

New Azulene Modified Electrodes for Heavy Metal Sensing

MARIA DANIELA POP¹, VERONICA ANASTASOAI¹, MARIANA APOSTOIU POPESCU¹, ALEXANDRA OPRISANU¹, ELEONORA MIHAELA UNGUREANU^{1*}, MIHAELA CRISTEA²

¹University Politehnica of Bucharest, 1-7 Gheorghe Polizu, 011061, Bucharest, Romania,

²Institute of Organic Chemistry C. D. Nenitzescu of Romanian Academy, 202B Spl. Independentei, 71141, Bucharest, Romania

The electrochemical characterization of 2,6-bis((E)-2-(furan-2-yl)vinyl)-4-(5-isopropyl-3,8-dimethylazulen-1-yl)pyridine has been performed by cyclic voltammetry, differential pulse voltammetry and rotating disk electrode. Modified electrodes were obtained by cycling the potential in the anodic scans or by controlled potential electrolysis (CPE) at different potentials and charges. The modified electrodes have been tested for mercury, cadmium, copper and lead ions detection.

Keywords: 2,6-bis((E)-2-(furan-2-yl)vinyl)-4-(5-isopropyl-3,8-dimethylazulen-1-yl)pyridine, voltammetric techniques, modified electrodes by electrooxidation, heavy metals detection

Azulenes have a five-member (electron-rich) cyclic moiety connected with a seven-member (electron-poor) cyclic moiety. In terms of electrochemical behavior, azulene derivatives present an irreversible electrooxidation, and a quasi-reversible reduction [1]. Polymeric films generated by electrooxidation can be used to create sensors, as shown in our recent works [2].

Determination of heavy metals from water samples is a very important task especially for application in food chemistry and environmental monitoring, due to their toxicity. This can be performed by using sensors based on azulene derivatives [3, 4], iron oxide/graphene composite [5], bismuth nanoparticle-porous carbon paste [6], zinc oxide graphene composite [7].

Our approach is based on complexing modified electrodes. 2,6-bis((E)-2-(furan-2-yl)vinyl)-4-(5-isopropyl-3,8-dimethylazulen-1-yl)pyridine (**L**) has been synthesized [8] and used to prepare modified electrodes with poly**L** (fig. 1). The investigated compound has been characterized by electrochemical techniques, and the preparation of the modified electrodes has been studied. The heavy metals recognition based on poly**L** modified electrodes has been tested.

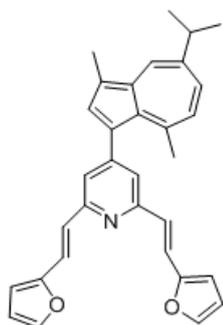


Fig. 1. Structure of **L**

Experimental part

The ligand **L** was synthesized according to the previously published procedure [8]. Electrochemical characterization of the ligand **L** and preparation of modified electrodes were performed in acetonitrile (CH₃CN) containing 0.1 M tetrabutylammonium perchlorate (TBAP), both from Fluka, and used as solvent and supporting electrolyte. Stock solutions (10⁻²M) of Cd(II), Pb(II), Cu(II) and Hg(II) have been freshly prepared before each experiment, using Cd(II) nitrate tetra hydrate, Pb(II) nitrate and Hg(II) acetate (all from Sigma Aldrich) and Cu(II) acetate monohydrate (from Fluka). 0.1 M buffer acetate (pH = 5.5) solution was

prepared from 0.2 M acetic acid solution and 0.2 M sodium acetate solution.

Electrochemical experiments have been performed using PGSTAT 12 AUTOLAB potentiostat connected to a three-electrode cell. The working electrodes were either a glassy carbon disk (with 3 mm diameter) (Metrohm), or poly**L** glassy carbon disk modified electrodes which were explored in characterization and recognition experiments, respectively.

The auxiliary electrode was a platinum wire, while the reference electrode was either Ag/10 mM AgNO₃ in 0.1 M TBAP/CH₃CN (in electrochemical experiments performed in acetonitrile solutions), or Ag/AgCl, 3 M KCl (in electrochemical experiments performed in aqueous solutions). The glassy carbon electrode was polished with diamond (2μm) paste before each experiment and cleaned with the solvent.

Cyclic voltammetry (CV), rotating disk electrode voltammetry (RDE) and differential pulse voltammetry (DPV) methods have been used for electrochemical characterizations. CV curves have usually been recorded at the scan rate of 0.1 V/s. DPV curves have been recorded at 0.01 V/s, with a pulse height of 0.025 V and step time of 0.2 s, while RDE curves were recorded at 0.01 V/s. All experiments have been recorded at 25°C, under argon atmosphere. For the experiments performed in acetonitrile solutions, the potentials were finally referred to the potential of the ferrocene/ferricinium redox couple (Fc/Fc⁺) equal to +0.07 V in our experimental conditions.

Electrochemical experiments for heavy metal ions detection have been performed in 0.1 M buffer acetate (pH = 5.5) solution as supporting electrolyte, at 25°C under argon atmosphere. Heavy metal ion solutions of different concentration (10⁻⁴ M - 10⁻⁷ M) were prepared by successive dilutions from their stock solutions (10⁻² M) in water.

Results and discussions

Electrochemical characterization of **L**

Electrochemical characterization of the azulene derivative **L** has been done by CV, DPV and RDE experiments on glassy carbon electrode. The CV and DPV oxidation and reduction curves have been recorded at different concentrations of **L** (1.4 - 5.4mM) in 0.1 M TBAP/CH₃CN, starting from the stationary potential (fig. 2). DPV curves in figure 2A show three oxidation peaks (a1 - a3) and four reduction peaks (c1 c2, c3 and c4). DPV peak currents for

*email: em_ungureanu2000@yahoo.com; Phone: (+40)724659287

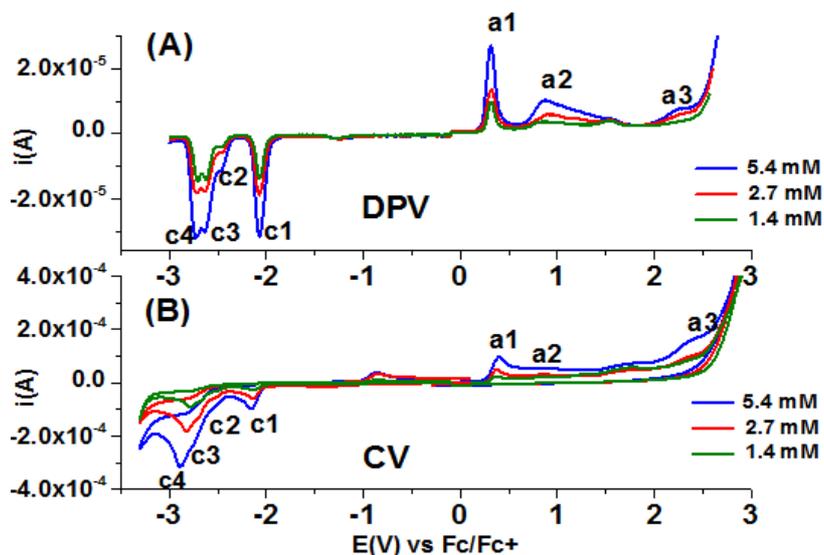


Fig. 2. DPV and CV curves on glassy carbon (3 mm in diameter) for **L** at different concentrations in 0.1 M TBAP, CH₃CN

anodic and cathodic peaks are increasing with the concentration of **L**. CV curves in figure 2B show 3 anodic peaks (a1 – a3) and 3 cathodic peaks (c1, c2, and c3), respecting the notation from DPV curves.

Figure 3A presents the CV curves obtained at different scan rates (0.1 – 1 V/s) within potential domains of the anodic peak a1 and cathodic peak c1 for 2.7 mM solution of **L**. Also, all current values increase with the scan rate.

irreversible, while in the cathodic domain, the peak c1 is reversible, while c2 is quasireversible.

Assigning the peaks appearing in voltammetric curves to specific reactions is difficult in the absence of laborious studies of the electrolysis products obtained at each potential.

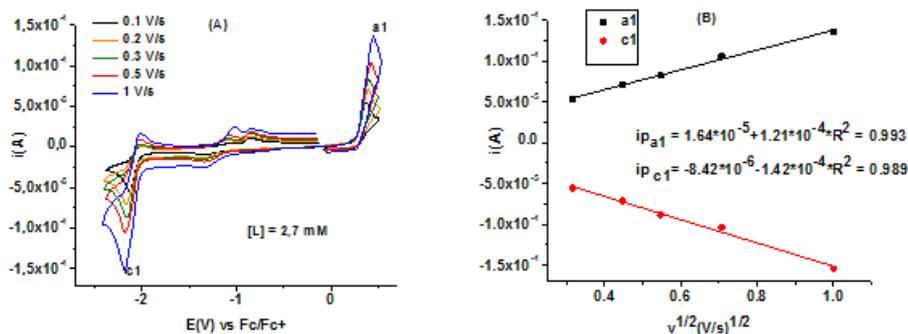


Fig. 3. CV curves at different scan rates of glassy carbon electrode in solution of 2.7 mM **L** in 0.1M TBAP/CH₃CN (A) and linear dependences of a1 and c1 peak currents on the square root of the scan rate (B)

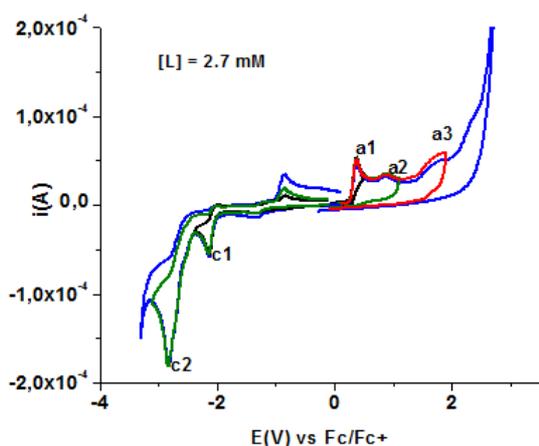


Fig. 4. CV curves at different potential scan domains of glassy carbon electrode for 2.7 mM **L** in 0.1M TBAP/CH₃CN

Linear dependences for the peak currents on the square root of the scan rate are obtained for a1 and c1 (fig.3B).

Figure 4 shows the CV curves (0.1 V/s) obtained on different scan potential domains for 2.7 mM solution of **L**, while Table 1 presents the characteristics of processes and potential values for each peak, all estimated from CV and DPV curves measured for 2.7 mM solution of **L**. It seems that all processes in the anodic domain are

Table 1
PEAK POTENTIALS (V) VS FC/FC⁺ FROM DPV AND CV CURVES FOR **L** (2.7 mM)

Peak	Method	
	CV	DPV
a1	0.374	0.318
a2	-	0.904
a3	2.426	2.277
c1	-2.136	-2.071
c2	-2.540	-2.457
c3	2.717	-2.632
c4	-2.820	-2.721

Figure 5 presents RDE curves on glassy carbon electrode obtained at different rotation rates (500 – 1500 rpm) and the DPV curve for 2.7 mM of **L** in 0.1 M TBAP/CH₃CN. One wave process in the anodic domain (corresponding to the DPV peaks a1, a2) and one wave in the cathodic domain (corresponding to the DPV peak c1) can be observed in figure 5A. They are denoted according to the notation given for the peaks of DPV curve

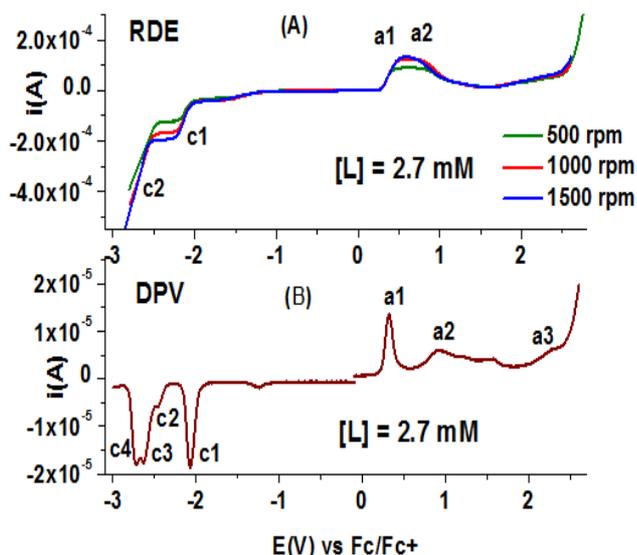


Fig. 5. (A) RDE curves (0.01 V/s) at different rotation rates (500 – 1500 rpm) and (B) DPV curves on glassy carbon electrode for 2.7 mM of **L** in 0.1 M TBAP/CH₃CN.

(shown in fig. 5B). The peculiar shape of RDE curves in the anodic scans is due to the formation of insulating polymer films that covers the electrode surface and leads to drop of the current to the baseline value. The current values from RDE curves increase with the rotation rate, more for the cathodic waves and less for the anodic processes. This behavior is also in agreement with the formation of insulating films in the anodic region of potentials.

Modified electrodes based on poly**L**

Poly**L** modified electrodes have been prepared from 1.4 mM **L** in 0.1 M TBAP/CH₃CN by either successive potential scans, or by controlled potential electrolysis (CPE). The prepared modified electrodes were transferred into a

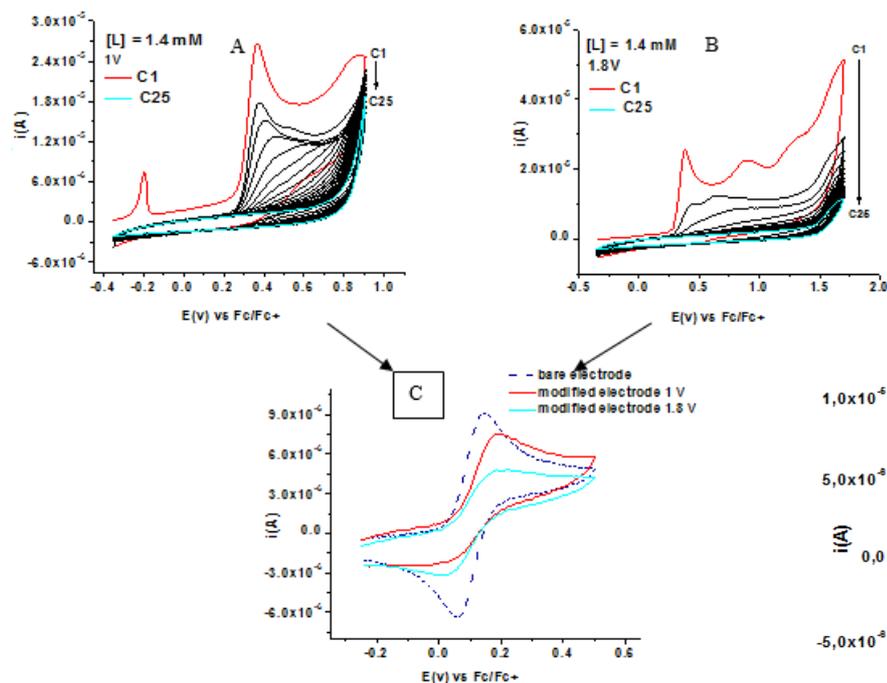


Fig. 6. A. CV curves (0.1 V/s) of poly**L** modified electrodes obtained by successive potential scanning between -0.3V and different anodic limits, +1 V (A) and +1.8 V (B), and the corresponding CV curves (0.1V/s) in 1mM ferrocene solution (C)

ferrocene solution (1 mM) in 0.1M TBAP/CH₃CN. The ferrocene signal in CV curves of modified electrodes has been compared with the ferrocene signal on the bare electrode (fig. 6).

CVs of two poly**L** modified electrodes obtained by 25 successive potential scans performed between -0.3V and the anodic limits of +1V and +1.8V, respectively, are shown in figures 6A and 6B. CV curves of these two modified electrodes in the ferrocene transfer solution are shown in figure 6C. It can be seen that the ferrocene signal is much more distorted for the poly**L** modified electrode prepared with the anodic limit of +1.8V. That is why this anodic limit of potential was chosen to prepare modified electrodes by the potential cycling procedure, because the electrode is better covered with the polymeric film. This fact ensures a bigger amount of complexing units in view of complexation and led to a better detection of heavy metals in our experiments.

The potential of 2.4 V has been selected for poly**L** modified electrodes prepared by CPE (fig. 7). At this potential value, different electropolymerization charges (1 and 6 mC) were used, and the CVs of CPE prepared modified electrodes are compared. The ferrocene signal for the modified electrode obtained at 6 mC is more flattened than at 1 mC (which is close to that of the bare electrode). Since better coverage of the electrode occurs at higher charge, the poly**L** modified electrode obtained at 6 mC was chosen for further recognition experiments.

Heavy metals sensing

For heavy metals recognition, the poly**L** modified electrodes obtained by CPE (2.4 V, 6 mC) from the solution of **L** (1.4 mM) in 0.1M TBAP/CH₃CN have been used. After cleaning with acetonitrile, the modified electrodes were immersed in the transfer solution containing 0.1 M acetate buffer at pH 5.5. After 15 cycles of equilibration (by CV with a the scan rate of 0.1 V/s between -0.9 V and +0.6 V) and

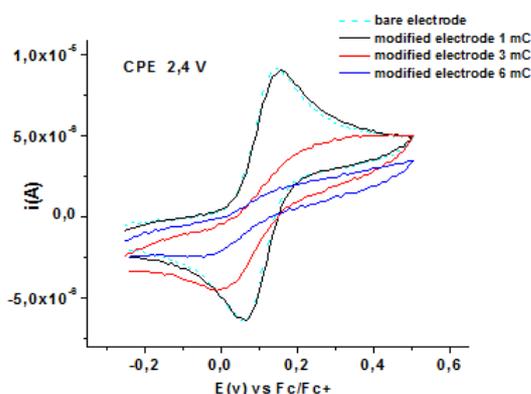


Fig. 7. CV (0.1 V/s) curves of poly**L** modified electrodes prepared by CPE at +2.4 V in 1.4 mM solution of **L** in 0.1 M TBAP/CH₃CN using different electropolymerization charges and measured in 1 mM ferrocene solutions in 0.1M TBAP/CH₃CN

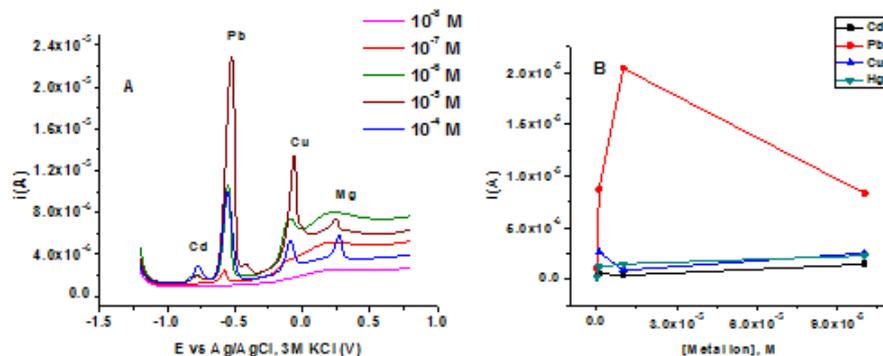


Fig. 8. DPV stripping currents for the polyL modified electrode obtained by CPE (2.4V,6mC) in 1,4 mM solution of L in 0.1M TBAP/CH₃CN, measured at different concentrations of heavy metals in acetate buffer at pH 5.5 (A) and DPV stripping currents in dependence on heavy metals concentration (B)

overoxidation (by CV with a the scan rate of 0.1 V/s between -0.2 V and +2.5 V), the modified electrodes were taken out from the cell, washed with water, and put in solutions containing heavy metals ions of different concentrations, under magnetic stirring for 15 min. Then, the modified electrodes were polarized at -1.2 V, where all cations were reduced, and their DPV stripping currents were recorded between -1.2 V and +0.5 V (fig. 8A). The calibration curves have been obtained for each heavy metal. The dependences of the DPV stripping currents on heavy metals concentration are shown in figure 8, suggesting that the best analytical signals have been obtained for Pb.

Several experiments using the polyL modified electrodes, obtained and conditioned in the same conditions, were performed for Pb²⁺ detection. The results are promising, and the work to evaluate the characteristic parameters of the method is in progress.

Conclusions

2,6-bis((E)-2-(furan-2-yl)vinyl)-4-(5-isopropyl-3,8-dimethylazulen-1-yl)pyridine (**L**) has been studied by electrochemical methods. The study led to the finding of the best potential at which this azulene could be polymerized. PolyL modified electrodes were characterized by cyclic voltammetry in ferrocene solutions. The modified electrodes were used for heavy metals recognition through preconcentration and anodic stripping. The best response has been obtained for Pb (detection limit of 10⁻⁷ M).

Acknowledgments: The authors are grateful for the financial support from: Executive Unit for Financing Education Higher, Research Development and Innovation (UEFISCDI) project ID PN-II-RU-TE-2014-4-0594 contract no. 10/2015, PN-II-PT-PCCA-2013-4-2151 contract no. 236/2014, and Romania-China bilateral project 68BM/2016.

References

1. UNGUREANU, E.-M., RAZUS, A.C., BIRZAN, L., CRETU, M.-S., BUICA, G.-O., Electrochemical study of azo-azulene compounds, *Electrochimica Acta*, vol. **53**, 2008, p. 7089.
2. DIACU, E., BUICA, G.-O., CHILIBON, I., BIRZAN, L., ARNOLD, G.-L., UNGUREANU, E.-M., Chemically Modified Electrodes Based on 5-(Azulen-1-yl)methylene)-2-thioxothiazolidin-4-one, *Journal of Solution Chemistry*, DOI 10.1007/s10953-016-0521-7.
3. BUICA, G.-O., UNGUREANU, E.-M., BIRZAN, L., RAZUS, A.C., MANDOC, L.-R. (POPESCU), Voltammetric sensing of lead and cadmium using poly(4-azulen-1-yl-2,6-bis(2-thienyl)pyridine) complexing films, *Journal of Electroanalytical Chemistry*, vol. **693**, 2013, p. 67.
4. UNGUREANU, E.-M., BUICA, G.-O., RAZUS, A.C., BIRZAN, L., WEISZ, R., BUJDUVEANU, M.-R., *Rev. Chim. (Bucharest)*, **63**, no. 1, 2012, p. 27.
5. LEE, S., OH, J., KIM, D., PIAO, Y., A sensitive electrochemical sensor using an iron oxide/graphene composite for the simultaneous detection of heavy metal ions, *Talanta*, vol. **160**, 2016, p. 528.
6. NIU, P., FERNÁNDEZ-SANCHEZ, C., GICH, M., AYORA, C., ROIG, A., Electroanalytical Assessment of Heavy Metals in Waters with Bismuth Nanoparticle-Porous Carbon Paste Electrodes, *Electrochimica Acta*, vol. **165**, 2015, p. 155.
7. LU, Y.-Y., CHEN, M.-N., GAO, Y.-L., YANG, J.-M., MA, X.-Y., LIU, J.-Y., Preparation of Zinc Oxide Graphene Composite Modified Electrodes for Detection of Trace Pb(II)", *Chinese Journal of Analytical Chemistry*, vol. **43** (9), 2015, p. 1395.
8. BIRZAN, L., CRISTEA, M., DRAGHICI, C. C., TECUCEANU, V., MAGANU, M., HANGANU, A., RAZUS, A. C., BUICA, G. O., UNGUREANU, E. M. *Dyes Pigm.*, **131**, 2016, p. 246.

Manuscript received: 27.02.2017