vertex potential of 2.0 V, lower vertex potential of 0.00 V (if investigating the process of reduction, then a lower vertex potential of -2.5 V), stop potential of 0.00 V, number of stop crossing of 6, and scan rate of 0.05 V/s.

2.5.1. In the section **Export ASCII data**, define a **filename** and choose a folder to save the data in, and push the **START** button (decrease or increase the lower and upper vertex potential to fit the electrochemical window or the sample electrochemical activity)

2.6. If any peaks are visible in the positive range of potential, then repeat the cleaning procedure. If there is a peak in the negative range potential, then put the argon (or nitrogen) pipe in the solution and start bubbling for an additional 5 min.

2.7. Add a drop of 1 mM ferrocene (in the solvent used to prepare the electrolyte) to the electrolyte solution by using a syringe.

2.8. Set the start potential to 0.00 V, the upper vertex potential to 0.85 V, the lower vertex potential to 0.00 V, the stop potential to 0.00 V, the number of stop crossing to 10, and the scan rate to 0.05 V/s. In the section **Export ASCII data**, change the **filename** and push the **START** button.

2.9. After the measurement, finish by repeating the cleaning procedures as mentioned in steps 1.2 and 1.3.

2.10. Prepare 4 mL of 1 mM test compound in the prepared electrolyte (step 1.1).

2.11. Fill the electrochemical cell with the test compound solution (1.5 mL); put all three electrodes in a cell and connect to the potentiostat (step 2.4). To investigate the process of reduction, remove the oxygen (step 2.5).

2.12. Set the start potential to 0.00 V, the upper vertex potential to 0.50 V (or 0.00 V in case of investigation of reduction process), the lower vertex potential to 0.00 V (-0.50 V in case of investigation of reduction process), the stop potential to 0.00 V, the number of stop crossing to 10, and the scan rate to 0.05 V. In the section **Export ASCII data**, change the **filename** and push the **START** button.

2.13. Repeat step 2.13 by increasing upper vertex potentials (or by decreasing the lower vertex potential) by 0.1 V until peak registration (**Figure 2a**). If the successive scan is shifted in potential (**Figure 2b**), then clean the RE and leave it in the electrolyte solution. Then, repeat the measurement.

2.14. Measure both oxidation and reduction processes on the same CV for the determination of

IP and EA: set the start potential to 0.00 V, the upper vertex potential to 1.00 V, the lower vertex potential to -2.70 V, and the stop potential to 0.00 V. Choose the upper and lower vertex potential in a way that registers full reduction and oxidation peaks and avoids further redox steps (if any exists) (**Figure 2a**).

Note: Estimate IP and EA by measuring the onset potential. There are a couple of ways to calculate these parameters from CV but the most useful is to calculate using the onset potential. Sometimes, it is not possible to observe reversible redox couple, especially for both  $n$  and  $p$  doping. Mixing of two different techniques is also undesirable as it may provide wrong results and conclusions.

2.14.1. To measure the onset potential, mark the tangent line to the CV peak (**Figure 3**). Calculate the desired values from the onset potential of the reduction or oxidation process using equations (**Equations 1 and 2**)<sup>10, 18, 19, 36–38</sup>.

$$IP [eV] = |e|E_{ox(onset)} + 5.1 \quad (1)$$

where  $E_{ox(onset)}$  is the onset of the oxidation potential calibrated with ferrocene\*

$$EA [eV] = -|e|(E_{red(onset)} + 5.1) \quad (2)$$

where  $E_{red(onset)}$  is the onset of the reduction potential calibrated with ferrocene\*

\*Potential calibrated with ferrocene means that the value of potential from the measurement is reduced by the oxidation potential of ferrocene.

2.15. Pull out the electrodes and pour out the test solution into the proper waste container.

2.16. Repeat the cleaning procedure (steps 1.2 and 1.3).

2.17. Repeat steps 2.9–2.12 with 0.25, 0.10, and 0.20 V/s scan rates.

2.18. Add one drop of 1 mM ferrocene (in the solvent used to prepare the electrolyte solution) to the test solution using a syringe. Set the start potential to 0.00 V, the upper vertex potential to 0.60 V, the lower vertex potential to 0.00, the stop potential to 0.00 V, the number of stop crossing to 6, and the scan rate to 0.05 V. Push the **START** button. After the measurement is completed, change the upper vertex potential to a value that registers the ferrocene couple with the first peak of oxidation of the test compound.

2.19. Pull out the electrodes and pour out the test solution into the proper waste container.

2.20. If the electropolymerization occurs during electrochemical oxidation, wash the WE carefully with the electrolyte solution using the syringe ( $3 \times 0.5$  mL). Clean the RE, AE, and electrochemical

cell using the standard procedure (steps 1.2-1.3).

2.21. To investigate electrochemical products deposited on WE, proceed to step 2.23. To investigate a solution, proceed to step 1.2.1 and start again from step 2.3.

2.22. Fill the electrochemical cell with an electrolyte solution. Then, put all the three electrodes in a cell and connect them to a potentiostat (step 2.4). To investigate the reduction process, deoxidate the solution (step 2.5).

2.23. Repeat steps 2.10–2.12 and then step 2.16.

### 3. UV-Vis-NIR Spectroelectrochemical Analysis

#### 3.1. Measurement preparation

3.1.1. Turn on the spectrometer and potentiostat.

3.1.2. Fill the spectroelectrochemical cell with 0.5 mL of electrolyte solution (step 1.1).

3.1.3. Put the PTFE seal on one side of the cell; then put the ITO electrode to the cell in this way to have a conductive side of the electrode touching the PTFE seal. Put the rest of the PTFE parts as shown in **Figure 1**. Put the RE and AE through the PTFE electrode holder and cover the upper side of the ITO electrode with copper foil as shown in **Figure 1** for better conductivity.

3.1.3.1. Put the assembled cell in the holder of the spectrometer and connect all the electrodes to a potentiostat. Follow the information regarding the connection of each wire of the potentiostat to its respective electrode.

3.1.4. Run the potentiostat and spectrometer software.

3.1.5. In the spectrometer software, choose **File | New | Absorbance** measurement.

3.1.6. Choose one of the listed detectors.

3.1.7. Make sure that the button on the detectors is in the “open” position. Then, click on the glowing light bulb; close the detector (move the button to the closed position) and then, click on the dark light bulb.

3.1.8. Select the second detector and repeat step 3.1.7.

3.1.9. Reconnect electrodes from the potentiostat and pull out the electrodes and other elements of the spectroelectrochemical cell.

3.1.10. Repeat cleaning procedures (steps 1.2 and 1.3).



3.1.11. Fill the spectroelectrochemical cell with a diluted ( $1 \times 10^{-5}$  M) solution of the test compound in the electrolyte solution if testing the small molecule. Fill the spectroelectrochemical cell with the electrolyte if testing the polymeric (oligomeric) layer deposited on the ITO electrode.

3.1.12. Assemble the spectroelectrochemical cell (step 3.1.3).

3.1.13. Click **Save**.

3.1.14. Select one of the listed detectors.

3.1.15. Define the save location and name the file (include the selected detector).

3.1.16. Select the second detector and repeat step 3.1.15.

## 3.2. Potentiostatic Analysis<sup>18</sup>.

3.2.1. Apply a neutral potential (*i.e.*, 0.00 V). This spectrum will be the starting spectra. Increase potential by 0.1 V and wait ca. 10 s until the process stabilizes and records absorption spectra (steps 3.1.13–3.1.16). Continue the measurement to the first change in UV-Vis-NIR spectra; wait for 10 s and then save the spectra (steps 3.1.13–3.1.16).

3.2.2. Increase potentials by 0.05 V; wait for 10 s and save (steps 3.1.13–3.1.16).

3.2.3. Repeat 3.2.2 until achieving the potential of the first or second oxidation potential (these potentials are known from the CV measurement); then, reverse the potential and go back to the starting potential.

3.3. When the measurements are completed, measure the CV of the test solution. Add 1 mM ferrocene (10  $\mu$ L) and measure the CV again. The value of ferrocene will help estimate the potential of the process and unify the data.

3.4. This analysis provides information regarding the optical band-gap, maximum wavelength of undoped and doped states, and isosbestic points of the electrochemical process. Calculate the optical band-gaps from onset values of  $\pi$ - $\pi^*$  bands on the UV-Vis spectra and using **Equation 3**<sup>18,19,23,24</sup>

$$E_g \text{ [eV]} = \frac{hc}{\lambda_{onset}} \quad (3)$$

where  $h$  is Planck's constant,  $\lambda_{onset}$  is compound absorption onset, and  $c$  is the speed of light in vacuum.

### 3.5. Time-Resolved Potentiostatic Analysis<sup>19,32,33</sup>

3.5.1. Prepare the measurement similar to the method described in 3.1.1–3.1.16 and put the argon (or nitrogen) pipe (through an additional hole in the electrode holder) and bubbling the solution at least 5 min prior to the measurement. After this, move the argon pipe above the solution level and keep the gas flow running for the measurement.

3.5.2. Run the potentiostat software, choose the chronoamperometry procedure with the following settings: potential start potential to 0.00 V, upper potential to 1.0 V, lower potential to –1.00 V, duration as 5 s, interval time as 0.010 s, number of repeats to 10, and delay time to 10 s. In the section **Export ASCII data**, define a **filename** and choose a folder to save the data.

3.5.3. In the spectrometer software, choose **File | New | High-speed Acquisition**. A new window will appear; set up the following parameters: Integration Time—10 ms, Scans to Average—1, Boxcar Wirth—0, Number of Scans—10000. Do not click the **Go** button.

3.5.4. In the potentiostat software, push the **START** button. When the countdown drops to 1 s, press the **Go** button in the spectrometer software.

3.5.5. Note that it is not possible to see absorption results until the process finishes.

3.5.6. Analyze the data to provide parameters. Use the information saved in the file such transmittance, current, voltage, and current density to provide working parameters:

3.5.6.1. Calculate Optical Density ( $\Delta OD$ ), the absorbance of the test compound during doping (dedoping) with **Equation 4**:

$$\Delta OD = \log \left( \frac{T_b}{T_c} \right) \quad (4)$$

where  $T_b$  is transmittance in doped form, a “bleach” state [%], and  $T_c$  is transmittance in undoped form, a “colored” state [%].

3.5.6.2. Calculate Coloration Efficiency (CE,  $\eta$ ), the amount of electrochromic color formed by the used amount of charge and as the connection between the injected/ejected charge as a function of electrode area ( $Q_d$ ) and the change in the optical density ( $\Delta OD$ ) value at a specific wavelength ( $\lambda_{\max}$ ) with **Equation 5**. Its value depends on the wavelength chosen for study, so the value is measured at  $\lambda_{\max}$  of the optical absorption band of the colored state.

$$CE = \frac{\Delta OD}{Q_d} \quad (5)$$

where  $\Delta OD$  is the optical density [-] and  $Q_d$  is the charge density [C/cm<sup>2</sup>].

3.5.6.3. Calculate the Contrast Ratio (CR), the measured intensity of color change during electrochemical doping and usually characterized by  $\lambda_{\max}$  of the colored form with **Equation 6**:

$$CR = \frac{T_b}{T_c} \quad (6)$$

where  $T_b$  is transmittance in doped form, “bleach” state [%], and  $T_c$  is transmittance in undoped form, “colored” state [%].

#### 4. EPR Spectroelectrochemical Analysis

##### 4.1. Measurement preparation

4.1.1. Turn on the spectrometer and the potentiostat.

4.1.2. Fill the spectroelectrochemical cell with electrolyte (step 1.1).

4.1.3. Set the power to 1 mW and tune the resonator to achieve a sharp, centered signal in Q-dip (use the autotuned option).

4.1.4. Set the Mn marker (manganese standard) to 600 and close the Q-dip window. If there is no Mn marker, then skip this step and go to step 4.8.

4.1.5. Set “sweep width  $\pm$ ” to  $2.5 \times 10$  mT, “mod width  $\pm$ ” to  $1.0 \times 0.1$  mT, “amplitude” to  $5 \times 100$ , “time constant” to 0.03 s, and “center field” value to *ca.* 338 mT and start the measurement.

4.1.6. If not registering six spectral lines of Mn marker, then change the “center field” value.

4.1.7. When registering six spectral lines of Mn marker (**Figure 4**), set the “center field” value between third and fourth line and decrease the value of “sweep width  $\pm$ ” to a value that covers only these two lines. Start the measurement again.

4.1.8. Go into the Q-Dip option, set the Mn marker to 0, and close the Q-dip window.

4.1.9. Measure the pure electrolyte as the background and check if there are any signals. If the signals are visible, then the signal may be from the contamination, low oxidation potential compounds, or from the glass.

4.1.10. Clean the spectroelectrochemical cell (step 1.3).

##### 4.2. Investigation of small molecules (solutions).

4.2.1. Fill the spectroelectrochemical cell with a diluted ( $1 \times 10^{-5}$  M) solution of the test compound in the electrolyte; put all three electrodes through the electrode holder to the cell in this manner

so that the WE and RE are inside the spiral AE (**Figure 1**).

4.2.1.1. Put the WE close to the bottom of the cell and the RE at the upper side of the active (metal not covered by PTFE) part of the WE (**Figure 1**). Place the cell equipped with an electrode inside in the sample cavity of the spectrometer and connect electrodes with a potentiostat (follow the information regarding the connection of each wire of the potentiostat to its respective electrode).

4.2.2. Apply the potential corresponding to the onset of the first redox peak (value known from CV measurement). If a signal appears, then the equipment is set up properly.

4.2.3. Go into the Q-Dip option, set the Mn marker to 600, close the Q-dip window, and start the measurement. The registration of signal with the signal of Mn marker allows calculation of the *g*-factor of the received signal.

4.2.4. Go into the Q-Dip option, set the Mn marker to 0, close the Q-dip window, and wait *ca.* 5 min.

4.2.5. Set the “center field” value in the center of the signal, decrease the value of “sweep width  $\pm$ ” to a value that covers the signal, but does not cut off the beginning and ending of the signal (when “sweep width  $\pm$ ” is changed, check entire signal), and decrease the value of “mod width  $\pm$ ” to get well-resolved spectra.

4.2.6. If the signal is small, then increase the “amplitude” value and “time” (acquisition time) of the measurement.

4.2.7. To decrease the signal to noise ratio, set the acquisition to 4, 9, or 16 depending on how noisy the signal is. If the signal is very noisy, select 16.

#### 4.3. Investigations of the polymeric layer deposited on the surface of the WE.

4.3.1. Fill the spectroelectrochemical cell with an electrolyte solution (step 1.1).

4.3.2. Put electrodes into the cell. Be careful not to destroy the polymeric layer on the WE. Connect the electrode with the potentiostat (step 4.2.1).

4.3.3. Apply neutral potential (*i.e.* 0.00 V) to ensure that the compound is in a neutral state; this spectrum will be the starting EPR spectra.

4.3.4. Increase potential by 0.10 V. Wait *ca.* 10 s until the process stabilizes and record the EPR spectra.

4.3.5. Repeat step 4.3.4 when the EPR signal appears.

4.3.6. Increase the potential by 0.05 V. Wait *ca.* 10 s until the process stabilizes and record the EPR spectra.

4.3.7. Repeat step 4.3.6 until the first or second oxidation potential is achieved and so on (values of these potentials are known from CV measurement); then, reverse the potential and go back to starting potential.

4.3.8. Apply the potential at which the EPR signal appeared in the previous cycle (4.3.5), go into the Q-Dip option, set the Mn marker to 600, close the Q-dip window, and start the measurement. Register the signal with the third and fourth spectral line of Mn marker (4.1.7).

4.4. When the measurement is completed, analyze the data.

4.5. Some of the analysis such as a number of spins can be only performed for the compounds deposited (insoluble polymers) on the WE. To calculate the number of spins, double-integrate the EPR signal, followed by a comparison of obtained value with calibrated Mn internal standard. Calculate the number of repeating units forming the polymer on the electrode using **Equation 7**<sup>24,32,33</sup>:

$$l_{mer} = \frac{1}{2} \cdot \frac{Q_{polym}}{F} \cdot N_A \quad (7)$$

where  $l_{mer}$  – number of repeating units in the polymer,  $Q_{polym}$  is the polymerization charge,  $F$  is the Faraday constant, and  $N_A$  is the Avogadro number.

4.6. To calculate doping charge, use the CV of deposited polymer recorded in a spectroelectrochemical cell before the EPR measurement, using **Equation 8**:

$$Q_d(E) = \frac{\int_{E_0}^E i dE}{v} \cdot e \quad (8)$$

where  $Q_d$  is the doping charge,  $i$  is the current,  $E$  is the set potential,  $E_0$  is the starting potential,  $v$  is the scan rate, and  $e$  is the elemental charge.

4.7. Use calculated doping charge to calculate doping level, using **Equation 9**:

$$\Delta D = \frac{Q_d}{l_{mer}} \quad (9)$$

where  $\Delta D$ - doping level,  $Q_d$  is the doping charge, and  $l_{mer}$  – number of repeating units in the polymer

4.8. To calculate the number of bipolarons, assume an initial doping level equal to zero. Use the number of polarons per unit from the concentration of spins, so the number of bipolarons should be calculated using **Equation 10**. In the calculations, assume that the initial amount of bipolarons

is zero and that faradaic current is much higher than that of non-faradaic current.

$$D = z_p n_p + z_b n_b \quad (10)$$

where  $z_i$  is the charge carrier's elemental charge,  $n_i$  is the number of charge carriers per polymer unit, ( $p$ ) is the polarons, and ( $b$ ) is the bipolarons.

**4.9.** Extract the  $g$ -factor value from the EPR spectra. Determine using Mn as an internal standard (steps 4.2.3 and 4.3.8), knowing that the fourth manganese line in it has a  $g$ -factor of 2.03324. Calculate the line width of EPR signal as the distance in mT between minimum and maximum of the EPR signal. This value is important as it may tell where (on which atom) the radicals are formed.

#### REPRESENTATIVE RESULTS:

The most common application of CV analysis is the estimation of IP and EA. Even though there are a couple ways to obtain CV data, it is strongly recommended to calculate them based on the onset of redox peaks (**Figure 3**). This approach allows unifying the calculation procedure. Not all of the tested materials undergo reversible oxidation/reduction processes (**Figure 3**); in such situations, it is not possible to calculate based on average potentials (average from potentials correspond to a maximum of cathodic-reduction and anodic-oxidation peaks). However, it is almost always possible to run the tangent to a peak as shown in **Figure 3**. With the intersection with the background line and use of **Equations 1 and 2**, the IP and EA values are estimated as 5.35 eV and -2.90 eV, respectively. There are also several different scales used to evaluate IP and EA based on CV measurements. The most commonly used scales for organic materials are -4.8 and -5.1 eV as equivalent to 0.00 V versus Normal Hydrogen Electrode (NHE). However, all of the scales are only an approximation; remember this when comparing different results. The crucial thing is to state what parameters were considered for calculations. In this case, the value -5.1 eV has been chosen as it should correspond to the formal potential of the ferrocene redox couple; in the Fermi scale, it is 0.40 V versus Saturated Calomel Electrode (SCE) in acetonitrile, which is in agreement with the previous measurement.

There are many articles published regarding the analysis of CV. Herein, we show when the process is not going to be as it is expected. The analysis is based on thiophene derivative: NtVTh (structure shown in **Figure 4**), which undergoes degradation upon oxidation (**Figure 5**).

NtVTh has two oxidation potentials: the first at 0.70 V and the second at 0.84 V (**Figure 5**). During the first cycle, the reduction peak is not observed, indicating an irreversible process. Electrochemical characteristics of NtVTh show that polymerization does not occur and after the first oxidation potential, some electro-inactive layer of reaction products deposits at the electrode surface, thus hindering the polymerization process. What is visible is the reaction with the radical cation on the vinyl bond, where the molecule is losing its conjugation and form dimers on the electrode.

While it is difficult to extract information about charge carriers from the CV, it is possible to

distinguish between polarons and bipolarons when supported by a UV-Vis-NIR spectrometer. The neutral poly(OiPrThEE) was characterized by two wide absorption  $\pi|\pi^*$  transitions bands with peaks maxima at  $\lambda_{\text{max}1} = 363$  nm and  $\lambda_{\text{max}2} = 488$  nm, related to the aromatic form of the undoped polythiophene derivative. During the oxidative doping, new polaronic and bipolaronic bands are generated. The UV-Vis spectrum obtained during the poly(OiPrThEE) oxidation revealed the diminishing the neutral polymer absorption band (300–550 nm) (**Figure 6**) together with the formation of a new absorption band (550–950 nm) of the radical cations of bithiophene and *p*-phenylenevinylene with maxima at 692 nm. The isosbestic point of the oxidation process was located at 604 nm. The bipolaronic band appeared between the 950 nm and 1700 nm with a maximum located at 1438 nm.

EPR spectroscopy is the technique that detects materials with an unpaired electron, this includes organic radicals<sup>39</sup>. There are several parameters that could be extracted from EPR spectra, but one of the most interesting is to estimate where the radicals are localized. Electrons, similar to protons, possess spin. By placing an electron in an external magnetic field, this spin can be split two ways: parallel and antiparallel to the magnetic field, giving two energy levels. This phenomenon is known as the Zeeman effect<sup>40,41</sup>. In case of organic radicals, the unpaired electron interacts not only with the external magnetic field but also with magnetic nuclei (nuclei which have a nonzero spin;  $I \neq 0$ ). A number of degenerate energy levels are equal to  $2I + 1$ , where  $I$  is the spin quantum number of the nucleus with which the unpaired electron interacts<sup>42</sup>. The interaction of the unpaired electron with a larger number of magnetic nuclei leads to further splitting of the energy levels and to hyperfine structure of EPR spectra registration<sup>43</sup> (**Figure 7**). For molecules where the unpaired electron interacts with an even larger number of nuclei, the individual spectral line could overlap, which results in registration of a single, broad signal<sup>44-46</sup> (**Figure 8**). This is typical for conjugated polymers, where the generated radical ion during a redox process is delocalized<sup>47,48</sup>.

The combination of EPR spectroscopy with electrochemical methods allows the characterization of charge carriers (radical ion) generated during the redox process as well as the determination of the mechanism of these processes<sup>49,50</sup>. If well-resolved (peaks are separated; not in the form of one broad peak) spectra are registered, as in the case of electrochemical reduction of *s*-tetrazine derivative (**Figure 7**), then the analysis of the hyperfine structure of spectra leads to conclusions about the localization of unpaired electron. One way to analyze this kind of spectra is to conduct simulation with special software and to fit simulated spectra with the experimental one<sup>51</sup>. This is especially helpful when the hyperfine structure is complex due to the interaction of the unpaired electron with large numbers of protons. In case of the *s*-tetrazine derivative shown in **Figure 7**, simulation of EPR spectra (red line) indicates the interaction of the unpaired electron with four nitrogen atoms of *s*-tetrazine.

#### FIGURE AND TABLE LEGENDS:

**Figure 1: Electrochemical and spectroelectrochemical cells used for measurements.** The figure presents the scheme setup of electrochemical/spectroelectrochemical cells using cyclic voltammetry, ultraviolet-visible and near-infrared (UV-Vis-NIR), and electron paramagnetic resonance (EPR) spectroelectrochemical measurements.

**Figure 2: Cyclic voltammetry (CV) of properly measured compound COPO1 (a) and the CV with an unstable reference potential dibenzothiophene-*S,S*-dioxide with ferrocene (b)<sup>52</sup>.** The figure shows two cyclic voltammograms. (a) presents correctly registered CV and (b) shows a voltammogram registered using a reference electrode with no stable potential.

**Figure 3: Cyclic voltammetry (CV) of compound COPO1 in a wide range of potentials.** Estimation of the onset potentials for EA and IP calculations of the COPO1 compounds<sup>52</sup>. EA = -2.90 eV and IP = 5.35 eV.

**Figure 4. EPR six spectral line of manganese standard.** The paramagnetic signal of manganese used for calibration of the signal shift.

**Figure 5: Cyclic Voltammetry (CV) of compound NtVTh.** Cyclic voltammograms of 15 mM NtVTh in 0.1 M Bu<sub>4</sub>NBF<sub>4</sub>/CH<sub>3</sub>CN and relative to ferrocene standard presenting the degradation process involved on working electrode. Scan rate 0.05 V/s: (a) was taken in the range -1.4 V to 0.8 V, and (b) in the range -1.4 V to 0.9 V.

**Figure 6: Ultraviolet-visible and near-infrared (UV-Vis-NIR) spectroelectrochemistry of poly(O/PrThEE) derivative.** UV-Vis-NIR spectra presenting the evolution of absorption band through the generation of charge carriers on polymer structure.

**Figure 7: EPR spectroelectrochemical analysis of tetrazine derivative.** (a) Structure of *s*-tetrazine derivative; (b) EPR spectra registered during electrochemical reduction of *s*-tetrazine derivative (black line-experimental and red line simulated spectrum).

**Figure 8: EPR spectroelectrochemical polaron signal of the conjugated polymer.** Electron paramagnetic resonance (EPR) spectra registered during the first step of oxidation of conjugated polymer (EPR spectra of polaron species).

**Figure 9: Cyclic voltammetry (CV) of ferrocene and decamethylferrocene.** Comparison of two electrochemical standards as pure and as mixture showing the shift of the potential.

## DISCUSSION:

Electrochemical and spectroelectrochemical techniques have no limitations; one can analyze both solid state and liquid solutions in a broad range of temperature and other conditions with these techniques. The important thing in all of these cases is that compounds/materials are analyzed under the applied potential, replicating real world conditions for working organic electronics devices. The only difference is that in electrochemistry, the formation of charge carriers, is observed.

The methods presented here show the usefulness of the analysis of charged carriers generated in organic compounds that correlate with their applicability in organic electronics. Moreover, the electrochemical and spectroelectrochemical techniques are cheaper and less demanding than



that of typical methods used in charge carrier analysis, but there are some critical steps and modifications to the protocol that are needed depending on the obtained results.

During electrochemical characterization, always start with a particular concentration. If a set of the compounds is compared, then all materials need to have the same molar concentration. The best is to start with 1 mM concentration and 50 mV/s scan rate as indicated in the protocol in this study, but it is good to know the concentration of the sample on the observed electrochemical behavior. Always try to measure at least three scans. The first two scans are usually different because the starting conditions (equilibrium) are different. The second and the third scans should be the same. If the second and third scans are the same, then there are probably no side reactions observed in this system (**Figure 2a**). In an oxidation process, a new peak at a lower potential appears showing that the conductive material was deposited on the WE<sup>18,19,24,25,29–32</sup>. If the height of the lower peak increases in successive scans, then probably the conjugated polymer was deposited<sup>18,19,24,25,29–32</sup>. If all the currents decrease in successive scans, then the nonconductive product of degradation was deposited on the electrode. If a very small peak is observed before the main oxidation or reduction peak (especially for polymers), then this is probably charge-trapping process<sup>19,23,31,34</sup>. If a very sharp dedoping peak of oxidation or reduction is observed, then this is probably caused by the decomposition of crystalline structures on an electrode formed through the electrocrystallization process during oxidation<sup>35</sup>.

Always check the behavior of the test compound before, during, and after redox peaks. It means that at least three CV scans should be registered: with upper (in the case oxidation) or lower vertex potential lower or higher, respectively, then the potential of peak maximum, with upper or lower vertex potential set to exactly on the peak maximum and with vertex potentials higher (oxidation) and lower (reduction) than potential of the peak maximum. The observed process may vary and sometimes two processes may be observed under one peak theoretically. Always compare the collected cyclic voltammograms of the electrolyte (step 2.6), the ferrocene (step 2.9), the compound (step 2.13), and the ferrocene with compound (step 2.19); there are several issues to be taken into account.

Always compare the CV signals of the electrolyte and the test compound, if any signals from the electrolyte is visible on the cyclic voltammogram of the measured compound, then the electrolyte must be changed because its electrochemical window is too low, or the electrolyte is contaminated. If the signal (redox couple) of ferrocene (step 2.9) and ferrocene with compound (step 2.19) are at the same position, then everything is performed properly. If the peaks are shifted between each other, then check the RE and repeat the measurement. If the signal (oxidation, reduction, or redox couple potential) of the test compound with added ferrocene (step 2.19) is at a higher potential than that of the pure compound (step 2.13), then consider the values (oxidation, reduction, or redox couple potential) from the cyclic voltammogram of the pure compound. The shift is caused by the higher amount of ferrocene in the solution. When two oxidation processes are observed, the first process (oxidation or reduction) which is always on the WE may affect the active surface; this may cause an increase in the oxidation potential of the second process (**Figure 9**).

**ACKNOWLEDGEMENTS:**

The authors gratefully acknowledge the financial support of “Excilight” project “Donor-Acceptor Light Emitting Exciplexes as Materials for Easy-to-tailor Ultra-efficient OLED Lightning” (H2020-MSCA-ITN-2015/674990) financed by Marie Skłodowska-Curie Actions within the framework programme for research and innovations “Horizon-2020”.

**DISCLOSURES:**

The authors have nothing to disclose.

**REFERENCES:**

- 1 O’Brien, D.F., Baldo, M.A., Thompson, M.E., Forrest, S.R. Improved energy transfer in electrophosphorescent devices. *Applied Physics Letters*. **74**, 442-444 (1999).
- 2 Chin, B.D. *et al.* Effects of interlayers on phosphorescent blue organic light-emitting diodes. *Applied Physics Letters*. **86**, 133505-133507 (2005).
- 3 Cardon, C.M., Li, W., Kaifer, A.E., Stockdale, D., Bazan, G.C. Electrochemical Considerations for Determining Absolute Frontier Orbital Energy Levels of Conjugated Polymers for Solar Cell Applications. *Advanced Materials* **23**, 2367-2371 (2011).
- 4 Bang, A.-M. *et al.* A novel random terpolymer for high-efficiency bulk-heterojunction polymer solar cells. *RSC Advances*. **7**, 1975-1980 (2017).
- 5 Tybrandt, K., Kollipara, S.B., Berggren, M. Organic electrochemical transistors for signal amplification in fast scan cyclic voltammetry. *Sensors and Actuators B: Chemical*. **195**, 651-656 (2014).
- 6 Schaur, S., Stadler, P., Meana-Esteban, B., Neugebauer, H., Sariciftci, N.S. Electrochemical doping for lowering contact barriers in organic field effect transistors. *Organic Electronics*. **13**, 1296-1301 (2012).
- 7 Mullen, K., Scherf, U. *Organic Light Emitting Devices. Synthesis, Properties, Applications*. Wiley-VCH. Weinheim. (2006).
- 8 Monk, P.M.S., Mortimer, R.J., Rosseinsky, D.R. *Electrochromism and Electrochromic Devices*. Cambridge University Press. Cambridge. (2007).
- 9 Skotheim, T.A., Elsenbaumer, R.L., Reynolds, J.R. *Handbook of Conducting Polymers*. Marcel Dekker. New York. (1998).
- 10 Data, P. *et al.* Kesterite Inorganic-Organic Heterojunction for Solution Processable Solar Cells. *Electrochimica Acta*. **201**, 78-85 (2016)
- 11 Data, P., Pander, P., Okazaki, M., Takeda, Y., Minakata, S., Monkman, A.P. Dibenzo[a,j]phenazine-Cored Donor–Acceptor–Donor Compounds as Green-to-Red/NIR Thermally Activated Delayed Fluorescence Organic Light Emitters. *Angewandte Chemie International Edition*. **55** (19), 5739-5744 (2016).
- 12 Jankus, V. *et al.* Highly Efficient TADF OLEDs: How the Emitter–Host Interaction Controls Both the Excited State Species and Electrical Properties of the Devices to Achieve Near 100% Triplet Harvesting and High Efficiency. *Advanced Functional Materials*. **24** (39), 6178-6186 (2014).
- 13 Data, P. *et al.* Exciplex Enhancement as a Tool to Increase OLED Device Efficiency *Journal of Physical Chemistry C*. **120** (4), 2070-2078 (2016).
- 14 Dias, F. B. *et al.* The Role of Local Triplet Excited States and D-A Relative Orientation in

Thermally Activated Delayed Fluorescence: Photophysics and Devices. *Advanced Science*. (2016).

15 Okazaki, M. *et al.* Thermally Activated Delayed Fluorescent Phenothiazine-Dibenzo[a,j]phenazine-Phenothiazine Triads Exhibiting Tricolor-Changing Mechanochromic Luminescence. *Chemical Science*. **8**, 2677-2686 (2017).

16 Data, P. *et al.* Efficient p-phenylene based OLEDs with mixed interfacial exciplex emission. *Electrochimica Acta* **182**, 524-528 (2015).

17 Goushi, K., Yoshida, K., Sato, K., Adachi, C. Organic light-emitting diodes employing efficient reverse intersystem crossing for triplet-to-singlet state conversion. *Nature Photonics*. **6**, 253-258 (2012).

18 Data, P., Lapkowski, M., Motyka, M., Suwinski, J. Influence of heteroaryl group on electrochemical and spectroscopic properties of conjugated polymers. *Electrochimica Acta*. **83**, 271-282 (2012).

19 Data, P., Motyka, M., Lapkowski, M., Suwinski, J., Monkman, A. Spectroelectrochemical Analysis of Charge Carriers as a Way of Improving Poly(p-phenylene) Based Electrochromic Windows. *Journal of Physical Chemistry C*. **119**, 20188-20200 (2015).

20 Enengl, C. *et al.* Explaining the Cyclic Voltammetry of a Poly(1,4-phenylene-ethynylene)-alt-poly(1,4-phenylene-vinylene) Copolymer upon Oxidation by using Spectroscopic Techniques. *ChemPhysChem*. **18**, 93-100 (2017).

21 Gudeika, D. *et al.* Hydrazone containing electron-accepting and electron-donating moieties. *Dyes Pigments*. **91**, 13-19 (2011).

22 Swist, A., Cabaj, J., Soloduch, J., Data, P., Lapkowski, M. Novel acridone-based branched blocks as highly fluorescent materials. *Synthetic Metals*. **180**, 1-8 (2013).

23 Data, P., Lapkowski, M., Motyka, M., Suwinski, J. Influence of alkyl chain on electrochemical and spectroscopic properties of polyselenophenes. *Electrochimica Acta*. **87**, 438-449 (2013).

24 Laba, K. *et al.* Electrochemically induced synthesis of poly(2,6-carbazole). *Macromolecular Rapid Communications*. **36**, 1749-1755 (2015).

25 Pluczyk, S. *et al.* Unusual Electrochemical Properties of the Electropolymerized Thin Layer Based on a s-Tetrazine-Triphenylamine Monomer. *Journal of Physical Chemistry C*. **120**, 4382-4391 (2016).

26 Blacha-Grzechnik, A., Turczyn, R., Burek, M., Zak, J. In situ Raman spectroscopic studies on potential-induced structural changes in polyaniline thin films synthesized via surface-initiated electropolymerization on covalently modified gold surface. *Vibrational Spectroscopy*. **71**, 30-36 (2014).

27 Laba, K. *et al.* Diquinoline derivatives as materials for potential optoelectronic applications. *Journal of Physical Chemistry C*. **119**, 13129-13137 (2015).

28 Enengl, S. *et al.* Spectroscopic characterization of charge carriers of the organic semiconductor quinacridone compared with pentacene during redox reactions. *Journal of Materials Chemistry C*. **4**, 10265-10278 (2016).

29 Data, P. *et al.* Electrochemically Induced Synthesis of Triphenylamine-based Polyhydrazones. *Electrochimica Acta*. **230**, 10-21 (2017).

30 Brzeczek, A. *et al.* Synthesis and properties of 1,3,5-tricarbazolylbenzenes with star-shaped architecture. *Dyes Pigments*. **113**, 640-648 (2015).

787 31 Data, P., Lapkowski, M., Motyka, M., Suwinski, J. Electrochemistry and  
788 spectroelectrochemistry of a novel selenophene-based monomer. *Electrochimica Acta*. **59**, 567  
789 – 572 (2012).

790 32 Data, P. *et al.* Electrochemical and spectroelectrochemical comparison of alternated  
791 monomers and their copolymers based on carbazole and thiophene derivatives. *Electrochimica*  
792 *Acta*. **122**, 118-129 (2014).

793 33 Data, P. *et al.* Evidence for Solid State Electrochemical Degradation Within a Small  
794 Molecule OLED. *Electrochimica Acta*. **184**, 86-93 (2015).

795 34 Data, P. *et al.* Unusual properties of electropolymerized 2,7- and 3,6-  
796 carbazole derivatives. *Electrochimica Acta*. **1282**, 430-438 (2014).

797 35 Etherington, M.K. *et al.* Regio- and conformational isomerization critical to design of  
798 efficient thermally-activated delayed fluorescence emitters. *Nature Communications*. **8**, 14987  
799 (2017).

800 36 Trasatti, S. The absolute electrode potential: an explanatory note. *Pure and Applied*  
801 *Chemistry*. **58**, 955-966 (1986).

802 37 Cardona, C.M. *et al.* Electrochemical Considerations for Determining Absolute Frontier  
803 Orbital Energy Levels of Conjugated Polymers for Solar Cell Applications. *Advanced Materials* **23**,  
804 2367-2371 (2011).

805 38 Bredas, J.-L. Mind the gap! *Mater Horiz*. **1**, 17-19 (2014).

806 39 Gerson, F., Huber, W. *Electron Spin Resonance Spectroscopy of Organic Radicals*; 2003.

807 40 Brustolon, M., Giamello, E. *Electron Paramagnetic Resonance. A Practitioner's Toolkit*.  
808 John Wiley & Sons Inc. New Jersey. (2009).

809 41 Weil, J., Bolton, J. *Electron Paramagnetic Resonance: Elementary Theory and Practical*  
810 *Applications*. John Wiley & Sons, Inc. (2007).

811 42 Rieger, P.H. *Electron Spin Resonance. Analysis and Interpretation*. The Royal Society of  
812 Chemistry. (2007).

813 43 Roznyatovskiy, V.V., Gardner, D.M., Eaton, S.W., Wasielewski, M.R., Radical Anions of  
814 Trifluoromethylated Perylene and Naphthalene Imide and Diimide Electron Acceptors. *Organic*  
815 *Letters*. **16**, 16–19 (2013).

816 44 Pluczyk, S., Kuznik, W., Lapkowski, M., Reghu, R. R., Grazulevicius, J. V. The Effect of the  
817 Linking Topology on the Electrochemical and Spectroelectrochemical Properties of Carbazolyl  
818 Substituted Perylene Bisimides. *Electrochimica Acta*. **135**, 487–494 (2014).

819 45 Ledwon, P. *et al.* A Novel Donor–acceptor Carbazole and Benzothiadiazole Material for  
820 Deep Red and Infrared Emitting Applications. *Journal of Materials Chemistry C*. **4**, 2219–2227  
821 (2016).

822 46 Heinze, J., Frontana-Urbe, B. A., Ludwigs, S. Electrochemistry of Conducting Polymers-  
823 Persistent Models and New Concepts. *Chemical Reviews*. **110**, 4724–4771 (2010).

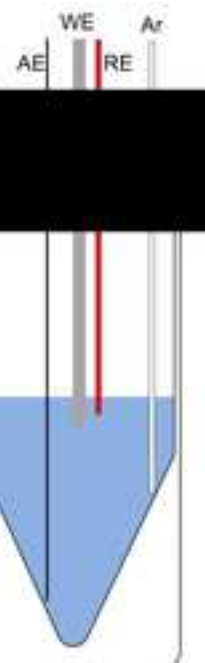
824 47 Kurowska, A., Kostyuchenko, A. S., Zassowski, P., Skorka, L., Yurpalov, V. L., Fisyuk, A. S.,  
825 Pron, A., Domagala, W. Symmetrically Disubstituted Bithiophene Derivatives of Properties.  
826 *Journal of Physical Chemistry C*. **118**, 25176–25189 (2014).

827 48 Zotti, G., Schiavon, G., Zecchin, S., Morin, J. F., Leclerc, M. Electrochemical, Conductive,  
828 and Magnetic Properties of 2,7-Carbazole-Based Conjugated Polymers. *Macromolecules*. **35**,  
829 2122–2128 (2002).

830 49 Kaim, W., Fiedler, J. Spectroelectrochemistry: The Best of Two Worlds. *Chemical Society*

831 *Reviews*. **38**, 3373–3382 (2009).  
832 50 Duling, D. R. Simulation of Multiple Isotropic Spin-Trap EPR Spectra. *Journal of Magnetic*  
833 *Resonance, Series B*. **104**, 105–110 (1994).  
834 51 Benson, C. R., et al. Multiplying the Electron Storage Capacity of a Bis-Tetrazine Pincer  
835 Ligand. *Dalton Transactions*. **43**, 6513–6524 (2014).  
836 52 Nobuyasu R. S. et al. Rational Design of TADF Polymers Using a Donor–Acceptor  
837 Monomer with Enhanced TADF Efficiency Induced by the Energy Alignment of Charge Transfer  
838 and Local Triplet Excited States. *Advanced Optical Materials*. **4**, 597–607 (2016).  
839

### Cyclic Voltammetry

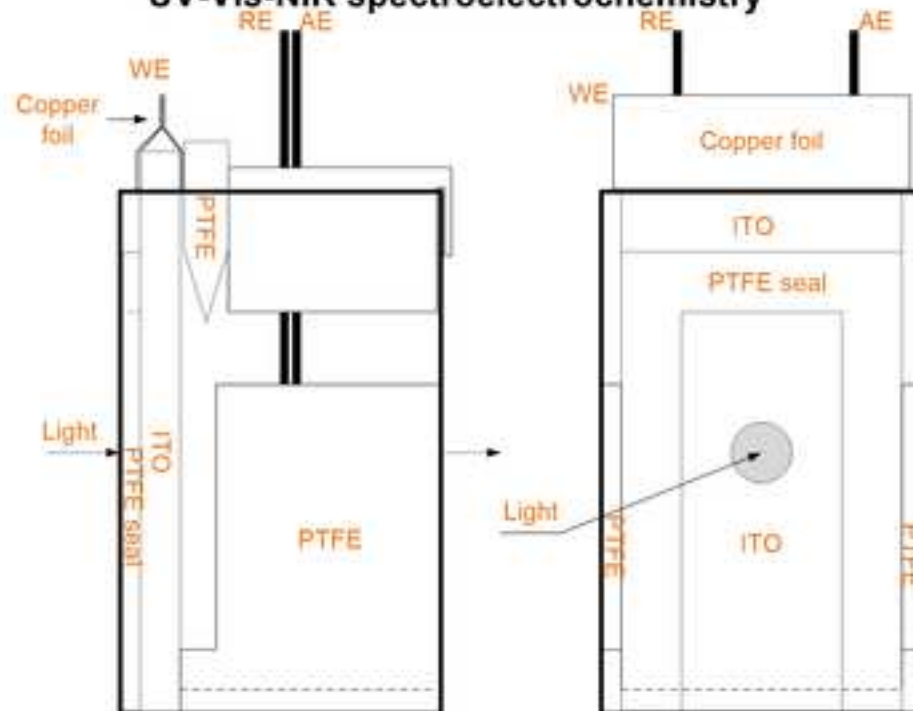


RE – Reference Electrode

WE – Working Electrode

AE – Auxiliary Electrode

### UV-Vis-NIR spectroelectrochemistry



### EPR spectroelectrochemistry

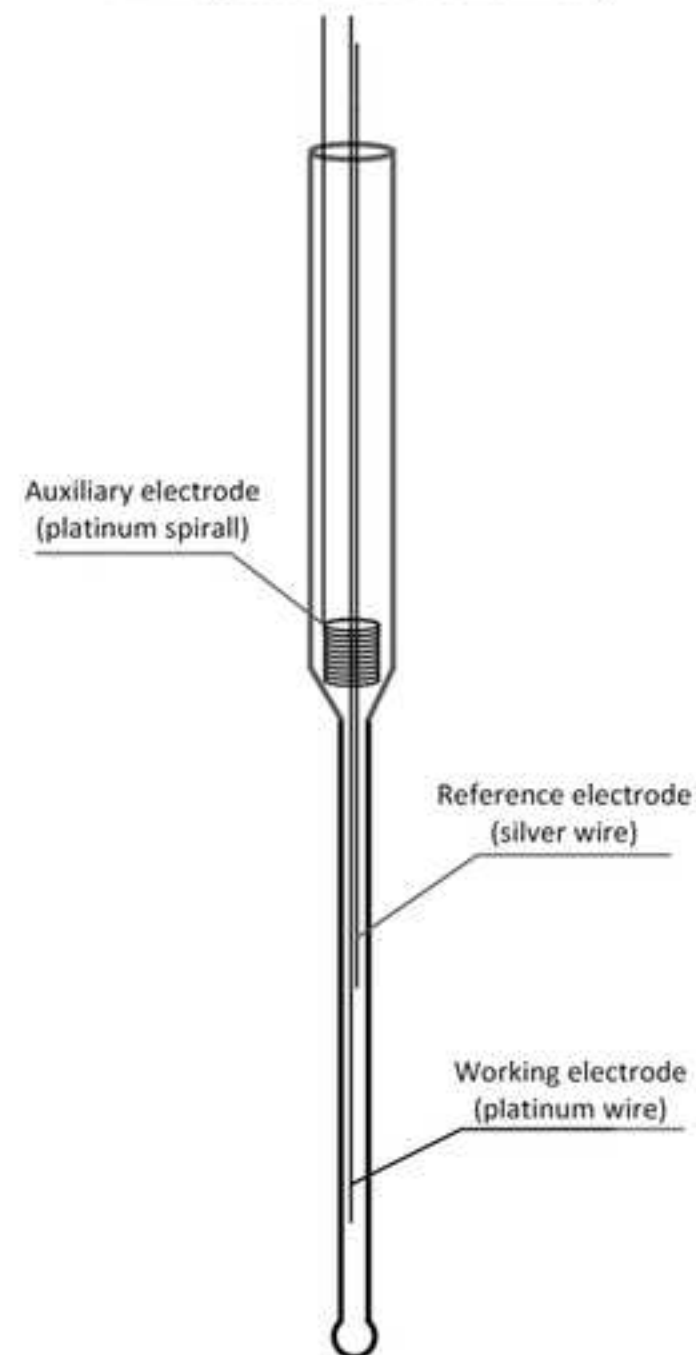


Figure 2

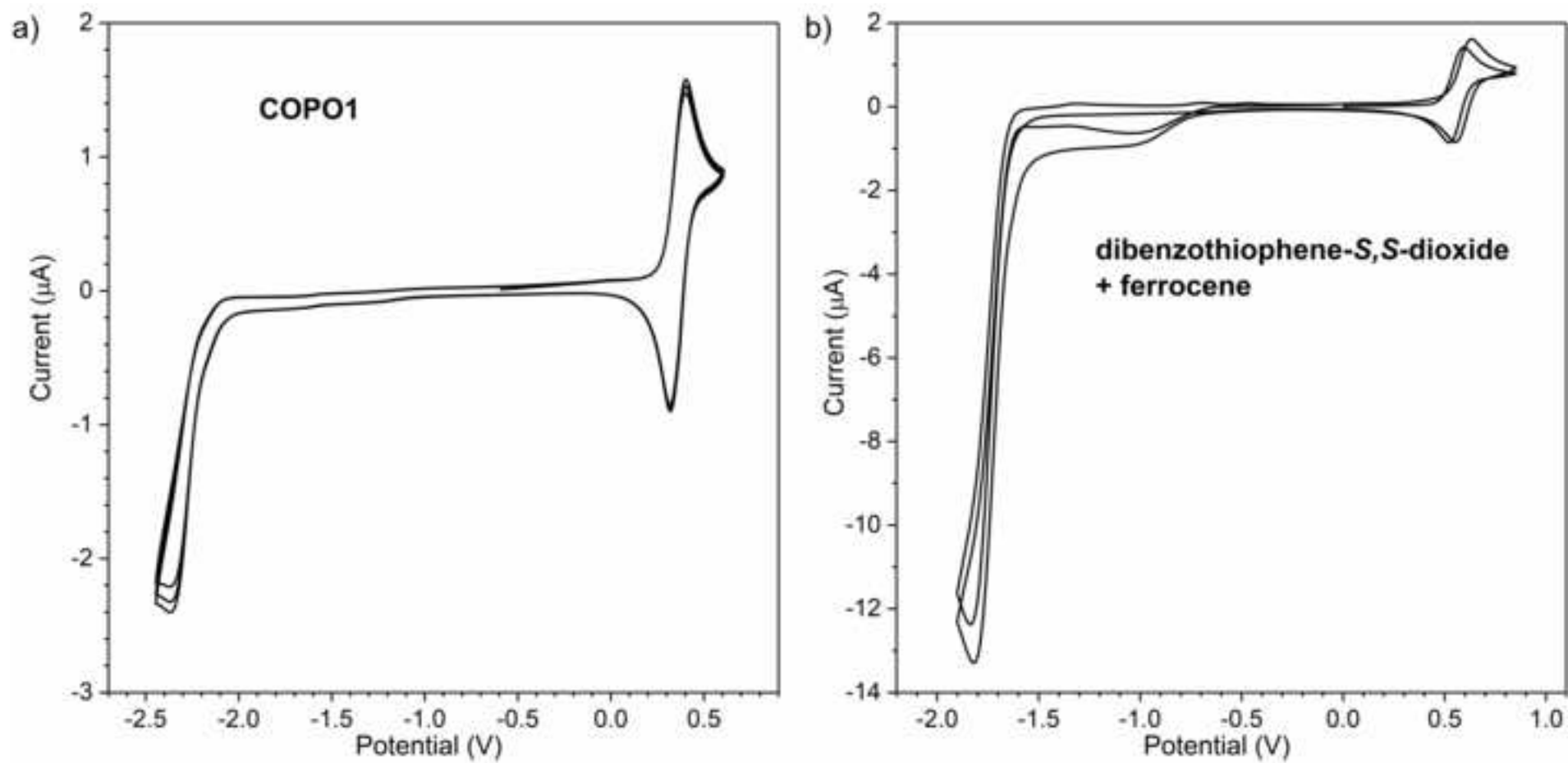


Figure 3

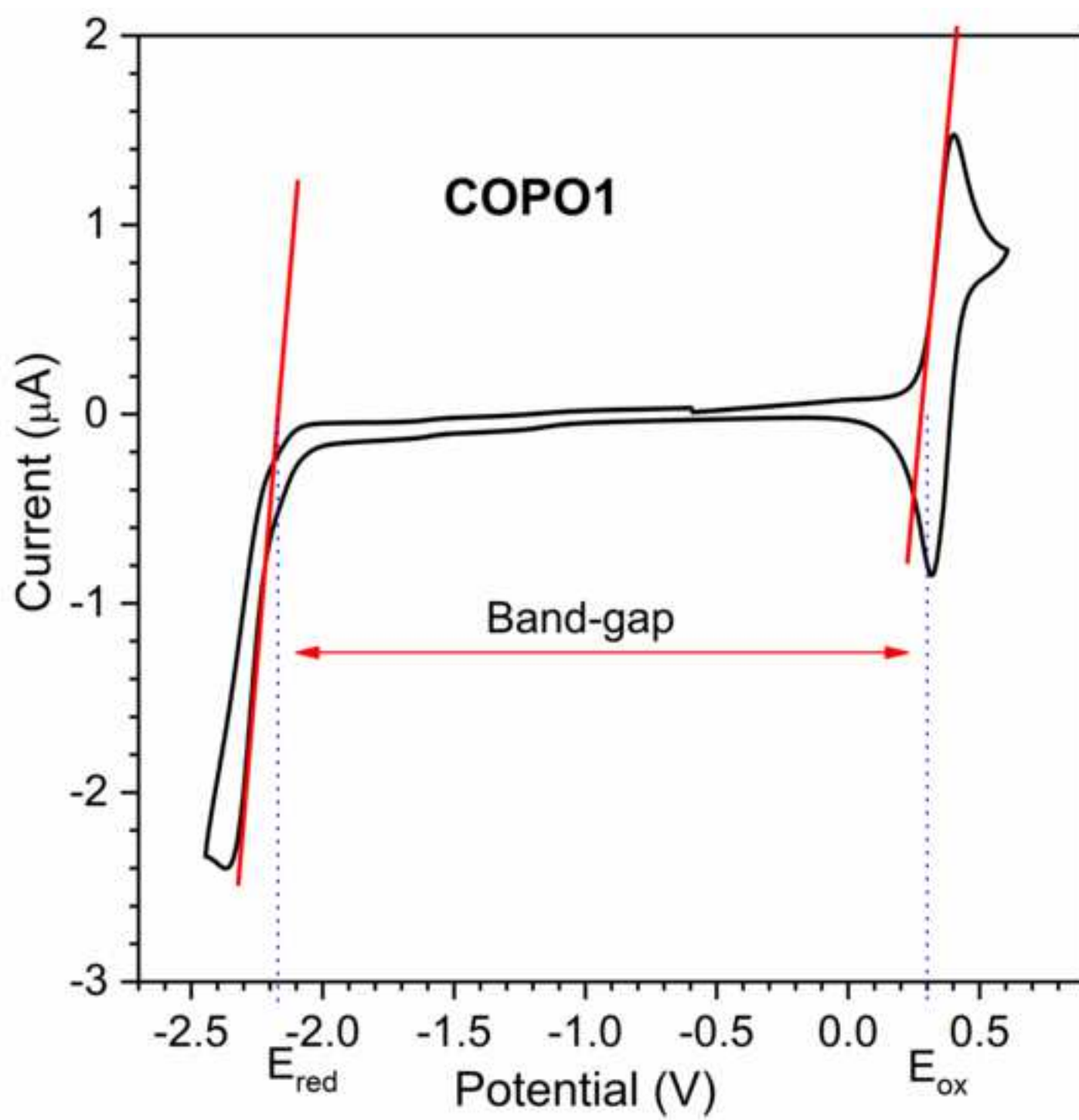




Figure 4

[Click here to download Figure Figure 4.tif](#)



Figure 5

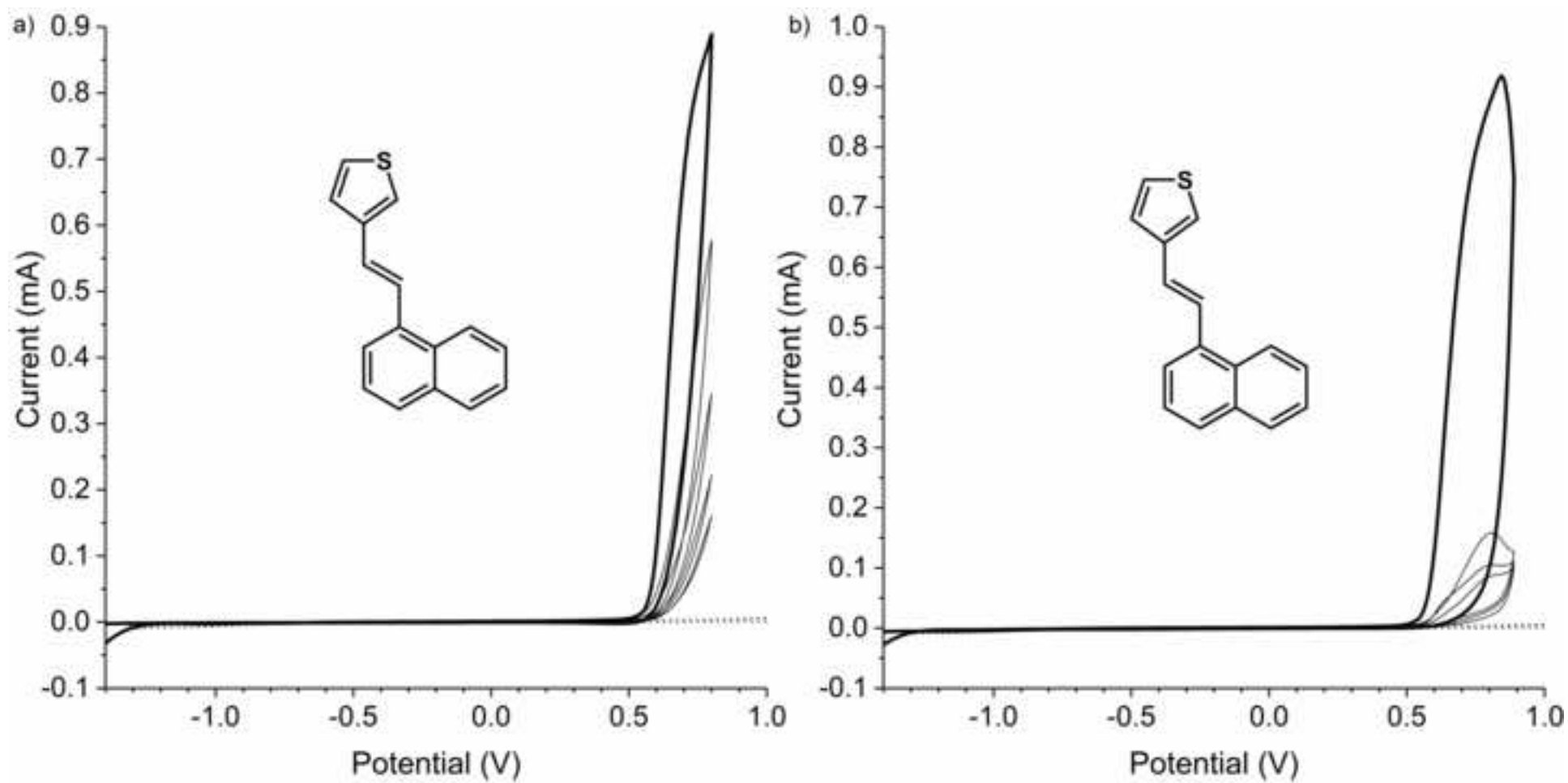
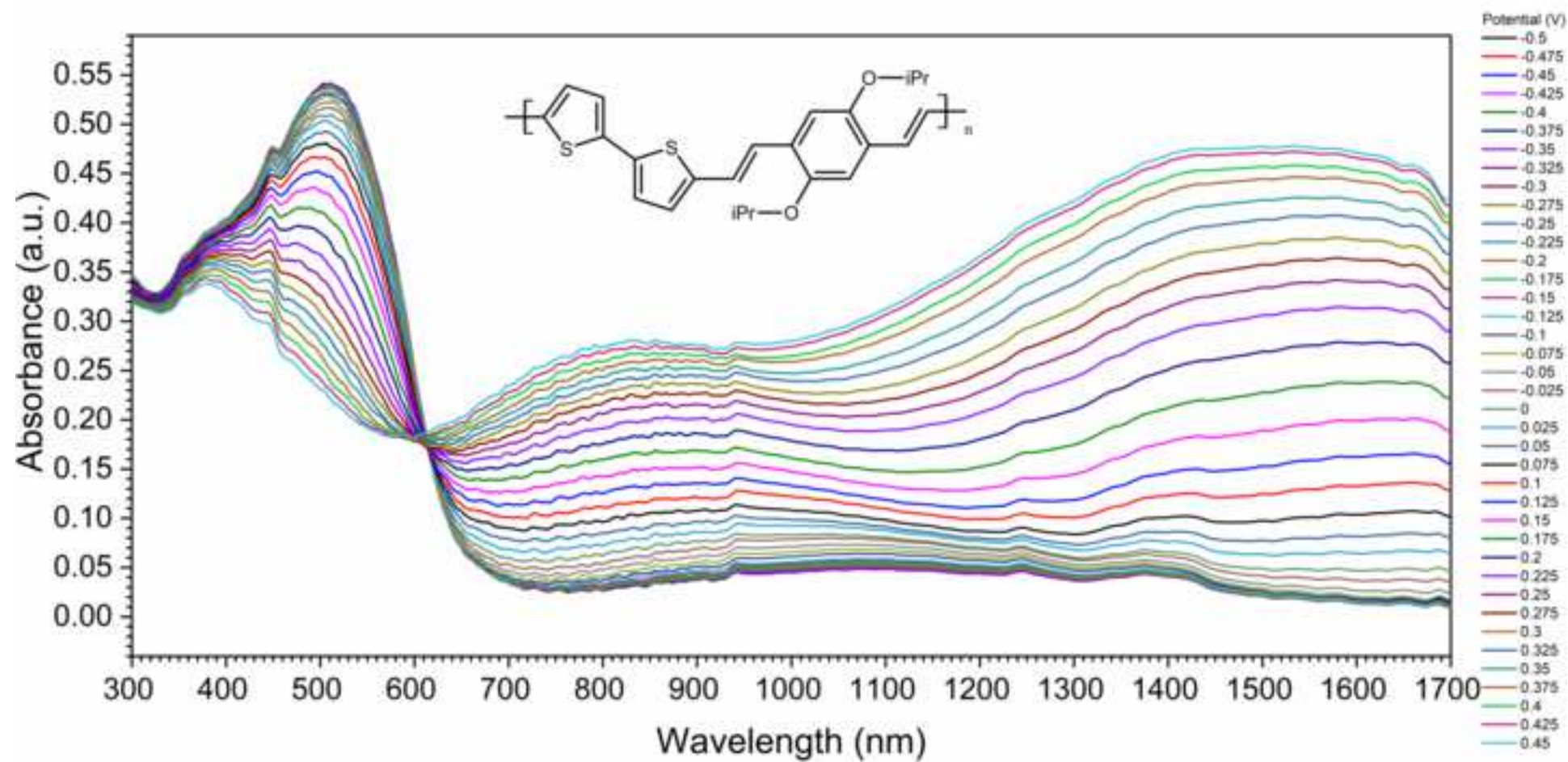


Figure 6

[Click here to download Figure Figure 6.tif](#)

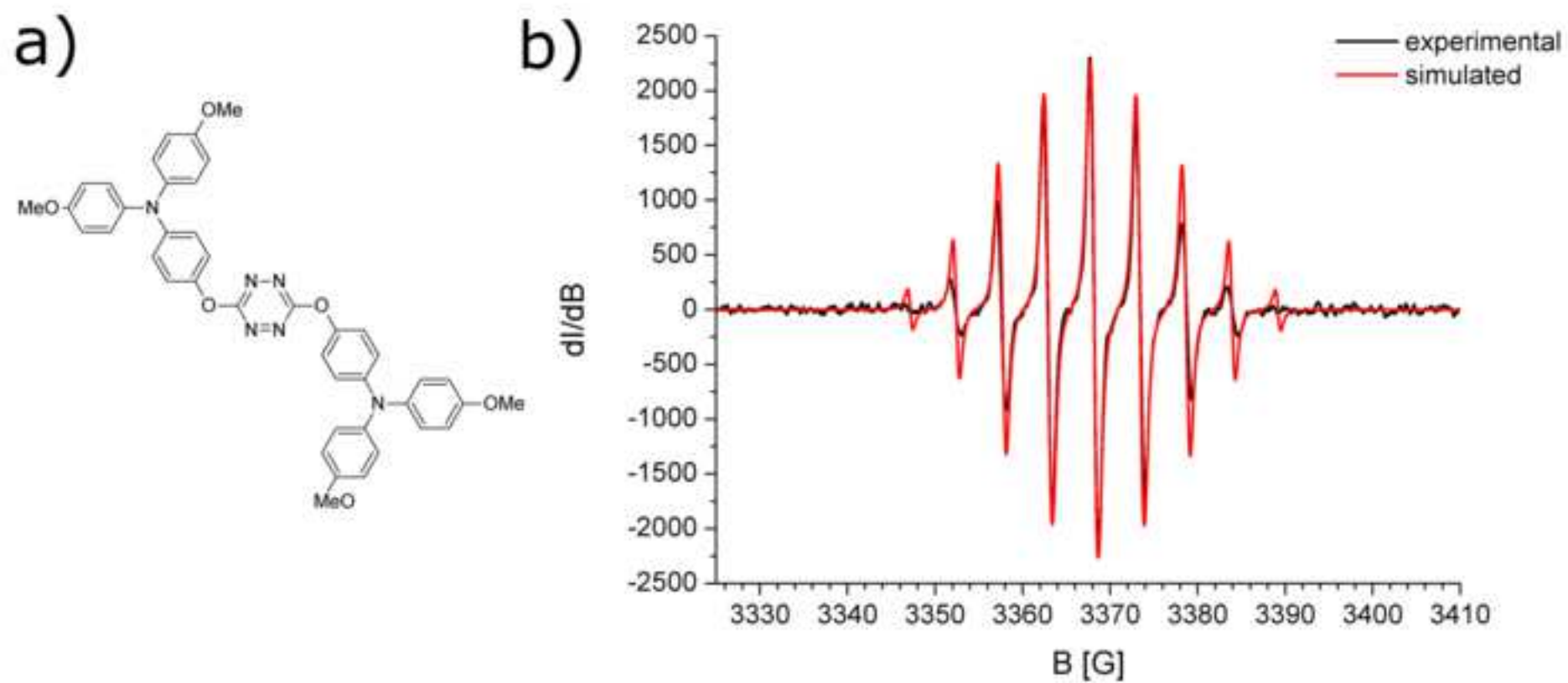
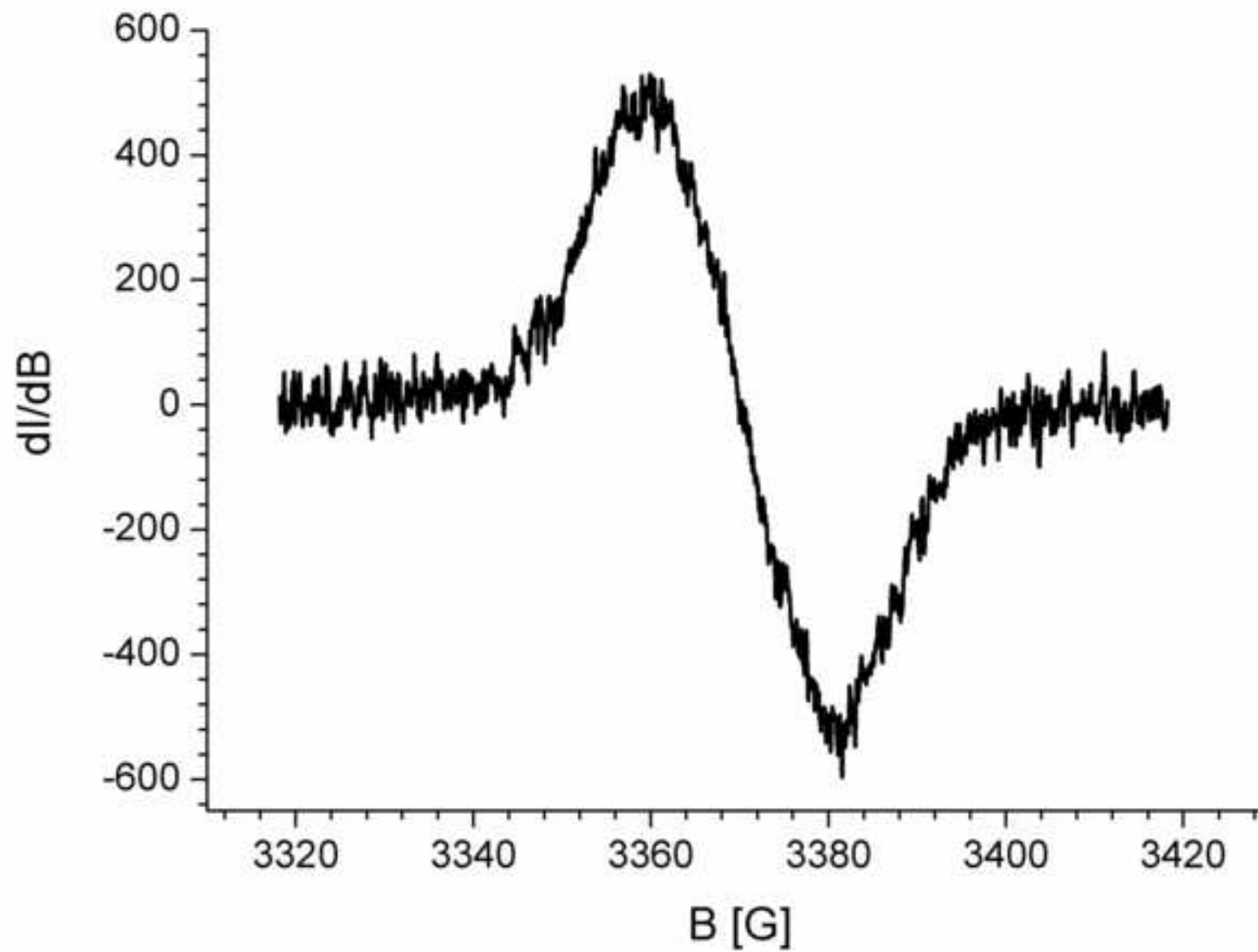
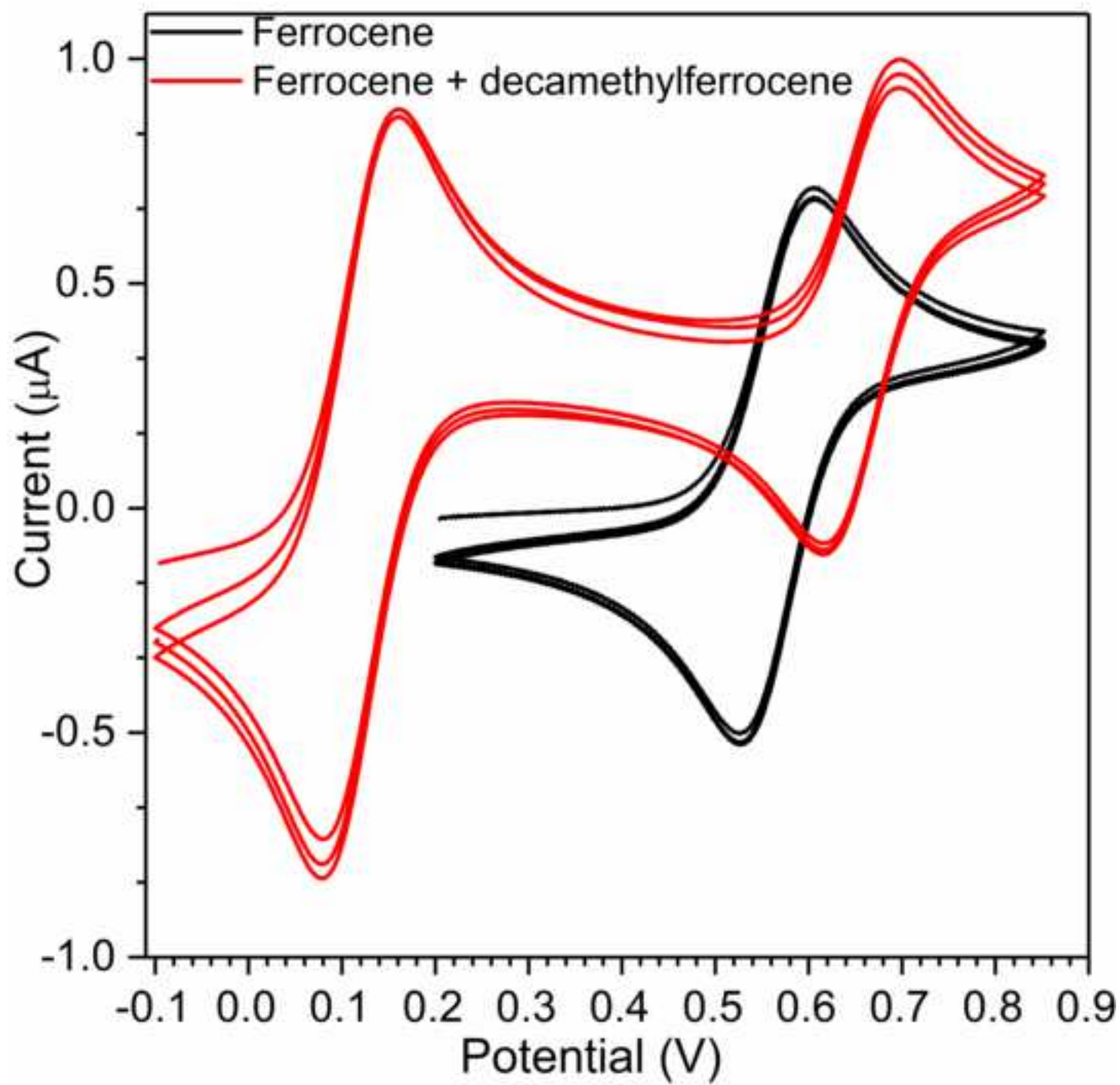


Figure 8





Name of Material/ Equipment	Company	Catalog Number	Comments/Description
Potentiostat	Metrohm	Autolab PGSTAT100	
EPR	JEOL	JES-FA200	
UV-Vis detector	Oceanoptics	QE6500	
NIR detector	Oceanoptics	NIRQuest	
Dichloromethane (DCM)	Sigma-Aldrich	106048	
Tetrabutylammonium tetrafluoroborate (Bu <sub>4</sub> NBF <sub>4</sub> )	Sigma-Aldrich	86896	
2-propanol, 99.9%	Sigma-Aldrich	675431	
Acetone, 99.9%	Sigma-Aldrich	439126	
Ultrasonic Bath	Elma	S30H	
Tetrahydrofuran >99.9%	Sigma-Aldrich	401757	
ferrocene >98%	Sigma-Aldrich	F408	
decamethylferrocene >97%	Sigma-Aldrich	378542	





1 Alewife Center #200  
Cambridge, MA 02140  
tel. 617.945.9051  
www.jove.com

## ARTICLE AND VIDEO LICENSE AGREEMENT - UK

Title of Article:	Using Cyclic Voltammetry, UV-Vis-NIR, and EPR spectroelectrochemistry to analyze organic compounds
Author(s):	Sandra Pluczyk, Marharyta Vasylieva, Przemyslaw Data

Item 1: The Author elects to have the Materials be made available (as described at <http://www.jove.com/publish>) via:

☐

Standard Access

☒

Open Access

Item 2: Please select one of the following items:

☒

The Author is **NOT** a United States government employee.

☐

The Author is a United States government employee and the Materials were prepared in the course of his or her duties as a United States government employee.

☐

The Author is a United States government employee but the Materials were NOT prepared in the course of his or her duties as a United States government employee.

### ARTICLE AND VIDEO LICENSE AGREEMENT

1. **Defined Terms.** As used in this Article and Video License Agreement, the following terms shall have the following meanings: "**Agreement**" means this Article and Video License Agreement; "**Article**" means the article specified on the last page of this Agreement, including any associated materials such as texts, figures, tables, artwork, abstracts, or summaries contained therein; "**Author**" means the author who is a signatory to this Agreement; "**Collective Work**" means a work, such as a periodical issue, anthology or encyclopedia, in which the Materials in their entirety in unmodified form, along with a number of other contributions, constituting separate and independent works in themselves, are assembled into a collective whole; "**CRC License**" means the Creative Commons Attribution 3.0 Agreement (also known as CC-BY), the terms and conditions of which can be found at: <http://creativecommons.org/licenses/by/3.0/us/legalcode>; "**Derivative Work**" means a work based upon the Materials or upon the Materials and other pre-existing works, such as a translation, musical arrangement, dramatization, fictionalization, motion picture version, sound recording, art reproduction, abridgment, condensation, or any other form in which the Materials may be recast, transformed, or adapted; "**Institution**" means the institution, listed on the last page of this Agreement, by which the Author was employed at the time of the creation of the Materials; "**JoVE**" means MyJoVE Corporation, a Massachusetts corporation and the publisher of The Journal of Visualized Experiments; "**Materials**" means the Article and / or the Video; "**Parties**" means the Author and JoVE; "**Video**" means any video(s) made by the Author, alone or in conjunction with any other parties, or by JoVE or its affiliates or agents, individually or in collaboration with the Author or any other parties, incorporating all or any portion

of the Article, and in which the Author may or may not appear.

2. **Background.** The Author, who is the author of the Article, in order to ensure the dissemination and protection of the Article, desires to have the JoVE publish the Article and create and transmit videos based on the Article. In furtherance of such goals, the Parties desire to memorialize in this Agreement the respective rights of each Party in and to the Article and the Video.

3. **Grant of Rights in Article.** In consideration of JoVE agreeing to publish the Article, the Author hereby grants to JoVE, subject to **Sections 4 and 7** below, the exclusive, royalty-free, perpetual (for the full term of copyright in the Article, including any extensions thereto) license (a) to publish, reproduce, distribute, display and store the Article in all forms, formats and media whether now known or hereafter developed (including without limitation in print, digital and electronic form) throughout the world, (b) to translate the Article into other languages, create adaptations, summaries or extracts of the Article or other Derivative Works (including, without limitation, the Video) or Collective Works based on all or any portion of the Article and exercise all of the rights set forth in (a) above in such translations, adaptations, summaries, extracts, Derivative Works or Collective Works and (c) to license others to do any or all of the above. The foregoing rights may be exercised in all media and formats, whether now known or hereafter devised, and include the right to make such modifications as are technically necessary to exercise the rights in other media and formats. If the "Open Access" box has been checked in **Item 1** above, JoVE and the Author hereby grant to the public all such rights in the Article as provided in, but subject to all limitations and requirements set forth in, the CRC License.



4. **Retention of Rights in Article.** Notwithstanding the exclusive license granted to JoVE in **Section 3** above, the Author shall, with respect to the Article, retain the non-exclusive right to use all or part of the Article for the non-commercial purpose of giving lectures, presentations or teaching classes, and to post a copy of the Article on the Institution's website or the Author's personal website, in each case provided that a link to the Article on the JoVE website is provided and notice of JoVE's copyright in the Article is included. All non-copyright intellectual property rights in and to the Article, such as patent rights, shall remain with the Author.

5. **Grant of Rights in Video - Standard Access.** This **Section 5** applies if the "Standard Access" box has been checked in **Item 1** above or if no box has been checked in **Item 1** above. In consideration of JoVE agreeing to produce, display or otherwise assist with the Video, the Author hereby acknowledges and agrees that, subject to **Section 7** below, JoVE is and shall be the sole and exclusive owner of all rights of any nature, including, without limitation, all copyrights, in and to the Video. To the extent that, by law, the Author is deemed, now or at any time in the future, to have any rights of any nature in or to the Video, the Author hereby disclaims all such rights and transfers all such rights to JoVE.

6. **Grant of Rights in Video - Open Access.** This **Section 6** applies only if the "Open Access" box has been checked in **Item 1** above. In consideration of JoVE agreeing to produce, display or otherwise assist with the Video, the Author hereby grants to JoVE, subject to **Section 7** below, the exclusive, royalty-free, perpetual (for the full term of copyright in the Article, including any extensions thereto) license (a) to publish, reproduce, distribute, display and store the Video in all forms, formats and media whether now known or hereafter developed (including without limitation in print, digital and electronic form) throughout the world, (b) to translate the Video into other languages, create adaptations, summaries or extracts of the Video or other Derivative Works or Collective Works based on all or any portion of the Video and exercise all of the rights set forth in (a) above in such translations, adaptations, summaries, extracts, Derivative Works or Collective Works and (c) to license others to do any or all of the above. The foregoing rights may be exercised in all media and formats, whether now known or hereafter devised, and include the right to make such modifications as are technically necessary to exercise the rights in other media and formats.

7. **Government Employees.** If the Author is a United States government employee and the Article was prepared in the course of his or her duties as a United States government employee, as indicated in **Item 2** above, and any of the licenses or grants granted by the Author hereunder exceed the scope of the 17 U.S.C. 403, then the rights granted hereunder shall be limited to the maximum rights permitted under such statute. In such case, all provisions contained herein that are not in conflict with such statute shall remain in full force and effect, and all provisions contained herein that do so conflict shall be

deemed to be amended so as to provide to JoVE the maximum rights permissible within such statute.

8. **Protection of the work.** The Author(s) authorize JoVE to take steps in the Author(s) name and on their behalf if JoVE believes some third party could be infringing or might infringe the copyright of either the Author's Article and/or Video.

9. **Likeness, Privacy, Personality.** The Author hereby grants JoVE the right to use the Author's name, voice, likeness, picture, photograph, image, biography and performance in any way, commercial or otherwise, in connection with the Materials and the sale, promotion and distribution thereof. The Author hereby waives any and all rights he or she may have, relating to his or her appearance in the Video or otherwise relating to the Materials, under all applicable privacy, likeness, personality or similar laws.

10. **Author Warranties.** The Author represents and warrants that the Article is original, that it has not been published, that the copyright interest is owned by the Author (or, if more than one author is listed at the beginning of this Agreement, by such authors collectively) and has not been assigned, licensed, or otherwise transferred to any other party. The Author represents and warrants that the author(s) listed at the top of this Agreement are the only authors of the Materials. If more than one author is listed at the top of this Agreement and if any such author has not entered into a separate Article and Video License Agreement with JoVE relating to the Materials, the Author represents and warrants that the Author has been authorized by each of the other such authors to execute this Agreement on his or her behalf and to bind him or her with respect to the terms of this Agreement as if each of them had been a party hereto as an Author. The Author warrants that the use, reproduction, distribution, public or private performance or display, and/or modification of all or any portion of the Materials does not and will not violate, infringe and/or misappropriate the patent, trademark, intellectual property or other rights of any third party. The Author represents and warrants that it has and will continue to comply with all government, institutional and other regulations, including, without limitation all institutional, laboratory, hospital, ethical, human and animal treatment, privacy, and all other rules, regulations, laws, procedures or guidelines, applicable to the Materials, and that all research involving human and animal subjects has been approved by the Author's relevant institutional review board.

11. **JoVE Discretion.** If the Author requests the assistance of JoVE in producing the Video in the Author's facility, the Author shall ensure that the presence of JoVE employees, agents or independent contractors is in accordance with the relevant regulations of the Author's institution. If more than one author is listed at the beginning of this Agreement, JoVE may, in its sole discretion, elect not take any action with respect to the Article until such time as it has received complete, executed Article and Video License Agreements from each such author. JoVE reserves the right, in its absolute and sole

## ARTICLE AND VIDEO LICENSE AGREEMENT - UK

discretion and without giving any reason therefore, to accept or decline any work submitted to JoVE. JoVE and its employees, agents and independent contractors shall have full, unfettered access to the facilities of the Author or of the Author's institution as necessary to make the Video, whether actually published or not. JoVE has sole discretion as to the method of making and publishing the Materials, including, without limitation, to all decisions regarding editing, lighting, filming, timing of publication, if any, length, quality, content and the like.

12. **Indemnification.** The Author agrees to indemnify JoVE and/or its successors and assigns from and against any and all claims, costs, and expenses, including attorney's fees, arising out of any breach of any warranty or other representations contained herein. The Author further agrees to indemnify and hold harmless JoVE from and against any and all claims, costs, and expenses, including attorney's fees, resulting from the breach by the Author of any representation or warranty contained herein or from allegations or instances of violation of intellectual property rights, damage to the Author's or the Author's institution's facilities, fraud, libel, defamation, research, equipment, experiments, property damage, personal injury, violations of institutional, laboratory, hospital, ethical, human and animal treatment, privacy or other rules, regulations, laws, procedures or guidelines, liabilities and other losses or damages related in any way to the submission of work to JoVE, making of videos by JoVE, or publication in JoVE or elsewhere by JoVE. The Author shall be responsible for, and shall hold JoVE harmless from, damages caused by lack of sterilization, lack of cleanliness or by contamination due to the making of a video by JoVE its employees, agents or independent contractors. All sterilization, cleanliness or


decontamination procedures shall be solely the responsibility of the Author and shall be undertaken at the Author's expense. All indemnifications provided herein shall include JoVE's attorney's fees and costs related to said losses or damages. Such indemnification and holding harmless shall include such losses or damages incurred by, or in connection with, acts or omissions of JoVE, its employees, agents or independent contractors.

13. **Fees.** To cover the cost incurred for publication, JoVE must receive payment before production and publication the Materials. Payment is due in 21 days of invoice. Should the Materials not be published due to an editorial or production decision, these funds will be returned to the Author. Withdrawal by the Author of any submitted Materials after final peer review approval will result in a US\$1,200 fee to cover pre-production expenses incurred by JoVE. If payment is not received by the completion of filming, production and publication of the Materials will be suspended until payment is received.

14. **Transfer, Governing Law.** This Agreement may be assigned by JoVE and shall inure to the benefits of any of JoVE's successors and assignees. This Agreement shall be governed and construed by the internal laws of the Commonwealth of Massachusetts without giving effect to any conflict of law provision thereunder. This Agreement may be executed in counterparts, each of which shall be deemed an original, but all of which together shall be deemed to be one and the same agreement. A signed copy of this Agreement delivered by facsimile, e-mail or other means of electronic transmission shall be deemed to have the same legal effect as delivery of an original signed copy of this Agreement.

A signed copy of this document must be sent with all new submissions. Only one Agreement is required per submission.

### CORRESPONDING AUTHOR

Name:	Przemyslaw Data		
Department:	Department of Physical Chemistry and Technology of Polymers		
Institution:	Silesian University of Technology		
Title:	Using Cyclic Voltammetry, UV-Vis-NIR, and EPR spectroelectrochemistry to analyze organic compounds		
Signature:		Date:	10.06.2018

Please submit a **signed** and **dated** copy of this license by one of the following three methods:

1. Upload an electronic version on the JoVE submission site
2. Fax the document to +1.866.381.2236
3. Mail the document to JoVE / Attn: JoVE Editorial / 1 Alewife Center #200 / Cambridge, MA 02140

**To the attention of editor of JOVE:**

Dear editor,

On behalf of the authors, I would like to submit the revised manuscript entitled: “*Using Cyclic Voltammetry, UV-Vis-NIR, and EPR spectroelectrochemistry to analyze organic compounds.*” by Sandra Pluczyk, Marharyta Vasylieva and Przemysław Data to be reconsidered for publication in the JOVE journal.

In the revised version of the manuscript we have introduced changes recommended by the JoVE Scientific Review Editor.

We hope that the revisions made will meet the editor recommendations.

Sincerely yours,

Przemysław Data

**Changes recommended by the JoVE Scientific Review Editor:**

1. Please revise the following lines to avoid previously published text: 575-584

**It's corrected**

2. As a UK author, please sign the UK Author License Agreement with open access selected.

**It's signed**