Recognition of Heavy Metal Ions by Using E-5-((5-Isopropyl-3,8-Dimethylazulen-1-yl) Dyazenyl)-1H-Tetrazole Modified Electrodes

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Abstract: Chemically modified electrodes (CMEs) based on polymeric films of E-5-((5-isopropyl-3,8-dimethylazulen-1-yl) diazenyl)-1H-tetrazole (L) deposited on the surface of the glassy carbon electrode have been used for the recognition of heavy metal (Me) ions. The electrochemical study of L was done by three methods: differential pulse voltammetry (DPV), cyclic voltammetry (CV), and rotating disk electrode voltammetry (RDE). The CV, DPV, and RDE studies for L were performed at different concentrations in 0.1 M tetrabutylammonium perchlorate solutions in acetonitrile. The polymeric films were formed by successive cycling or by controlled potential electrolysis (CPE). The film formation was proven by recording the CV curves of the CMEs in ferrocene solution. The CMEs prepared at different charges or potentials were used for detection of heavy metal ions. Synthetic samples of heavy metal ions (Cd(II), Pb(II), Cu(II), Hg(II)) of concentrations between 10⁻⁸ and 10⁻⁴ M were analyzed. The most intense signal was obtained for Pb(II) ion (detection limit of about 10⁻⁸ M). Pb(II) ion can be detected by these CMEs in waters at such concentrations. The ability of the ligand L to form complexes with Pb(II) and Hg(II) ions was also tested by UV-Vis spectrometry. The obtained results showed the formation of Me(II)L₂ complexes.

Keywords: azulene derivative; chemically modified electrodes; voltammetric techniques; complexing polymeric films; UV-Vis spectrometry; heavy metal ions

1. Introduction

Chemically modified electrodes (CMEs) with complexing properties are alternative tools for the recognition of heavy metal ions which can be done by using very sensitive methods such as atomic absorption spectroscopy [1], emission spectroscopy [2], cold vapor atomic fluorescence spectrometry [3] and inductively coupled mass spectrometry [4]. The last techniques require laborious sample preparation and well-controlled experimental conditions being also expensive tools. That is why electrochemical detection, which uses methods such as anodic stripping voltammetry, is a promising answer, its main advantage being the fact that it is a portable method at a low cost. Regarding to toxicity concerns, solid electrodes which can be further modified to increase the selectivity and sensitivity can replace the toxic mercury electrodes usually used for stripping [5]. The CMEs can be prepared by physical absorption of several compounds or by electropolymerization of specific complexing monomers on solid electrodes. For instance, Zhou [6] developed a sensor for the specific detection of Cd(II) and Pb(II) by using amino acids that have cysteine as a functional side chain. The use of graphene oxide nanoparticles led to the increase the electrochemical signal. Complexing CMEs can be obtained by covering the electrode surface with polymer complexing films. The most efficient preparation is the direct electropolymerization of a complexing monomer [7]. This allows for the obtaining of...
a film with a thickness that is easy to control [8] in a single step; the method is generally reliable and reproducible. Different monomers have been used for modification of electrode surfaces to detect heavy metals (pyrrole, thiophene). Compared to them, azulene has special properties, such as an easy polymerization due to its polar character. Its push-pull structure with separate loads on the two cycles (a cyclopentadienyl anion joined with a cycloheptatrienyl cation having 6 π electrons in each ring [9]) allows for the use of azulene derivatives in oxidation and reduction processes. Due to their particular chemistry, such azulene derivatives have been little used in applications such as the electroanalysis of heavy metal ions. However, the CMEs with polymeric azulene derivative films can be used as sensing tools for monitoring the concentrations of different targets, such as heavy metals in wastewater samples [10].

The monomer used to prepare the complexing films in this paper is a tetrazole azulene (Figure 1). Our research led to obtaining new CMEs based on the azulene derivative L (L-CMEs) and testing their ability to complex heavy metals. The electrooxidative polymerization of L was used to cover the electrode surfaces with complexing polymeric films by which the recognition of heavy metal cations (Hg(II), Cu(II), Pb(II), Cd(II)) became possible.

2. Materials and Methods

The synthesis of azulene derivative L shown in Figure 1 was performed according to the described methodology [11]. Tetrabutylammonium perchlorate (TBAP, Fluka, Munich, Germany, analytical purity ≥ 99.0%) and acetonitrile (CH₃CN, Sigma Aldrich, electronic grade 99.999% trace metals) were used as supporting electrolyte and solvent, respectively. 0.1 M acetate buffer solution (pH = 4.5) was prepared from 0.2 M acetic acid solutions (Fluka, Munich, Germany, >99.0%, trace select), 0.2 M sodium acetate (Riedel de Haën, Seelze, Germany), and ultrapure water. Stock solutions of heavy metal salts were prepared by dissolving salts of mercury (II) acetate, cadmium acetate dihydrate (Fluka, Munich, Germany, ≥ 98%), lead (II) acetate trihydrate (Fluka, Munich, Germany, ≥ 98%), and copper (II) acetate monohydrate (Fluka, Munich, Germany, ≥ 98%) in ultrapure water.

For the electrochemical experiments cells with three electrodes were connected to an AUTOLAB potentiostat. For the preparation of CMEs, the working electrode were glassy carbon disks (d = 3 mm, Metrohm, Herisau, Switzerland), the reference electrode was Ag/10 mM AgNO₃, 0.1 M TBAP/CH₃CN, and the counter electrode a Pt wire. The potentials were finally referred to the reversible system ferrocene/ferricenium (Fc/Fc⁺). Before each experiment, the glassy carbon electrode was polished with diamond paste and rinsed with acetonitrile. CV curves were recorded at a scan rate of 0.1 V/s or at different potential scan rates (0.1–1 V/s) when the influence of this parameter was particularly studied. DPV curves were obtained at the scan rate of 0.01 V/s. RDE curves were recorded at 0.01 V/s by using different electrode rotation rates (500, 1000, 1500 rpm). For the recognition experiments using CMEs, the reference electrode was Ag/AgCl and the counter electrode was a Pt wire.

UV-Vis absorption spectra were recorded between 800 and 200 nm on JASCO V-670 spectrophotometer at room temperature, using acetonitrile as solvent.

L-modified electrodes were prepared in solutions of the ligand L in 0.1 M TBAP/CH₃CN. After preparation, each CME was taken out from the monomer solution, equilibrated and tested in 0.1 M acetate buffer solution (pH = 4.5), according to previously described procedure [12,13]. Then, this L-CME was immersed for 15 min under stirring in a solution of heavy metal ions. After that the modified electrode having the accumulated ions was
taken out, cleaned with distilled water and immersed in 0.1 M acetate buffer solution (pH = 4.5), where it was polarized for 3 min to −1.2 V and the stripping curves were recorded between −1.2 V and +0.8 V. The method used for recognition was based on the stripping analysis on L-CME complexing modified electrodes using the DPV technique available in the potentiostat software.

3. Results
3.1. Electrochemical Study of L

Three methods have been used to study the electrochemical behavior of L: DPV, CV and RDE. Figure 2 shows the DPV and CV curves registered at oxidation and reduction for different concentrations of L in the supporting electrolyte (0.1 M TBAP/CH₃CN). The curves at the bottom (A) are the DPV curves, and present 2 main anodic peaks (a1, a2) for L and 3 secondary peaks (a3–a5) which overlap the oxidation domain of the solvent. When scanning in the cathodic direction, 5 DPV cathodic peaks (c1–c5) are noticed, of which the highest (in absolute value) are c1, c2, and c3. The CV curves represented at the top of Figure 2B show two oxidation peaks corresponding to a1 and a2 DPV peaks and a large peak on the potential domain covering a3–a5 DPV peaks. In the cathodic scans in the CV, five peaks are noticed in good agreement with c1–c5 DPV peaks. The anodic and cathodic peak currents in the CV and DPV curves increase with the concentration of L. The other small signals at negative potentials (−1.2 V−−1.4 V) are attributed to the reduction of oxygen traces (secondary process) from residual water (O₂/O₂⁻).

![Figure 2](image)

Figure 2. (A)—DPV (with currents in absolute value) and (B)—CV (0.1 V/s) curves on glassy carbon for L in 0.1 M TBAP/CH₃CN at different concentrations (mM): 0 (dotted blue line), 1 (green line), 2 (red line).

Figure 3A shows CV curves at different scan rates (V s⁻¹) in L solution (1 mM) that tested, the appearance of a cathodic peak c1’ corresponding to the return scan was noticed, attesting to the fact that c1 is a quasi-reversible process. The peak-to-peak separation between c1 and c1’ is about 200 mV, while for ferrocene/ferrocenium reversible couple this value is in the same conditions (without IR compensation, in the same cell) of about 90 mV (see further). That is why the process c1 has been considered as quasi-reversible (Table 1).
of the square root of the scan rate ($v^{1/2}$) has been done for the anodic (a1) and cathodic (c1) peaks. The comparison of potentials of the first cathodic peak of the same oxidation potentials (0.36 V) is higher than that for reduction potentials (0.15 V in absolute value), the first reduction peak for this unsubstituted derivative being at −1.91 V. It means that a1, c2, c5 correspond to irreversible processes, and a2, c1, c3, and c4 to quasi-reversible processes (Table 1).

Figure 3. CV curves on glassy carbon at different scan rates (A); the dependence of current ($i_p$) on the square root of the scan rate for a1 and c1 peaks in L solution (1 mM) in 0.1 M TBAP/CH$_3$CN (B).

Table 1. Values (in V) of anodic (a) and cathodic (c) peak potentials from CV and DPV curves and half-wave potential ($E_{1/2}$) from RDE for L (1 mM), and the associated processes characteristics obtained from the CV curves on different scanning domains and rates.

| Peak  | Method | Process Characteristics |
|-------|--------|-------------------------|
| a1    | CV     | 0.57                    | Irreversible            |
| a2    | CV     | 0.93                    | Quasireversible         |
| c1    | CV     | −1.95                   | −1.867 (500 rpm)        |
|       | DPV    | −1.91                   | −1.888 (1000 rpm)       |
|       | RDE    | −1.906                  | −1.906 (1500 rpm)       |
| C’1   | CV     | −1.70                   | Quasireversible         |
| c2    | CV     | −2.26                   | −2.288 (500 rpm)        |
|       | DPV    | −2.23                   | −2.292 (1000 rpm)       |
|       | RDE    | −2.330                  | −2.330 (1500 rpm)       |
| c3    | CV     | −2.34                   | Quasireversible         |
| c4    | CV     | −2.57                   | Quasireversible         |
| c5    | CV     | −3.11                   | Irreversible            |

In order to check the diffusion control, the plots of the peak current ($i_p$) as a function of the square root of the scan rate ($v^{1/2}$) has been done for the anodic (a1) and cathodic (c1) peaks (Figure 3B). The linear dependency of the peak currents on $v^{1/2}$ can be noticed:

- $i_{pa1} (\mu A) = 1.00 + 60 \cdot v^{1/2}$ ($R^2 = 0.997$); $i_{pc1} (\mu A) = 8.05–95 \cdot v^{1/2}$ ($R^2 = 0.994$). The slope for c1 is almost double compared to that for a1, which indicates a different number of electrons involved in these processes. From the slope of the a1 line vs. $v^{1/2}$ the diffusion coefficient (of about 2.5 × 10$^{-4}$ cm$^2$·s$^{-1}$) for L was calculated using the Randles-Sevcik equation for a three electrons transfer. The value of 3 for the number of electrons involved in the first peak a1 agrees with the mechanism for oxidation and reduction proposed for an azulene derivative [13] with similar structure.

The CV curves for the azulene derivative L in 0.1 M TBAP/CH$_3$CN solution (1 mM) on different scan domains are presented in Figure 4. Based on the shape of the CV peaks in Figures 3 and 4 obtained from the CV curves on different scanning domains and rates, and the peak-to-peak separation for the direct and reverse processes (such as c1 and c1’), it can be appreciated that a1, c2, c5 correspond to irreversible processes, and a2, c1, c3, and c4 to quasi-reversible processes (Table 1).
Figure 4. CV curves (0.1 V s\(^{-1}\)) on glassy carbon at different potential domains for L (1 mM) in 0.1 M TBAP/CH\(_3\)CN.

The values of the peak potentials from the CV and DPV curves measured for L solution (1 mM) are also presented in Table 1. The potential of the first oxidation peak for L is +0.55 V. This value is clearly lower than that obtained for a similar unsubstituted derivative [13], which has the potential of a1 peak at the potential of +0.91 V. It means that L oxidizes much easier. The comparison of potentials of the first cathodic peak of the same derivatives shows that L is reduced more hardly (−1.91 V). The difference between their oxidation potentials (0.36 V) is higher than that for reduction potentials (0.15 V in absolute value), the first reduction peak for this unsubstituted derivative being at −1.76 V [13]. The values obtained for L are explained by the effects of alkyl groups that increase the electron density on azulene nucleus, making the oxidation easier and the reduction harder.

Figure 5 shows the RDE (A) curves at different rotation rates for L at concentration of 1 mM compared to the corresponding anodic and cathodic DPV curves plotted on the top (B). The anodic RDE curves show only one wave corresponding as potential to a1 peak in DPV. The cathodic curves show two clear waves (w1, w2) which correspond to the DPV peaks c1, and c2–c3 (which are situated to very close potentials to be separated through RDE, but they can be distinguished by DPV), respectively. The increase of the rotation rate of the electrode leads to the increase of the limiting currents for the cathodic waves. The anodic RDE wave does not increase with the rotation rate of the electrode. At more positive potentials than that for a2 DPV peak, the current decreases suddenly. The same behavior has been noticed in other cases of azulene derivatives when the electrode was covered with a film. The values of the RDE half-wave potential for the cathodic processes presented in Table 1 agree with the peak potentials obtained through DPV and CV methods.
3.2. Preparation of L-CMEs

The glassy carbon electrodes were modified with polyL films in 1 mM L solution in 0.1 M TBAP/CH$_3$CN by successive cycling of the potential in the anodic domain with different potential limits (0.75 V, 1 V) or by CPE using different charges and potentials (1 mC, 0.75 V/1 V; 2 mC, 1 V). The number of cycles has not been optimized, and 20 cycles were usually used, as shown in Figure 6A. The CMEs were transferred after preparation to a cell containing ferrocene solution (1 mM) in 0.1 M TBAP/CH$_3$CN to record the CV curves and compare them with those on bare electrode (Figure 6A,B). It can be seen that the ferrocene signal for the polyL film on CME prepared by successive cycling or CPE is slightly shifted as anodic and cathodic peak potential, and the peak currents remain practically the same. The ferrocene/ferrocenium system has a peak-to-peak separation of about 100 mV on both CMEs and on bare electrode. This indicates the formation of thin films.

The film formation on L-CME was evidenced by electrochemical experiments (see Figures S1–S7) by CV in the supporting electrolyte (S1) and ferrocene solution in supporting electrolyte (S2). The peaks corresponding to the polymer oxidation and reduction are situated at 0.052 and 0.038 V (S3). However, much more systematic studies and statistical analysis on several sets of electrodes for different film thicknesses are needed.
Supplementary Figure S4 shows the chronoamperograms of films of different thicknesses. Supplementary Figure S5 shows the CV curves by which the electrode is equilibrated, and Supplementary Figure S6 the CV curves by which the film is overoxidized on the electrode. However, there is no expected concordance between the charge used to prepare the film and the peak current heights obtained for different film thicknesses (S7). Supplementary Figure S8 shows the CV curves during the formation of L-CMEs by successive potential scanning (20 cycles) with anodic limit in the potential domain of a1 and a2 processes. As shown in Supplementary Figure S8, the peak current for a2 decreases in successive cycles especially when the potential is scanned in the domain of a2 process. This is a proof of a covering of the electrode with the polymeric film. The transfer in ferrocene solution of the modified electrodes obtained by cycling in the domain of a1 and a2 processes led to the cyclic voltammograms showed in Figure 6. All these studies will be the subject of systematic investigations related to the optimization of the conditions for the preparation and use of future sensors based on chemically modified electrodes with L. The research is in progress.

### 3.3. Recognition of Heavy Metal Ions Using Poly L

For the recognition of heavy metal ions, the L-CME were prepared by CPE in 1 mM L solution in 0.1 M TBAP/CH3CN at a potential of 1 V and using a charge of 1 mC. The used procedure was the same as in the case of other azulene derivatives [13]; after that, the L-CME was introduced in the conditioning cell containing 0.1 M acetate buffer solution (pH 4.5) and was equilibrated (15 CV cycles at 0.1 V s\(^{-1}\) between −0.9 V and +0.6 V) and overoxidized (15 CV cycles at 0.1 V s\(^{-1}\) between −0.2 V and +1.5 V). Afterwards, the L-CME was cleaned with distilled water and introduced into the accumulation solution containing a mixture of heavy metal ions (Cd(II), Pb(II), Hg(II) and Cu(II)) at a given concentration under magnetic stirring for 15 min. Different concentrations of accumulation solutions were tested in this order: 10\(^{-8}\), 10\(^{-7}\), 10\(^{-6}\), 10\(^{-5}\), 10\(^{-4}\) (mol L\(^{-1}\)). After accumulation, the CME complexed with metal ions was rinsed with distilled water and introduced into the analysis cell filled with 0.1 M acetate buffer, pH 4.5, where it was polarized for 3 min at −1.2 V to reduce the accumulated cations. Afterwards, the anodic redissolution curves were recorded between −1.2 V and 0.8 V using DPV (Figure 7).

![Figure 7. DPV curves (0.01 V s\(^{-1}\)) recorded on L-CME for different concentrations (M) of mixed metal ion accumulation solutions.](image)

The recorded DPV curves show peaks for all metal ions in solution (Cd(II), Pb(II), Cu(II), Hg(II)) that occur at about −0.76 V, −0.55 V, −0.10 V and +0.25 V, respectively, vs. Ag/AgCl (Figure 7). The dependence of the DPV peak currents on the concentration of the cations in the accumulation solutions is presented in Figure 8. It can be observed
that the most intense signals were obtained for the Pb(II) ion in solutions of $10^{-8}$ to $10^{-4}$ M concentrations. From the linearity of the points in the graph $i_{\text{peak}} = f (c_{\text{Pb}^{2+}})$ for Pb (Figure 8) in the interval $10^{-8}$–$10^{-5}$ M, it can be concluded that the L-CMEs can be used for the analysis of the Pb (II) ion in waters, even at low concentrations.

![Dependence of the stripping currents from DPV on the metallic ions' concentration.](image)

**Figure 8.** Dependence of the stripping currents from DPV on the metallic ions’ concentration.

### 3.4. UV-Vis Study of Hg(II) and Pb(II) Metal ion Complexation Using L

In order to follow the interaction of L with the metal ions of Pb(II) and Hg(II), the spectrophotometric titration was performed in acetonitrile solutions of L (from $10^{-6}$ M concentration solution). Changes in the spectra were found following the addition of increasing concentrations of Pb(II) and Hg(II) solutions (several µL of metal salts $10^{-3}$ M in water) to 3 mL solution of L in 7 µM CH₃CN. The hypo-, batho- and hypsochromic shifts in respect to the initial spectrum of L (Figures 9A and 10A) represent evidence of the formation of complexes between Me and L. A significant hypsochromic shift of the ligand λₘₐₓ ~ 487.7 nm is observed in the UV-Vis spectra recorded when increasing $[\text{Me(II)}]/[\text{L}]$ ratio.

The calibration curves (Figures 9B and 10B) for the formation of complexes with Hg(II), and Pb(II), respectively, were obtained from the decrease of the absorbance peak at 487.7 nm when the metal concentration increases. The increase in the $[\text{Me(II)}]/[\text{L}]$ molar ratio results initially in a linear decrease in absorbance, followed by a saturation stage (with plateau) in which the ligand was fully complexed with Pb(II) or Hg(II) metal ions. The absorbances are practically constant after the addition of 0.6 equivalents of Pb(II), but decrease slowly (descending plateau) for Hg(II).

![Absorbance vs. wavelength for the UV-Vis study of Hg(II) and Pb(II) metal ion complexation using L.](image)

**Figure 9.** Absorbance vs. wavelength for the UV-Vis study of Hg(II) and Pb(II) metal ion complexation using L.

**Figure 9. Cont.**
Using the method of absorbance variation on the molar ratio \([\text{Me(II)}]/[\text{L}]\) [14], from Figure 11A the probable formula of the complexes formed with Pb(II) and Hg(II) were obtained. Since \([\text{Pb(II)}]/[\text{L}] = 0.53 \approx 1/2\) and \([\text{Hg(II)}]/[\text{L}] = 0.61 \approx 1/2\), it follows that the probable formula of the formed complexes is \(\text{Me(II)L}_2\). The same stoichiometric formula of the complex was obtained using the method of continuous variations (Job) of the absorbance with the molar fraction \(X = [\text{Me(II)}]/([\text{Me(II)}] + [\text{L}])\) of the metal [14] from a series of solutions (Figure 11B), in which \(X\) varied between 0 and 0.75. For both Pb(II)
and Hg(II): \([\text{Me(II)}]/([\text{Me(II)}] + [\text{L}]) = 0.472 \approx 1/2 \rightarrow\) the probable formula of the formed complexes is \([\text{Me(II)}\text{L}^2]\).

Figure 10. (A) UV-Vis titration spectra for \(\text{L}\) (1 mM) with 0–3 equivalents of Pb(II) ions in solution; the black arrows indicate the isosbestic points, the red arrows indicate the direction in which the absorbance values shift with the increase of Pb(II) concentration; (B) Maximum visible peak absorbance vs. \([\text{Pb}] / [\text{L}]\), \([\text{L}] \approx \text{constant}\).

Figure 11. Absorbance vs. \([\text{Me(II)}]/[\text{L}]\) (A) and absorbance vs. \([\text{Me(II)}]/([\text{L}] + [\text{Me(II)}])\) (B) for the visible peak of \(\text{L}\) during the complexations with Pb(II) (blue stars) and Hg(II) (red squares).

4. Conclusions

The electrochemical study of compound E-5-((5-isopropyl-3,8-dimethylazulen-1-yl)diazeneyl)-1H-tetrazole (\(\text{L}\)) in 0.1 M TBAP/CH\(_3\)CN showed that a polymeric film which can complex the heavy metal cations can be obtained through the oxidative polymerization of \(\text{L}\) on a glassy carbon electrode. By recording the CV curves of the ferrocene signal for the CME with poly\(\text{L}\) prepared by CPE or successive cycling, it has been shown that the electrode was covered with a thin insulating film. The recognition of heavy metal ions using L-CME was performed by chemical preconcentration and anodic stripping from aqueous solutions of metal cations (Cd(II), Pb(II), Cu(II), and Hg(II)) with concentrations between \(10^{-8}\) and \(10^{-4}\) M. Pb(II) and Hg(II) ions have shown the best signals. The detection limit was estimated at \(10^{-8}\) M for Pb(II) ion. The UV-Vis absorption spectra of \(\text{L}\) solutions in presence of heavy metal ions confirmed the formation of \([\text{Me(II)}\text{L}^2]\) complexes with Pb(II) and Hg(II). It was shown through voltammetric techniques and UV-Vis spectroscopy that \(\text{L}\) can be used to detect Pb(II) and Hg(II) ions, with these methods being of interest for the analysis of these ions in different water samples.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/sym13040644/s1, Figure S1: CV curves for L-CME in 0.1 M TBAP, CH\(_3\)CN at different scan rates (V/s): 0.01—green; 0.05—red; 0.1—blue; 0.2—magenta; 0.3—navy; 0.5—cyan; 1—olive; L-CME was prepared in 1 mM solution of \(\text{L}\) in 0.1 M TBAP, CH\(_3\)CN by CPE at 1 V, 1 mC. Figure S2. CV curves for L-CME in 1 mM ferrocene in 0.1 M TBAP, CH\(_3\)CN at different scan rates (V/s): 0.01—blue; 0.02—red; 0.025—green; 0.03—wine; 0.05—cyan; 0.1—magenta; 0.2—black; L-CME was prepared in 1 mM solution of \(\text{L}\) in 0.1 M TBAP, CH\(_3\)CN by CPE at 1 V, 1 mC. Figure S3. CV curves (0.05 V/s) for L-CME (red line) and GC (blue dashed line) in 0.1 M TBAP, CH\(_3\)CN; L-CMEs was prepared in 1 mM solution of \(\text{L}\) in 0.1 M TBAP, CH\(_3\)CN by CPE at 1 V, 1 mC. Figure S4. Chronoamperograms during the preparation of L-CMEs in 1 mM solution of \(\text{L}\) in 0.1 M TBAP, CH\(_3\)CN by CPE at 1 V and using different charges: 0.5 (blue short line—electrode E1), 1 (blue longer line—electrode E2),
and 6 (red line—electrode E3). Figure S5. CV curves (0.1 V/s) during the equilibration of the electrode E3, prepared as shown in Figure S4 in 0.1 M acetate buffer solution (pH = 4.5), according to previously described procedure [12,13] giving the electrode E3e. Figure S6. CV curves (0.1 V/s) during the overoxidation in 0.1 M acetate buffer solution (pH = 4.5), according to previously described procedure [12,13] giving the electrode L-CME (E3eo). Figure S7. DPV curves (0.01 V/s) recorded for L-CMEs prepared as in Figure S4 (electrodes E1, E2, E3), equilibrated and overoxidized in 0.1 M acetate buffer solution (pH = 4.5), according to the previously described procedure [12,13], after their immersion in a mixed metal ion accumulation solution of 10^{-5} M concentration (for each cation); L-CMEs were prepared in 1mM solution of L in 0.1 M TBAP, CH$_3$CN by CPE at 1V and using different charges: 0.5 (green line), 1 (blue line), and 6 (red line). Figure S8. CV curves (0.1 V/s) during the formation of L-CMEs by successive potential scanning (20 cycles) with anodic limit in the potential domain of a1 and a2 processes; L-CME 1 mM solution of L in 0.1 M TBAP/CH$_3$CN.

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