New Azulene Modified Electrodes for Heavy Metal Sensing

MARIA DANIELA POP1, VERONICA ANASTASOAE2, MARIANA APOSTOIU POPESCU1, ALEXANDRA OPRISANU1, ELEONORA MIHAELA UNGUREANU3*, MIHAELA CRISTEA4

1University Politehnica of Bucharest, 1-7 Gheorghe Polizu, 011061, Bucharest,Romania,
2Institute of Organic Chemistry C. D. Nenitzescu of Romanian Academy, 2028 Spl. Independentei, 71141,Bucharest, Romania
3*email: em_ungureanu2000@yahoo.com; Phone: (+40)724659287
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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 polyL (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 polyL modified electrodes has been tested.

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 (10⁻² M) 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 polyL 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 (10⁻⁶ M – 10⁻³ M) were prepared by successive dilutions from their stock solutions (10⁻¹ 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 – 5.4 mM) 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

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

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 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.
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 polyL

PolyL 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 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 polyL 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 polyL 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 polyL 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 polyL modified electrode obtained at 6 mC was chosen for further recognition experiments.

Heavy metals sensing

For heavy metals recognition, the polyL 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
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).

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