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ADVANCED MATERIALS BASED ON 4-(AZULEN-1-YL)-2,6-BIS((E)-2-(THIOPHEN-2-YL)VINYL)PYRIDINE

Alina Giorgiana BROTEA[1], Ovidiu Teodor MATICA[2], Cornelia Elena MUSINA (BORSARU)[3], Eleonora-Mihaela UNGUREANU[4]

*The electrochemical study of 4-(azulen-1-yl)-2,6-bis((e)-2-(thiophen-2-yl) vinyl)pyridine (**L**) was performed on glassy carbon working electrode by using three methods: differential pulse voltammetry (DPV), cyclic voltammetry (CV) and rotating disk electrode voltammetry (RDE). The CV, DPV and RDE curves for **L** were recorded at different concentrations in 0.1M TBAP/ CH_3CN. Polymeric films were formed by electrochemical oxidation. The film formation was proved by recording the CV curves of the chemically modified electrodes (CMEs) in transfer solutions containing ferrocene in 0.1M TBAP/ CH_3CN. The obtained CMEs were used for the detection of heavy metal ions in synthetic samples. The most intense signal was obtained for Pb(II) ion (estimated detection limit of $5 \cdot 10^{-8}$ M), which shows that these CMEs can be used for Pb(II) ion detection in waste waters.*

Keywords: 4-(azulen-1-yl)-2,6-bis((e)-2-(thiophen-2-yl)vinyl)pyridine, cyclic voltammetry, differential pulse voltammetry, rotating disk voltammetry, chemically modified electrodes, heavy metal ions detection

1. Introduction

Functionalized polymer films have aroused much research interest due to their great potential as materials for analytical electrodes [1, 2]. These films are most efficiently produced by the electrochemical polymerization of a monomer with properties suitable for the analysis of the target compound. The structure of the monomer is important because electropolymerization must lead to a stable polymeric compound. Basically, modified electrodes are produced that contain covalently attached functions capable of sensing the target. For example, for

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[1] PhD student, Dept. of Inorganic Chemistry, Physical Chemistry and Electrochemistry, University POLITEHNICA of Bucharest, Romania, e-mail: brotea_alina@yahoo.com

[2] PhD student, Dept. of Inorganic Chemistry, Physical Chemistry and Electrochemistry, University POLITEHNICA of Bucharest, Romania, e-mail: maticaovidiu@yahoo.co.uk

[3] PhD student, Dept. of Inorganic Chemistry, Physical Chemistry and Electrochemistry, University POLITEHNICA of Bucharest, Romania, e-mail: borsaru_cornelia@yahoo.com

[4] Emeritus Professor, Dept. of Inorganic Chemistry, Physical Chemistry and Electrochemistry, University POLITEHNICA of Bucharest, Romania, e-mail: em_ungureanu2000@yahoo.com

heavy metal (HM) analysis, films were obtained by derivatizing films previously coated by electropolymerization using dithiocarbamate- [3] or EDTA-based monomers [4], capable of detecting copper, cadmium, or lead. These can be obtained by chemical processes, such as the derivatization of films previously deposited by electropolymerization on electrodes. The incorporation of complexing fragments into polymeric materials can be achieved alternatively by doping or ion exchange procedures [5]. However, the most effective approach in obtaining chelated modified electrodes is direct electropolymerization of monomers on which complexing fragments are grafted.

Thus, stable functionalized polymer films with controlled dimensions and known concentrations of complexing sites can be produced in a single stage. This simple approach has, however, been rarely applied to the determination of trace metals and only a few examples can be found in the literature [6 - 9].

This work presents the electrochemical study of 4-(azulen-1-yl)-2,6-bis((e)-2-(thiophen-2-yl)vinyl)pyridine (**L**) (Fig. 1) that was performed on glassy carbon working electrode in 0.1 M TBAP/ CH_3CN. Similar compounds with 4,6,8-trimethylazulene instead of azulene were proposed as chelating ligands for heavy metals (HMs) ions. The study of HMs ions recognition from aqueous solutions using modified electrodes led to estimate the detection limits for Cd (II), Pb(II), Hg(II), and Cu(II) of about 10^{-8} M, $5{\cdot}10^{-6}$ M, $5{\cdot}10^{-6}$ M, $5{\cdot}10^{-6}$ M, respectively [10]. Another similar derivative 2,6-bis((E)-2-(thiophen-2-yl)vinyl)-4-(4,6,8-trimethylazulen-1-yl)pyridine was electrochemically characterized and electropolymerized to give modified electrodes. The study of HMs recognition from aqueous solutions using these modified electrodes led to estimate low detection limits for Cd(II), Pb(II), Hg(II), and Cu(II) of about 10^{-8} M, $5{\cdot}10^{-6}$ M, $5{\cdot}10^{-6}$ M, $5{\cdot}10^{-6}$ M, respectively [11]. A comparison with the unsubstituted compound **L** could be useful in the prediction of their complexing properties.

After the electrochemical characterization of **L**, polymeric films were formed by its electrochemical oxidation.

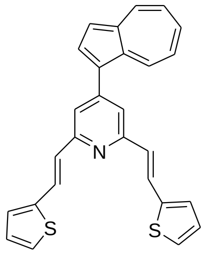

Fig. 1. 4-(azulen-1-yl)-2,6-bis((E)-2-(thiophen-2-yl)vinyl)pyridine (**L**)

The obtained CMEs were used for the detection of HMs ions in synthetic samples. Their detection limits recommend them as advanced materials based on azulene-thiophene-vinyl-pyridines.

2. Experimental Section

L was synthesized according to previously published procedure [12, 13]. Acetonitrile (CH_3CN) and tetrabutylammonium perchlorate (TBAP) from FLUKA were used as received. Mercury (II) acetate (Fluka, ≥98%), cadmium nitrate tetrahydrate (Fluka, ≥98%), copper (II) acetate monohydrate (Fluka, ≥98%) and lead (II) nitrate (Fluka, ≥99.5%) were used as received to prepare the synthetic stock solutions (10^{-3} M) of heavy metal (HM) ions. HM solutions with different concentrations were prepared by successive dilution.

The electrochemical experiments were carried out on PGSTAT302N AUTOLAB potentiostat coupled to a three-compartment cell. The working electrode was a glassy carbon disk (3 mm in diameter, from Metrohm). Before each experiment its surface was polished with diamond paste (0.25 μm) and cleaned with CH_3CN. The reference electrode was Ag/10 mM $AgNO_3$ in 0.1 M TBAP, CH_3CN. At the end of experiments the potentials were referred to the ferrocene/ferricinium redox couple (Fc/Fc^+) potential (+0.07 V). The auxiliary electrode was a platinum wire. The experiments were performed at 25ºC under argon atmosphere.

The cyclic voltammetry (CV) curves were recorded at 0.05 and 0.1 V/s scan rates. The differential pulse voltammetry (DPV) curves were recorded at 0.01V/s with a pulse height of 0.025V and a step time of 0.2 s. The rotating disk electrode voltammetry (RDE) experiments were performed at 0.01 V/s with rotation rates of 1000 rpm. Chemically modified electrodes (CMEs) have been prepared from millimolar solutions of L in 0.1 M TBAP/CH_3CN by scanning or controlled potential electrolysis (CPE). Then, each modified electrode was washed with acetonitrile and introduced in 0.1 M acetate buffer solution (pH = 4.5) where it was equilibrated and overoxidized as previously described [14]. The resulting modified electrodes were immersed for 15 min under stirring in synthetic aqueous solutions containing HM ions (Hg(II), Cd(II), Cu(II) and Pb(II)). After that, the electrodes were taken out and cleaned with deionized water, then immersed in a cell containing 0.1 M acetate buffer solution (pH = 4.5). Here, they were polarized for 3 min at −1.2 V, and then their DPV curves were recorded between −1.2 and +0.6 V.

3. Results and discussion

3.1. Electrochemical Study

The electrochemical behavior of **L** was studied by CV, DPV, and RDE in 0.1 M TBAP, CH_3CN. The oxidation and reduction curves were recorded starting from the equilibrium potential to more positive or negative potentials, respectively. The curves for the supporting electrolyte were also recorded. They are shown with dotted lines in the following Figures.

Study by CV and DPV

The electrochemical characterization of **L** was performed by CV and DPV on glassy carbon electrode in solutions with millimolar concentrations of **L** (Fig. 2), and at different scan domains (Fig. 3). Anodic and cathodic curves were recorded individually, starting from the stationary potential. Their starting points are marked by arrows. To compare the currents values for anodic (a1 – a3) and cathodic (c1 – c2) processes, the cathodic CV currents were shown in absolute values in Fig. 2. The curves for the supporting electrolyte ([**L**] = 0 mM) are shown with dotted lines. Three anodic and two cathodic processes are noticed, denoted in the order in which they appear in the voltammograms. The CV curves are shown in parallel with those obtained by DPV to compare their peak potentials.

Study by RDE

Fig. 4 presents RDE curves on GC electrode for three different concentrations of **L** in 0.1 M TBAP/CH_3CN obtained at 1000 rotation rates having comparison (on top) the DPV curves also shown in Fig. 2.

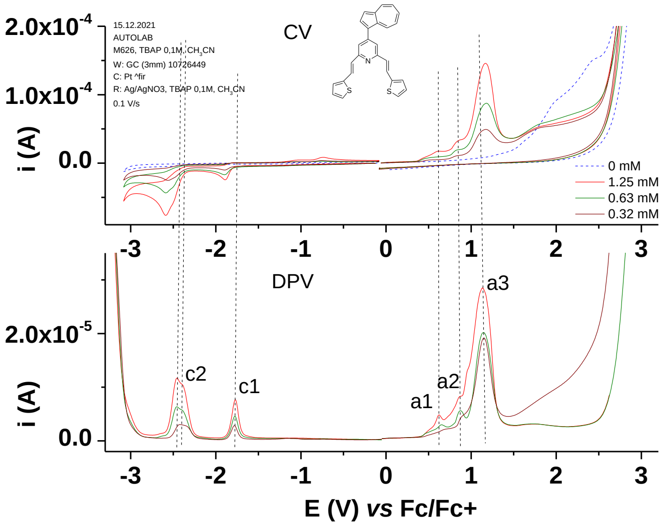

Fig. 2. DPV (0.01 V/s) and CV (0.1 V/s) curves (with currents in absolute values) on glassy carbon for **L** in 0.1 M TBAP/ CH_3CN at different concentrations (mM): 0 (dotted blue line), 1.25 mM (red line), 0.63 mM (wine line), 0.32 mM (olive line)

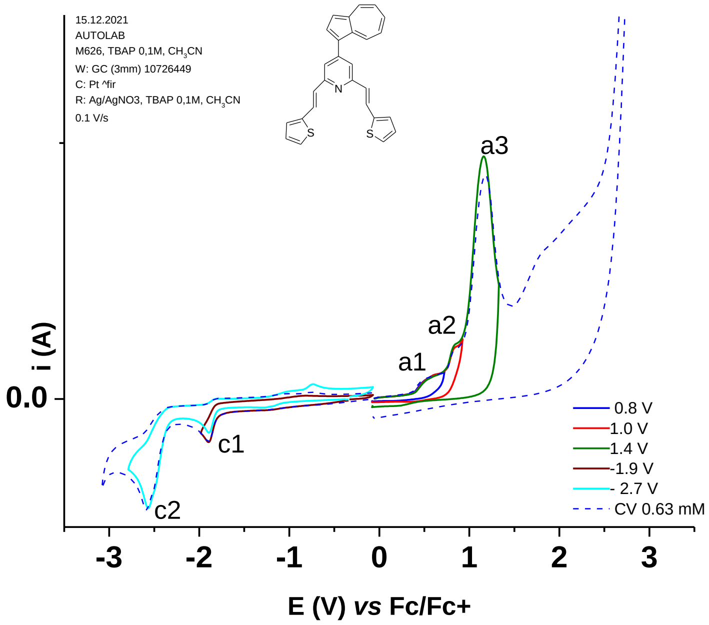

Fig. 3. Anodic and cathodic CV (0.1 V/s) curves for **L** (0.63 mM) in 0.1M TBAP/ CH_3CN on different scan domains

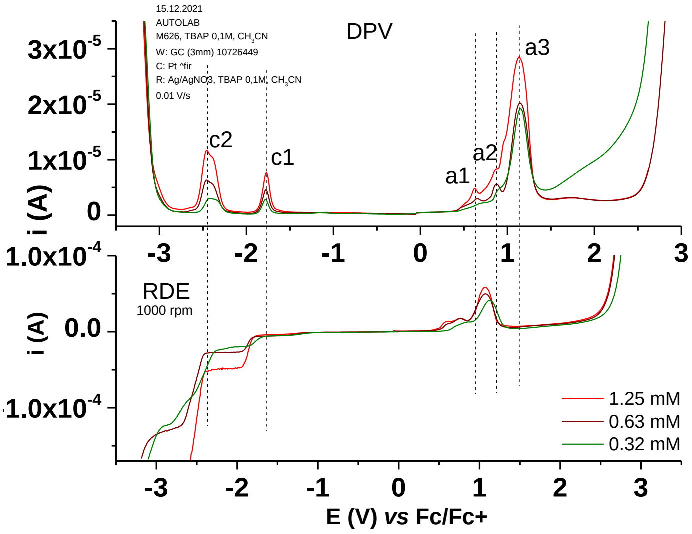

Fig. 4. RDE curves at 1000 rpm and DPV curves on glassy carbon for **L** at different concentrations (mM) in 0.1M TBAP/ CH_3CN;

A normal behaviour of RDE waves, *i.e.*, the increase of limiting current with **L** concentration, for the processes in the cathodic domain (corresponding to the DPV peaks c1 – c2) can be noticed. For c2 the RDE wave for 1.25 mM **L** is superimposed over the discharge of the supporting electrolyte. However, the normal behavior is evident at lower concentration (0.32 and 0.63 mM) of **L**. There is no regular RDE wave for the processes in the anodic domain (corresponding to the DPV peaks a1- a3). The “peak” shape of RDE curves in the anodic scan is certainly due to the formation of films that cover the electrode surface.

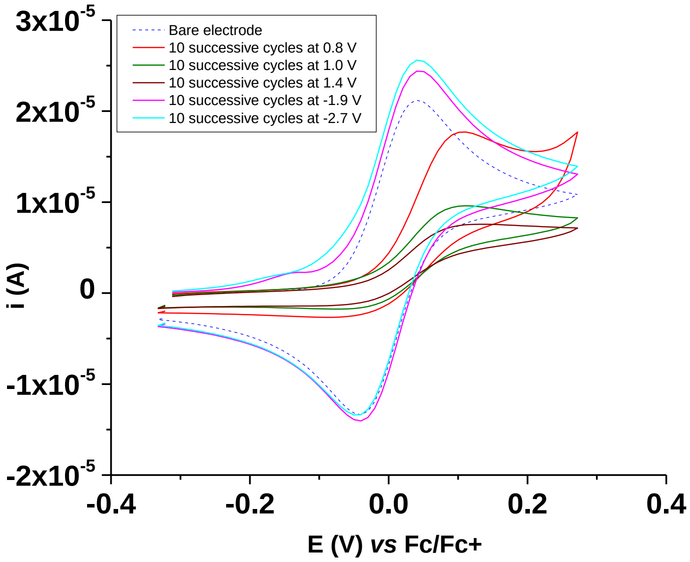

Fig. 5. CV curves (0.1 V/s) of the modified poly**L** electrode recorded in ferrocene solution (1 mM) in 0.1M TBAP/ CH_3CN compared to CV curve recorded on bare electrode. Films were formed by scanning the potential up to different values of switching.

3.2. Evidence of HMs films formation

CMEs prepared from millimolar solutions of L in 0.1 M TBAP/CH_3CN by scanning up to different values of switching or controlled potential electrolysis (CPE) were checked by ferrocene redox probe as previously described [14]. CV curves were recorded after the transfer of the modified CME in ferrocene solution in 0.1M TBAP/ CH_3CN and ferrocene signals were compared to CV curve recorded on bare electrode. Fig. 5 shows that the ferrocene signal is very disturbed when the scanning is done in the range of anodic potentials (to 0.8, 1.0, 1.4 V). The potential of the ferrocene is shifted with 0.063 V to more positive values for CMEs prepared by scanning (up to these anodic potentials) in respect to bare electrode. This indicates the formation of films by cycling at anodic potentials.

Conversely, the potential of the ferrocene is not shifted, and the peaks currents have higher values for CMEs prepared by scanning up to cathodic potentials in respect to bare electrode. This indicates the formation of other type of films by cycling at cathodic potentials than at anodic potentials. We have investigated only the films formed at anodic potentials. In order to perform HMs recognition experiments, the films were obtained not by the method of scanning, but by controlled potential electrolysis (CPE), which ensures the control of the charge used when forming the films, in order to compare the films prepared/conditioned in different ways.

3.3. HMs recognition experiments using polyL films

For HMs ions recognition, **L**-CMEs obtained by CPE in 0.63 mM solution of **L** in 0.1 M TBAP/CH_3CN were tested by the procedure already described [2]. After preparation and careful cleaning with acetonitrile, the modified electrodes were introduced in acetate buffer (0.1 M) at pH 4.5 and cycled for equilibration and overoxidation. After that, they were immersed for 15 minutes in synthetic solutions in water containing a mixture of HM ions under magnetic stirring, then they were introduced in acetate buffer (pH 4.5) and polarized at −1.2 V (3 min), and finally linearly swept in anodic scans using DPV (Fig. 6). The DPV stripping peak currents were recorded for each investigated ion *vs.* HM ion concentration (c) in accumulation solutions. The DPV curves show striping peaks for all investigated ions (Cd at -0.776 V, Pb at -0.546 V, Cu at -0.148 V, Hg at 0.208 V), indicating that these ions have been retained by complexation in the electrogenerated films, ensuring the immobilization of **L** complexing units. The signal for Pb is by far the highest in intensity among the other metals.

Influence of film thickness on HMs DPV response

The peak currents of HMs ions are very different in the DPV curves obtained on **L**-CMEs (Fig. 6). It shows a selective complexation for Pb, which has the highest signal. The peak for Pb(II) is influenced by the film thickness which is conditioned by the electropolymerization charge (Fig. 6). Fig. 7 shows the optimum value for the charge of 0.5 mC. Consequently, the **L**-CMEs have been prepared at this charge for the other experiments.

Influence of HMs concentration on DPV response

L-CMEs have been prepared and tested in different accumulation solutions having HMs concentrations between $5 \cdot 10^{-8}$ M and 10^{-5}M (Fig. 7). Examples of plots for the dependence of peak current vs. HM ion concentration are shown in Fig. 7 for Cd(II) and Pb(II) ions. It seems that a linear correlation can be assumed at these low concentrations of HM ions, and the slope (selectivity) for an imaginary straight line is clearly higher for Pb(II): 1.662 $A \cdot M^{-1}$ (for Pb) > 0.0315 $A \cdot M^{-1}$ (for Cd).The signal for Pb(II) on L-CMEs is visible at $5 \cdot 10^{-8}$ M, but the detection limit could be optimized especially by variation of L-CMEs' electropolymerization potential. The signals for Cd(II) appear only when their concentrations in accumulation solutions overcome 10^{-7} M. These values indicate a high selectivity of L-CMEs with respect to Pb(II) ions vs. Cd(II) ions (Fig. 7).

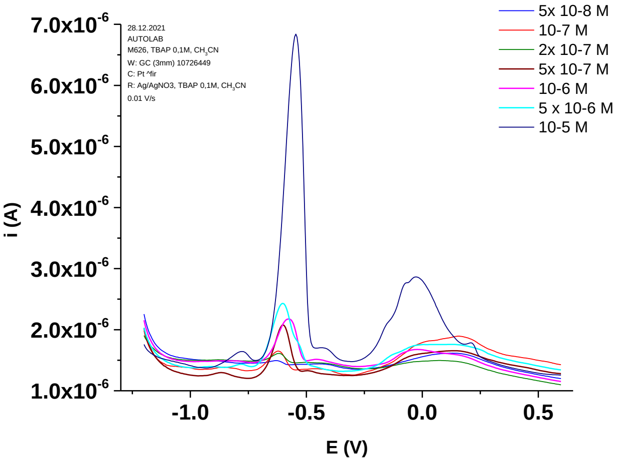

Fig. 6. DPV curves (0.01 V s^{-1}) recorded on poly**L**-modified electrodes for different concentrations (M) of mixed metal at 15 minutes.

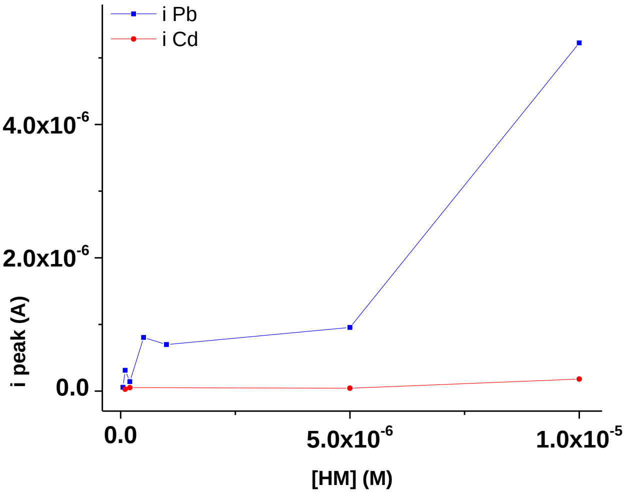

Fig. 7. Dependence of the stripping current from DPV on the metallic ion’s concentration [HM]

4. Conclusions

The electrochemical characterization of 4-(azulen-1-yl)-2,6-bis((E)-2-(thiophen-2-yl)vinyl)pyridine (**L**) was performed by cyclic voltammetry, differential pulse voltammetry and rotating disk electrode methods. The anodic and cathodic processes have been put in evidence, and the conditions for obtaining electrodes modified with **L** have been identified. The films formation on the surface of the electrode was confirmed by the transfer of the modified electrodes in ferrocene solutions, when the CV signals were found attenuated in intensity proportionally to the charge used for electropolymerization and displaced as anodic potential. The cathodic peak of ferrocene did not appear anymore for CMEs potentials .

L-CMEs were tested for analysis of synthetic solutions containing heavy metal ions by the anodic stripping method. The DPV stripping peak currents were recorded for each investigated ion *vs.* HM ion concentration in accumulation solutions. The DPV curves show striping peaks for all investigated ions, but their intensity was higher by far for Pb ion.

Influence of film thickness on HMs DPV response showed a selective complexation for Pb(II). The peaks for Pb(II) increased with the film thickness which is connected to the electropolymerization charge. Influence of HMs concentration on the **L**-CMEs DPV response has been tested in different accumulation solutions having HMs concentrations between $5\cdot10^{-8}$ M and 10^{-5} M. The plot of Pb(II) stripping currents on **L** concentration in accumulation solutions has been found linear at concentrations below $5\cdot10^{-7}$ M, but the estimated detection limit ($5\cdot10^{-8}$ M) can be optimized especially by varying the electropolymerization potential when preparing **L**-CMEs.

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