MODIFIED ELECTRODES BASED ON 2,6-BIS((E)-2-(THIOPHEN-2-YL)VINYL)-4-(4,6,8-TRIMETHYLAZULEN-1-YL)PYRIDINE FOR HEAVY METALS SENSING

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This paper presents the electrochemical characterization of 2,6-bis((E)-2-(thiophen-2-yl)vinyl)-4-(4,6,8-trimethylazulen-1-yl)pyridine using cyclic voltammetry, differential pulse voltammetry and rotating disk electrode. Modified electrodes were obtained by successive scanning or by controlled potential electrolysis using different electrode potentials or charges.

The modified electrodes were tested in solutions containing different concentrations of heavy metal ions (Cd^{2+}, Pb^{2+}, Hg^{2+} and Cu^{2+}). The best response was obtained for Pb^{2+} ions.

Keywords: 2,6-bis((E)-2-(thiophen-2-yl)vinyl)-4-(4,6,8-trimethylazulen-1-yl)pyridine, electrochemical characterization, modified electrodes, heavy metals

1. Introduction

Nowadays food products contain chemicals in varying proportions. Food products could have substances that are beneficial for the human body, such as calcium, magnesium, sodium, potassium, etc., but also some toxic substances that in small concentrations can affect the body, due to the raw materials from which the food is made or food preparation process. Among the last ones, the heavy metals such as copper, cadmium, mercury, and lead are the most dangerous [1].

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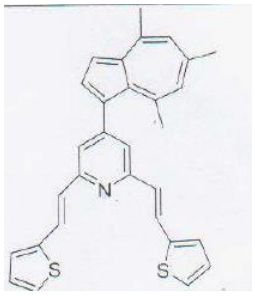
For instance, some studies associate *Itai–itai* desease, which appeared for the first time in Japan, with an increased concentration of cadmium in rice [2–4]. Alzheimer disease is associated with copper presence [5, 6], lead and mercury are considered as one of the main causes of autism [7, 8], and lead is also related to Parkinson disease [9].

The most used and optimized techniques for heavy metal determination are the spectrometric methods (graphite furnace atomic absorption spectroscopy, flame atomic absorption spectrometry, inductively coupled plasma mass spectrometry, atomic fluorescence spectrometry, inductively coupled plasma atomic emission spectroscopy), or chromatography methods (gas chromatography, high performance liquid chromatography, etc.). All these methods require a complex equipment, are expensive to maintain, and need well trained people [10–16].

Nowadays, new electrochemical methods have been developed for heavy metals detection [17,18]. The glassy carbon electrode is the most commonly used, usually modified with bismuth film [19, 20], with magnetite–reduced graphene oxide nanoparticles [21], or with bismuth film and poly (violet pyrocatechol) composite with multi-wall carbon nanotubes [22]. Several examples of polyazulene films have been investigated by our group [23, 24-26].

This paper concerns the electrochemical behaviour of a new synthetized azulene compound, namely 2,6-bis((E)-2-(thiophen-2-yl)vinyl)-4-(4,6,8-trimethylazulen-1-yl)pyridine (**L**), which is proposed as chelating ligand for heavy metal ions.



L

2. Experimental

Acetonitrile (CH_3CN, 99.999% electrochemical grade) and tetra-*n*-butylammonium perchlorate (TBAP, 99%) from Sigma-Aldrich were used as solvent and supporting electrolyte, respectively. For heavy metals recognition commercial metal salts: mercury(II) acetate (99.999%, cadmium nitrate tetrahydrate (≥99.0%), and lead(II) nitrate (≥99.0%) from Sigma Aldrich, and copper(II) acetate monohydrate (≥99.0%) from Fluka were used.

A potentiostat PGSTAT 12 AUTOLAB connected to a three-electrode cell was used in all experiments; the cell contains a glassy carbon electrode from Metrohm (diameter of 3 mm) as working electrode (its active surface was polished before each determination with diamond paste of 0.25 μm, and cleaned with the solvent), a platinum wire as auxiliary electrode, and Ag / 10 mM $AgNO_3$, 0.1 M TBAP, CH_3CN as reference electrode. All the curves obtained for electrochemical characterization and for poly**L** modified electrodes preparation were finally referred to the potential of the ferrocene/ferricinium redox couple (Fc/Fc^+) which in our experimental conditions was +0.07 V.

Cyclic voltammetry (CV) curves were recorded at different scan rates (between 0.1 V/s and 1.0 V/s). Differential pulse voltammetry (DPV) curves were recorded at 0.01 V/s with a pulse height of 0.025 V and a step time of 0.2 s. Rotating disk electrode (RDE) curves were recorded at 0.01 V/s.

For the heavy metals ions detection, the electrochemical cell contained 0.1 M acetate buffer at pH = 5.5 as supporting electrolyte (prepared from 0.2 M acetic acid and 0.2 M sodium acetate solutions). During the detection, a glassy carbon disk (3 mm diameter) modified with poly**L** was the working electrode, the reference electrode was Ag/AgCl, 3 M KCl from Metrohm, and the counter was a platinum wire. The standard solutions for the heavy metals recognition had concentrations between 10^{-4} and 10^{-8} mol/L of mixtures of heavy metal ions; they were prepared by successive dilutions from a stock solution containing all cations at the same concentration (10^{-2} M).

All electrochemical experiments have been performed at 25ºC under argon atmosphere.

3. Results and Discussion

3.1. Electrochemical characterization of L

The electrochemical characterization of **L** on glassy carbon electrode was performed by CV, DPV and RDE at different concentrations of **L** in 0.1 M TBAP/CH_3CN as supporting electrolyte.

The CV and DPV anodic and cathodic curves at (0–2) mM concentrations of **L**, recorded from the stationary potential toward anodic or cathodic potential limits, respectively, are presented in Fig. 1. DPV curves show three oxidation peaks (a1, a2, a3) and five reduction peaks (c1 – c5), in the four in which they appear in the voltammograms. Three anodic peaks (a1, a2, a3) and four cathodic peaks (c1, c2, c4, c5) can be seen in the CV curves, respecting the notations given for the processes from DPV curves.

The peak currents are increasing with **L** concentration for both DPV and CV curves. Fig. 2 shows the linear dependences of the total currents *vs* **L**

concentration from DPV and CV curves, for both anodic and cathodic peaks. The equations and their correlation coefficients for the main peaks are presented in Table 1.

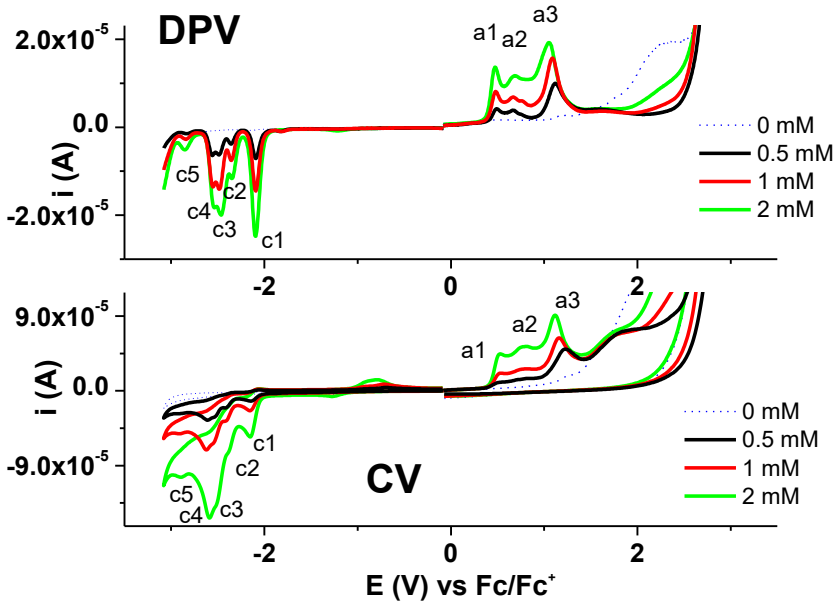


Fig. 1. DPV (0.01 V/s) and CV (0.1 V/s) anodic and cathodic curves on glassy carbon electrode (3 mm diameter) for different **L** concentrations in 0.1 M TBAP/CH_3CN

Good coefficient correlation for all peaks were obtained in case of CV peaks, whereas for DPV peaks high correlation coefficients were obtained only for a1, a2, c1, c2, c3, c4, and c5.

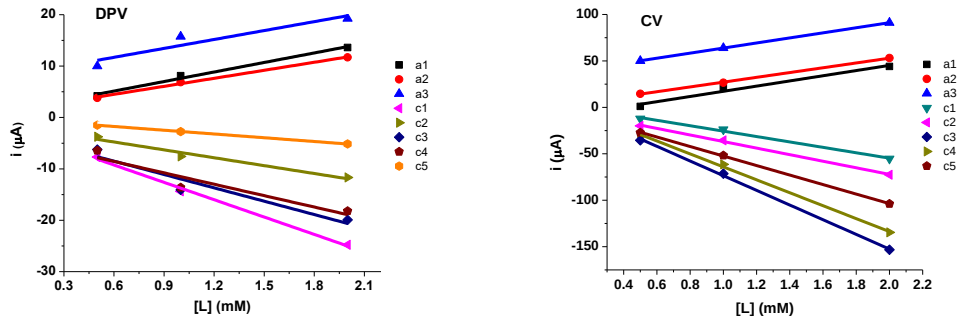


Fig. 2. Linear dependences of the total peak currents *vs* **L** concentration for DPV and CV curves

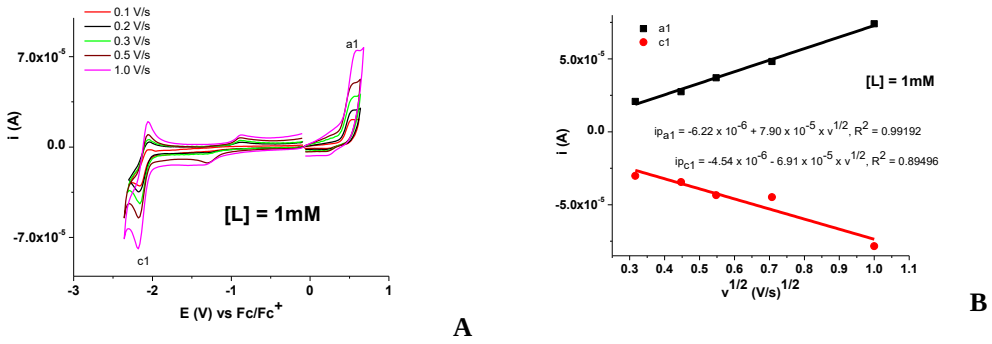
Table 1

Equations and their correlation coefficients for the linear dependences of the total peak currents *vs* L concentration for DPV and CV curves

Method	Equation	Correlation Coefficient
DPV	$i_{peak\ a1} = 1.43 + 6.17 \cdot [\mathbf{L}]$	0.981
	$i_{peak\ a2} = 1.38 + 5.19 \cdot [\mathbf{L}]$	0.992
	$i_{peak\ c1} = -2.5 - 11.25 \cdot [\mathbf{L}]$	0.991
	$i_{peak\ c2} = -1.70 - 5.11 \cdot [\mathbf{L}]$	0.942
	$i_{peak\ c3} = -3.305 - 8.65 \cdot [\mathbf{L}]$	0.854
	$i_{peak\ c4} = -4.12 - 7.39 \cdot [\mathbf{L}]$	0.807
	$i_{peak\ c5} = -0.29 - 2.43 \cdot [\mathbf{L}]$	0.997
CV	$i_{peak\ a1} = -10.64 + 27.91 \cdot [\mathbf{L}]$	0.960
	$i_{peak\ a2} = 1.35 + 25.79 \cdot [\mathbf{L}]$	0.999
	$i_{peak\ a3} = 36.51 + 27.31 \cdot [\mathbf{L}]$	0.999
	$i_{peak\ c1} = 3.54 - 29.12 \cdot [\mathbf{L}]$	0.992
	$i_{peak\ c2} = -1.44 - 35.34 \cdot [\mathbf{L}]$	0.997
	$i_{peak\ c3} = 5.48 - 79.03 \cdot [\mathbf{L}]$	0.997
	$i_{peak\ c4} = -5.60 - -69.67 \cdot [\mathbf{L}]$	0.996
	$i_{peak\ c5} = -1.18 - 51.22 \cdot [\mathbf{L}]$	0.999

*i_{peak} is expressed in μA, and [**L**] in mmol/L

CV curves for the first anodic and cathodic scans recorded at different scan rates (0.1 – 1 V/s) in 1 mM solution of **L** in 0.1 M TBAP/CH_3CN are presented in Fig. 3A. Fig. 3B shows their linear dependences of the peak currents *vs* the square root of the scan rate; the current values increase with the scan rate. **L** diffusion coefficient (D_L) has been calculated from the slope of a1 current *vs* the square root of scan rate using the Randles–Sevcik equation.



A **B**

Fig. 3. (A) CV anodic and cathodic curves recorded on glassy carbon electrode (3 mm diameter) at different scan rates (0.1 – 1.0 V/s) for **L** (1 mM) in 0.1 M TBAP/CH_3CN on glassy carbon electrode (3 mm diameter) and (B) the linear dependences of the total peak currents *vs* the square root of the scan rate

The experiment was performed at room temperature (298.2 K) and the number of transferred electrons was taken 1. The value resulted was D_L = 1.76 x 10^{-5} cm^2/s.

The scan limit domain (Fig. 4) influence was also investigated by CV for **L** solution (1 mM) in 0.1 M TBAP/CH_3CN. It can be noticed that the first two anodic peaks (a1 and a2) belong to quasireversible processes, while the third anodic peak (a3) to an irreversible process. The peak a1 has a pre-wave, which is evident especially at high scan rates. The processes in the cathodic domain are quasi–reversible. The values of peak potentials from CV and DPV curves and the process characteristics are presented in Table 2.

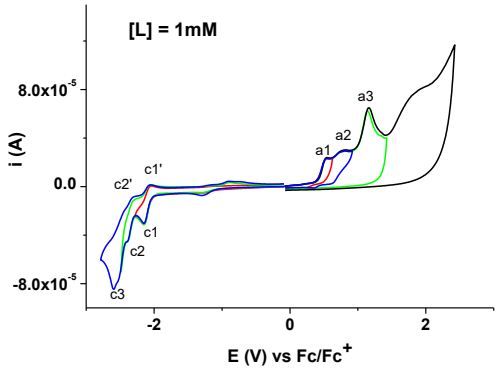


Fig. 4. CV curves (0.1 V/s) on glassy carbon electrode (3 mm diameter) at different scan rates in **L** solutions (1 mM) in 0.1 M TBAP/CH_3CN solution

Table 2

Peak potentials (V) *vs* Fc/Fc^+ and characteristics for CV and DPV curves

Peak	DPV	CV	Process type
a1	0.47	0.51	irreversible
a2	0.67	0.78	irreversible
a3	1.08	1.15	irreversible
c1	-2.09	-2.15	quasi–reversible
c2	-2.35	-2.4	quasi–reversible
c3	-2.48	-2.5	-
c4	-2.55	-2.62	irreversible
c5	-2.84	-2.9	-

RDE anodic and cathodic curves were also recorded at different rotations rates on glassy carbon disk electrode. A comparison with DPV anodic and cathodic curves at different **L** concentrations in 0.1 M TBAP/CH_3CN is given for 0.5 mM solutions of **L** in Fig. 5. RDE currents increase with the scan rate. It can be seen that the anodic waves for a1 and a2 are merged into a single process,

which is not the case for the anodic peaks from DPV curves. After the peak a2 the currents drop suddenly to values close to zero. This drop is characteristic for the electrode coverage with insulating films. Their formation occurs at potentials more positive than a2 potential, in the domain of a3 process. In the cathodic domain, there can be observed two waves which correspond to c1 and c4 peaks from DPV curves. Fig. 6 presents the RDE anodic and cathodic curves at different **L** concentrations (0.5–2 mM) at 1000 rpm and the DPV anodic and cathodic curves at different **L** concentrations. In the anodic domain, a single wave corresponding to a2 (from DPV curves) appeared. RDE anodic currents slightly increase with **L** concentration in the domain of a1 and a2 processes, and at potentials more positive than a2, being not affected at potentials in the domain of a3 process (delimited by two isosbestic points).

The cathodic domain shows three main waves. The first one is connected to c1 DPV peak, the second one to c2 DPV peak, and the third one to c3-c6 peaks.

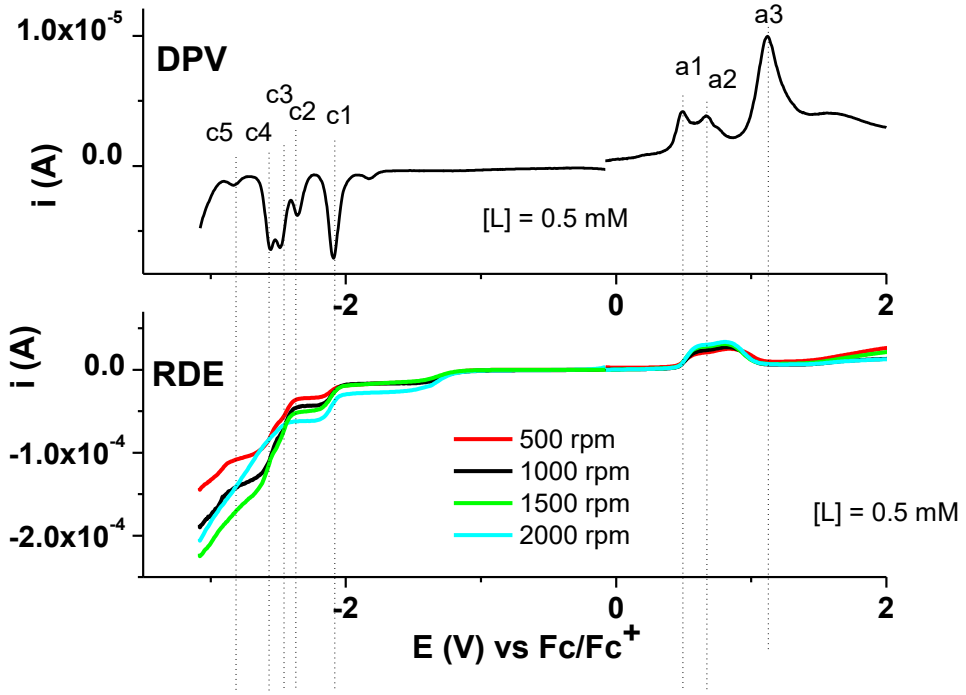


Fig. 5. RDE anodic and cathodic curves at different rotation rates (500–2000 rpm) for **L** solution (0.5 mM) –down, and their corresponding DPV anodic and cathodic curves on glassy carbon electrode (3 mm diameter)

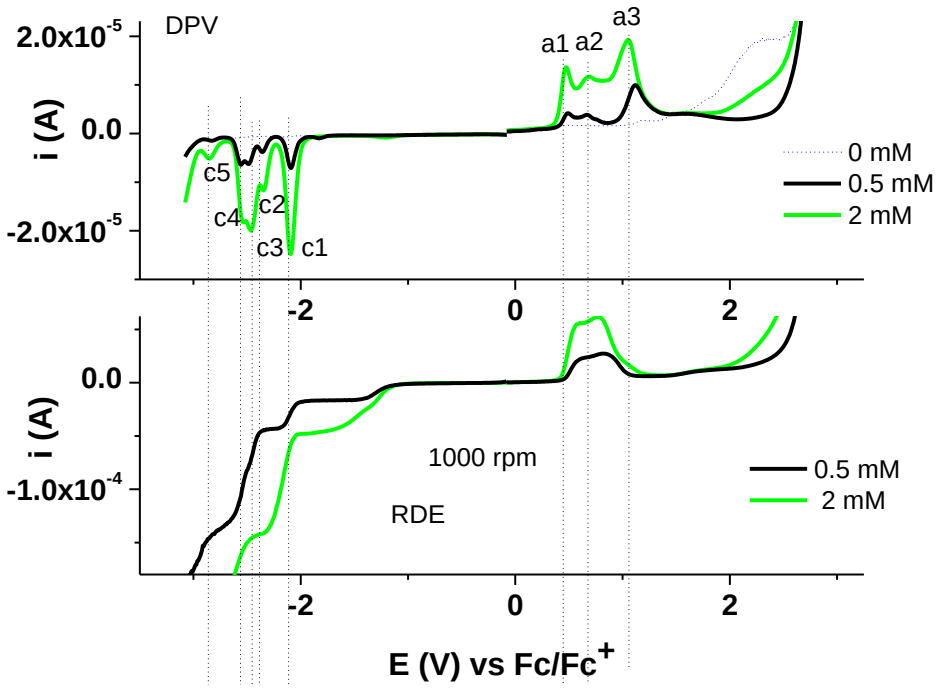


Fig. 6. RDE anodic and cathodic curves (for 1000 rpm) at different concentrations (0.5–2 mM) of **L** in 0.1 M TBAP/CH_3CN and their corresponding DPV anodic and cathodic curves on glassy carbon electrode (3 mm diameter)

3.2. Modified electrodes based on L

Poly**L** modified electrodes were obtained by successive scanning (20 cycles) at different anodic potential limits or by controlled potential electrolysis (CPE) at different potentials or charges in 1 mM solution of **L** in 0.1 M TBAP/CH_3CN. After preparation, the poly**L** modified electrodes were transferred in 1 mM ferrocene solution in 0.1 M TBAP/CH_3CN and their CV curves were recorded.

Fig. 7 presents the CV (0.1 V/s) curves for the preparation of the modified electrodes by scanning to different anodic limits of potential: 0.62 V (a), 0.92 V (b), 1.42 V (c), as well as the CV curves obtained after the transfer of the poly**L** modified electrodes in ferrocene solution (d). From Fig. 7d, it has been observed that as the anodic sweep limit increases, the ferrocene signal is shifted to more positive potentials and lower intensity currents, indicating the formation of an insulating film.

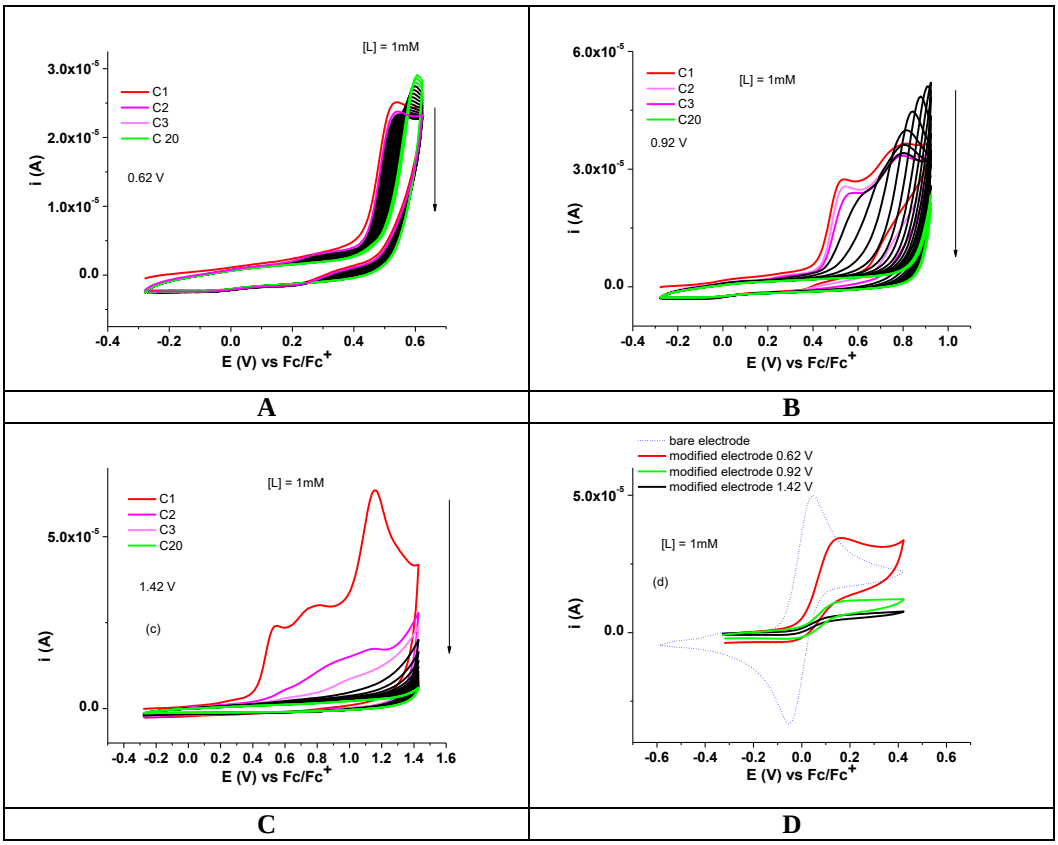


Fig. 7. CV successive curves (0.1 V/s) during the preparation of the modified electrode by 20 cycles in 0.5 mM solution of **L** in 0.1M TBAP, CH_3CN at different potential limits: 0.62 V (a); 0.92 V (b); 1.42 V (c) and CV curves (0.1V/s) recorded in 1mM ferrocene solution in 0.1M TBAP/CH_3CN on bare and on each modified electrode obtained after the 20th cycle (d), respectively.

The preparation of poly**L** modified electrodes has been performed also by controlled potential electrolysis (CPE) at different anodic potentials. The modified electrodes were also transferred in 1 mM ferrocene solution. CV curves recorded in transfer solution for poly**L** modified electrodes are shown in Fig. 8. The curbes (Fig. 8A) correspond to the modified electrodes obtained by CPE 0.62 V using different electropolymerization charges (0.5 mC, 0.8 mC, 1 mC) and to the modified electrodes obtained at different electropolymerization potentials (0.62 V, 0.92 V, 1.42 V) for 1 mC constant charge (Fig. 8B).

From Fig. 8A it can be seen that the ferrocene anodic peak is shifted to more positive values, and the cathodic peak is decreased in intensity when increasing the CPE oxidation charge. This corresponds to an increase of the amount of film deposited during CPE when the charge is increasing. From Fig. 8B it can be observed that as the electrolysis potential increases, at a charge of 1mC,

the modified electrodes obtained by CPE are not so different from the bare electrode. This behaviour is certainly related to the fact that polymerization is rather slow and it takes some time to be achieved. For higher positive potentials in CPE (1.42 V) the time of CPE is quite short, and the film is less formed. Looking to the ferrocene signal, it can be seen that only at 0.62 V the film formation was more efficient. That is why this potential has been chosen for the study of recognition event, as it can be seen further. Also, the charge has been increased to 2 mC in order to get thicker films.

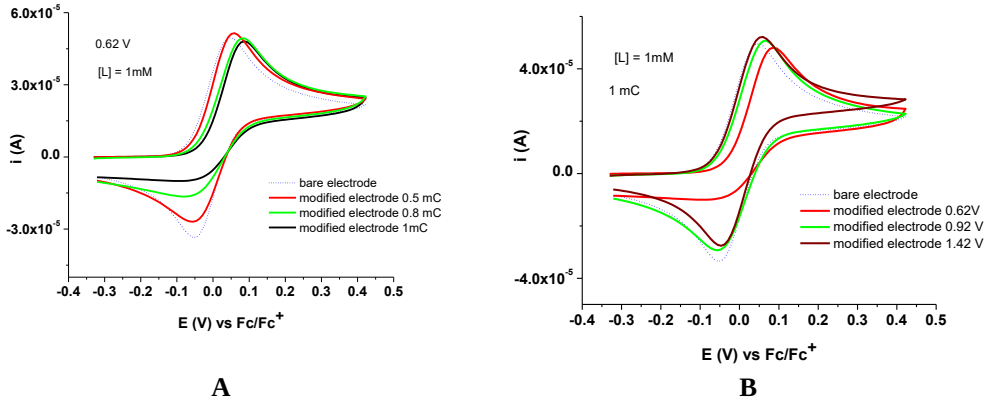


Fig. 8. CV curves (0.1 V/s) of modified electrodes recorded in transfer solution (1 mM ferrocene in 0.1M TBAP, CH_3CN); the modified electrodes were prepared by CPE at 0.62 V using different electropolymerization charges (A) and at different electropolymerization potentials for 1 mC constant charge (B)

3.3. Recognition properties using modified electrodes based polyL

Poly**L** modified electrodes were obtained by CPE at 0.62 V with 2 mC in 1 mM solution of **L** in 0.1 M TBAP/CH_3CN. After preparation, each electrode was cleaned with distilled water and introduced in a three-electrode cell containing 0.1 M acetate buffer, at pH 5.5. For the recognition process, the modified electrodes have been equilibrated by CV between –0.9 V and +0.6 V (15 cycles)) and overoxidized (15 CV cycles between -0.2 V and +2.5 V), then they were introduced in mixtures of heavy metal ions (Cd^{2+}, Pb^{2+}, Hg^{2+} and Cu^{2+} at different concentrations) in distilled water under magnetic stirring for 15 minutes. Then, each electrode was cleaned with distilled water and introduced in a three-electrode cell containing 0.1 M acetate buffer, at pH 5.5. A potential of -1.2 V was applied for 2 minutes, and then a potential scan (0.01 V/s) from -1.2 V to +0.8 V was performed. The resulted DPV curves are shown in Fig. 9. The stripping currents have been measured. Their dependence on cations concentration is given in Fig. 10. Significant stripping peaks have been obtained for all metal ions. Pb

ion presents the best response, followed by for Cu, Hg, Cd ions (with detection limits of about 10^{-8} M, $5x10^{-6}$ M, $5x10^{-6}$ M, $5x10^{-6}$ M, respectively).

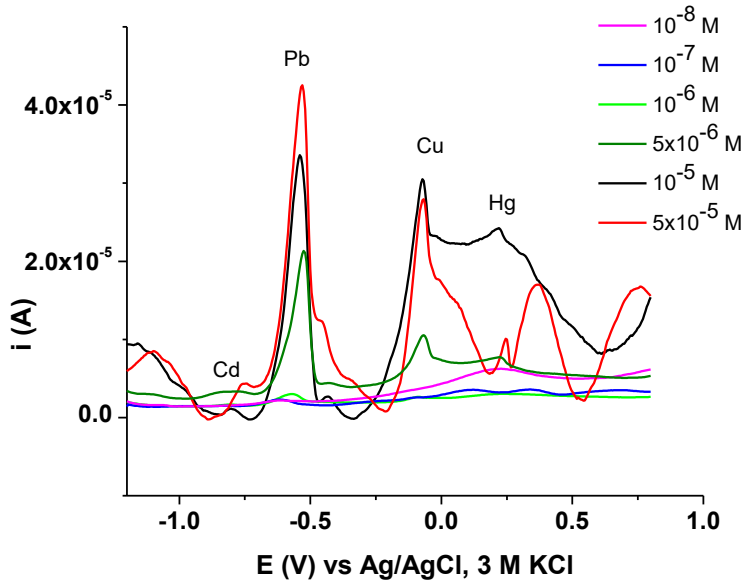


Fig.9. Stripping DPV curves recorded on poly**L** modified electrodes obtained by CPE (0.62 V, 2 mC); accumulation for 15 min in Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+} ions at different concentrations; stripping in acetate buffer at pH 5.5

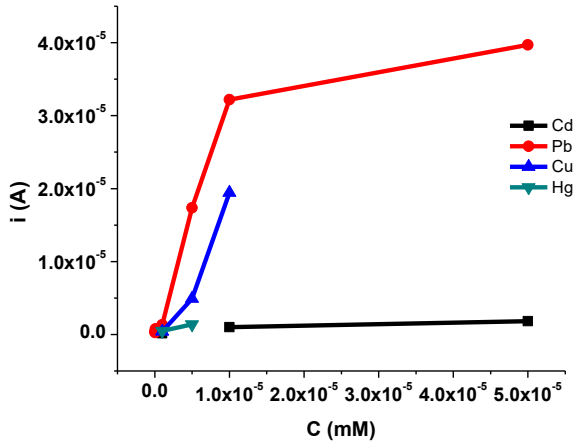


Fig.10. Dependences of the DPV stripping currents on each heavy metal ion concentration

4. Conclusions

2,6-bis((E)-2-(thiophen-2-yl)vinyl)-4-(4,6,8-trimethylazulen-1-yl)pyridine (**L**) was electrochemically characterized using different methods (cyclic voltammetry, differential pulse voltammetry, rotating disk electrode) at different concentrations, scan rates, and scan domains. Poly**L** modified electrodes were obtained by successive scans or by controlled potential electrolysis at anodic potentials using different charges.

The study of heavy metal ions recognition from aqueous solutions using poly**L** modified electrodes led to estimate the detection limits for Cd^{2+}, Pb^{2+}, Hg^{2+} and Cu^{2+} of about 10^{-8} M, $5x10^{-6}$ M, $5x10^{-6}$ M, $5x10^{-6}$ M, respectively.

Acknowledgements

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