

**National University of Science and Technology
POLITEHNICA Bucharest**

Doctoral School of Chemical Engineering and Biotechnologies



SUMMARY OF PhD THESIS

**Electrochemical and spectral studies on organic ligands in view of
heavy metal determination using chemically modified electrodes**

Supervisor:

**Prof. Emeritus Dr.Eng. Eleonora-
Mihaela UNGUREANU**

**PhD Student:
Cornelia Elena Mușină
(married Borșaru)**

**Bucharest
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Keywords: 5-(5-isopropyl-3,8-dimethyl-azulen-1-ylmethylene)-2-thioxo-thiazolidin-4-one; 2-thioxo-5-(4,6,8-trimethyl-azulen-1-ylmethylene)-thiazolidin-4-one; 1,4,6,8-tetrakis((E)-2-(thiophen-2-yl)vinyl)azulene; 2-(azulen-1-yldiazenyl)-5-(thiophen-2-yl)-1,3,4-thiadiazole; chemically modified electrodes; voltametric methods; SEM; AFM; Raman; colorimetric sensors; electrochemical sensors; heavy metal ions.

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I would like to thank to the members of the doctoral thesis guidance committee for their availability and advice during the doctoral internship: Prof. Emeritus Elena DIACU, Prof. Emeritus Olga IULIAN, Associated Prof. Dr. Eng. George-Octavian BUICĂ, Dr. Eng. CS I Amalia ȘTEFANIU, mentioning here also the regretted Prof. Emeritus Teodor VIȘAN from whom I received valuable advice.

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With special gratitude and love, I would like to thank to my family who stood by me, surrounded me with affection and accepted all the sacrifices required by my involvement in the activities related to the preparation and elaboration of this thesis.

Cornelia Elena MUȘINĂ (BORȘARU)

Introduction

The doctoral thesis was developed in the Laboratory of Electrochemical Processes in Organic Solvents (PESO) within the Department of Inorganic Chemistry, Physical Chemistry, and Electrochemistry of the Faculty of Chemical Engineering and Biotechnology, POLITEHNICA National University of Science and Technology Bucharest. The thesis is part of this group's research into new organic compounds from an electrochemical point of view.

The doctoral thesis is written in "article" format and is structured in two main parts. The first part, represented by Chapter 1 entitled PRESENTATION OF THE DOCTORAL THESIS TOPIC, METHODS AND CONCEPTS, presents a literature review on the research topic, the methods and concepts used to describe the ligands studied, as well as the preparation and characterization of chemically modified electrodes with azulene ligands and their analytical applications. The second part of the thesis, entitled Chapter 2. ARTICLES PUBLISHED IN EXTENSO WITH THE MAIN SCIENTIFIC RESULTS OF THE DOCTORAL THESIS, consists of three articles published with the main scientific results of the doctoral thesis. Chapter 2.1 is entitled STUDIES ON THE COMPLEXATION OF AZULENE-RODADINE DERIVATIVES WITH Pb(II) BY UV-Vis. This paper is dedicated to the optical characterization of two related azulene-rhodanines and their interaction with Pb(II) ions in acetonitrile solution. The investigations were carried out by UV-Vis. The main wavelengths for each compound were determined, evaluated, and compared with those for unsubstituted azulene-rhodanine.

Chapter 2.2 is entitled ELECTROCHEMICAL AND OPTICAL EXPERIMENTS AND DFT CALCULATIONS FOR 1,4,6,8-TETRAKIS((E)-2-(THIOPHEN-2-YL)VINYLAZULENE. Due to its conjugated structure, 1,4,6,8-tetrakis((E)-2-(thiophen-2-yl)vinyl)azulene (L) has high potential for nonlinear optics and dyeing. This compound was studied electrochemically using cyclic voltammetry, differential pulse voltammetry, and rotating disk electrode voltammetry in organic electrolytes. The main processes that occurred during the oxidation and reduction scans were highlighted and characterized. Calculations based on density functional theory (DFT) were performed to evaluate the chemical reactivity of this compound. UV-Vis studies of L in acetonitrile were performed to establish the optical parameters in this solvent and its complexing power towards heavy metal (HM) ions.

In Chapter 2.3, entitled POLYMER FILMS OF 2-(AZULENE-1-YLDIAZENYL)-5-(THIOPHENE-2-YL)-1,3,4-THIADIAZOLE: SURFACE CHARACTERIZATION AND ELECTROCHEMICAL DETECTION OF HEAVY METALS, the ligand 2-(azulen-1-yl-diazenyl)-5-(thiophen-2-yl)-1,3,4-thiadiazole (L) is presented as a functional monomer capable of forming stable, redox-active films with high affinity for lead in aqueous solutions.

The general conclusions of the doctoral thesis are presented in Chapter 3, the original contributions in Chapter 4, and the dissemination of the results in Chapter 5. The thesis ends with 79 bibliographical references and totals 102 pages written in single-spaced TNR12 font.

The main results obtained in this thesis are presented below. The figures, tables, and diagrams are numbered in accordance with the numbering in the thesis, to which a number related to the structure of the abstract has been added at the beginning.

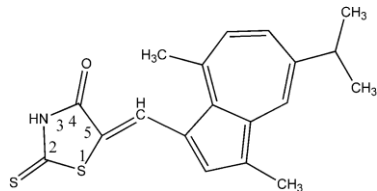
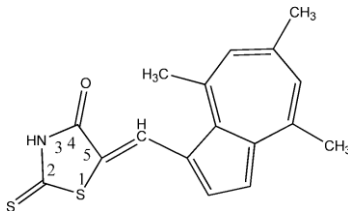
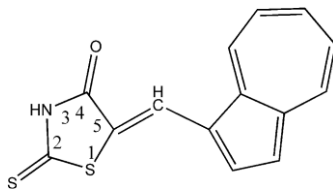
CHAPTER 1. PRESENTATION OF THE DOCTORAL THESIS TOPIC, METHODS, AND CONCEPTS

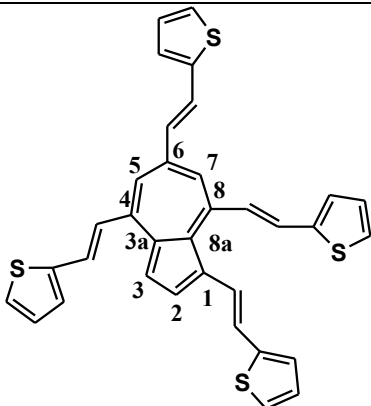
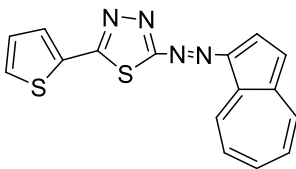
1.1. INVESTIGATED AZULENYL LIGANDS - POTENTIAL APPLICATIONS

The doctoral thesis is part of the preoccupations of the Electrochemical Processes in Organic Solvents (PESO) group from the Department of Inorganic Chemistry, Physical Chemistry and Electrochemistry from the Faculty of Chemical Engineering and Biotechnology of the National University of Science and Technology.

The studies developed during the doctoral internship were mainly related to the evaluation of the electrochemical properties of some azulene ligands synthesized at the “C. D. Nenitescu” Institute of Organic and Supramolecular Chemistry”, Romanian Academy, in Bucharest (CCO). The ligands studied (Table 1.1.1) contain azulene nuclei substituted with fragments with different chromophore groups, which exhibit complexing properties towards heavy metal ions, such as the rhodanine azulene derivatives: (5-(5-isopropyl-3,8-dimethyl-azulen-1-ylmethylene)-2-thioxo-thiazolidin-4-one (**T1**), 2-thioxo-5-(4,6,8-trimethyl-azulen-1-ylmethylene)-thiazolidin-4-one (**T2**), (Z)-(azulen-1-ylmethylene)-2-thioxo-thiazolidin-4-one (**T3**), the vinyl-thiophen derivative 1,4,6,8-tetrakis((e)-2-(thiophen-2-yl)vinyl)azulene (**L2064**), and the thiadiazol 2-(azulen-1-yl-diazenyl)-5-(thiophen-2-yl)-1,3,4-thiadiazole (**L2548**).

Table 1.1.1. Ligand structures studied in the articles in the thesis.

		
(T1)	(T2)	(T3)

	
(L2064)	(L2548)

Due to their dipole structure ($\mu = 1.08$ D)[1,2], azulene (Figure 1), a nonalternant bicyclic aromatic hydrocarbon, formed by the condensation of an electron-deficient seven-membered ring (tropylium cation) with an electron rich five-membered ring (cyclopentadienyl anion), is a structural block for obtaining of push-pull systems with advanced optoelectronic properties [3–5].

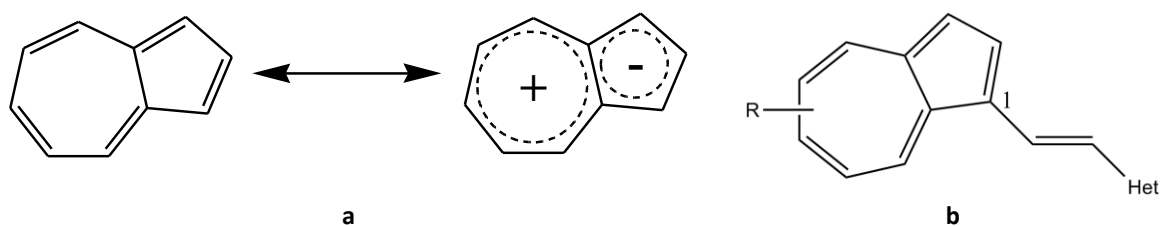


Figure 1. The dipole structure of azulene (a); general structure of 1-vinylazulenes with an azulen-1-yl moiety as EDG, and a heteroaryl as EWG (b).

Because azulene exhibits a good electron-donating capability [6], a series of push-pull compounds from the class of 1-vinylazulenes with the general structure shown in Figure 2, containing the azulen-1-yl moiety as electron-donating group (EDG) or linked via a C=C bond to a heteroaryl electron-withdrawing group (EWG) have been reported in the literature [7–15].

Rhodanine ring which is one of the substituents of rhodanine in thioxo-thiazolidin-4-onele studiate (**T1** -**T3**) is known for its complexing properties towards heavy metals [16]. Rhodanine derivatives are used also in the medical field, as antimicrobial [17,18], antiviral [19], anti-cancer [20,21], antibacterial [22,23], pan-assay interference compounds (PAINS) [24,25] or with anti-diabetic activity [26], in the detection of Alzheimer's markers [27], and they are materials with applications in biomedicine [28]. New materials have been developed with applications in the production of supercapacitors [29], and for the protection of various surfaces [30–32] and for the manufacture of photovoltaic cells [33,34].

In this thesis several optical properties are studied for two rhodanine-linked azulene structures having different alkyl groups (methyl = Me, i-propyl = i-Pr) as substituents and binding positions on the two azulene rings: 5-(5-isopropyl-3,8-dimethyl-azulen-1-ylmethylene)-2-thioxo-thiazolidin-4-one (**T1**) and 2-thioxo-5-(4,6,8-trimethyl-azulen-1-ylmethylene)-thiazolidin-4-one (**T2**). They were compared with the unsubstituted compound, (Z)-5-(azulen-1-ylmethylene)-2-thioxo-thiazolidin-4-one (**T3**) previously studied [35]. Their proprieties, such as dipole moment (in D), were calculated by DFT methods, which varied in the order **T1**>**T2**>**T3** (9.04>8.84>7.83, respectively, using the B3LYP functional) [16].

The organic push-pull systems derived from 1-vinylazulenes class exhibit high hyperpolarizability and the investigation of them is of great research interest in the electrochemistry application field, due to their valuable technical properties. According to literature data, these azulene derivatives can be used as non-linear optical (NLO) systems or as building blocks for other molecules with potential technical applications [3,15,36,37]. In the field of electrochemistry, 1-vinylazulenes exhibit interesting electrochemical properties, being able to be used as modified electrodes with complexing properties [12,37,38] and as electrochemical sensors for the detection of heavy metal ions in water [38–40].

In continuation of our concern regarding the obtaining, through electrochemical polymerization, of new modified electrodes for the detection of heavy metal ions and contaminants (Cd^{2+} , Cu^{2+} , Co^{2+} , Ni^{2+} , Pb^{2+} , Hg^{2+} , Cr^{3+}) in water at very low concentrations, several azulene monomers based on thiophenvinyl azulene have been tested and reported in our previous papers [39–41].

The ligand (L2064), namely 1,4,6,8-tetrakis((E)-2-(thiophen-2-yl)vinyl)azulene (Figure 1) is an azulene derivative substituted with (thiophen-2-yl)vinyl moieties. Like other azulene derivatives studied in our group it can have potential nonlinear optical responses and staining properties [42], due to the presence in its molecule of an azulene moiety and of 3 thienyl groups connected by 4 conjugated vinyl bonds. Both thienyl [41] and azulene [11] groups could polymerize leading to films.

The contamination of environmental matrices with heavy metals such as lead (Pb(II)), cadmium (Cd(II)), mercury (Hg(II)), and copper (Cu(II)) has become a major public health and ecological concern due to their toxicity, persistence, and bioaccumulation [43]. These metals can interfere with biological processes even at low concentrations, necessitating the development of analytical tools that are not only sensitive and selective but also capable of functioning in situ, especially in complex or turbid samples [44–46]. Compared to traditional spectroscopic or chromatographic techniques, electrochemical sensors offer numerous advantages, including low cost, portability, rapid response, and minimal sample preparation [47–49].

Chemically modified electrodes (CMEs) have attracted considerable attention due to their capacity to be molecularly engineered for targeted detection. Incorporation of electron-rich or electron-deficient ligands into sensor surfaces enhances selectivity and signal response for specific analytes [49]. Among these, 1,3,4-thiadiazole derivatives have emerged as efficient chelating ligands for soft heavy metal ions such as Pb(II) and Cd(II), owing to the presence of sulphur and nitrogen donor atoms in their structure [48–50]. These hetero-cycles have been successfully employed in voltammetric platforms for metal-ion sensing, especially when integrated into nanostructured films or polymers.

A particularly relevant compound, 2-(azulen-1-yl-diazenyl)-5-phenyl-1,3,4-thiadiazole (**T**), has been previously shown to electropolymerize under controlled potential electrolysis, forming films with increased conductivity and up to sixfold greater electroactive surface area [57]. However, the monomeric structure of **T** lacks the tunability required to optimize film conductivity, redox activity, and metal-ion specificity simultaneously.

To address these limitations, in this thesis was tested a novel hybrid monomer, 2-(azulen-1-yl-diazenyl)-5-(thiophen-2-yl)-1,3,4-thiadiazole (**L**) with structure the shown in Figure 1, that combines (i) a thiophene group to improve charge transport, (ii) a thiadiazol moiety for metal binding, and (iii) an azulene core to support redox-active electropolymerization. While some analogues such as **T** have been investigated, this is the first study on the electropolymerization, poly**L** film formation, and analytical application of poly**L** in heavy metal sensing.

1.2. PHYSICAL-CHEMICAL METHODS USED FOR CHARACTERIZATION OF INVESTIGATED LIGANDS

The ligands used in this thesis were synthesized according to previously published methods. For instance, 1,4,6,8-tetrakis((E)-2-(thiophen-2-yl)vinyl)azulene (**L2064**), was synthesized by the sequence Vilsmeier - Wittig reactions, according to the previously published procedure [13]. The main characteristics of each ligand were carefully checked by elemental analysis, UV-Vis spectra, ¹H-NMR spectra, ¹³C-NMR spectra, IR spectra, and MS spectra in the appropriate solvents and conditions.

1.2.1. Electrochemical methods for ligands investigation

The electrochemical methods for the investigation of organic ligands in this thesis were cyclic voltammetry (CV), differential pulse voltammetry (DPV) and voltammetry with rotating disk electrode (RDE).

Chemically modified electrodes (CMEs) were prepared either by controlled potential electrolysis (CPE) or scanning the potential (using CV). CPE was achieved by chronoamperometry. Cyclic voltammetry was used also for their characterization.

Electrochemical experiments were performed on Autolab PGSTAT302N potentiostat connected to three-electrode electrochemical cells. For electrochemical characterization and preparation of CMEs, the working electrode (WE) was a glassy carbon (GC) disk (Metrohm, Herisau, Switzerland) with a diameter of 3 mm, the counter electrode (CE) was a platinum wire, and the reference electrode (RE) was Ag/10 mM AgNO₃, 0.1 M TBAP/CH₃CN. All potentials were reported to the ferrocene/ferrocenium redox couple potential (Fc/Fc⁺) at the end of each experiment. For the electrochemical analysis of HMs ions in aqueous solutions using CMEs a three-electrode cell (transfer cell) was used, in which the WE was a GC disk modified with **L** films, the reference electrode was Ag/AgCl, 3 M KCl, and the auxiliary electrode was a platinum wire. Electrochemical experiments for the characterization of the ligands were carried out in a controlled argon atmosphere.

The electrooxidation and electroreduction curves were recorded on glassy carbon (GC) electrode in millimolar solutions of each ligand in organic solvents such as ACN or mixtures 2:1 (in volumes) of ACN and DMF (ACN-DMF) using tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. The background was initially recorded separately on the freshly cleaned GC electrode in the supporting electrolyte. The ligand was then added to the electrochemical cell, and the curves were recorded in its solutions in anodic or/and cathodic scan. Then the electrode was polished again on electrochemical velvet with diamond paste, clean with the solvent and dried, and the curves were recorded again in its solutions in cathodic or/and anodic scan. CV), DPV and RDE methods were used for testing various solutions of each ligand in millimolar concentrations, and in different conditions according to the applied method. The CV curves were recorded at scan rates between 0.05 and 0.5 V/s. DPV curves were obtained with a pulse height

of 0.025 V and a time step of 0.2 s at 0.01 V/s. RDE curves were recorded with the electrode rotation rates from 500 to 1500 rpm at 0.01 V/s.

The chemically modified electrodes based on the ligand **L** (L-CME) were prepared from millimolar solutions of **L** in 0.1 M TBAP in ACN or DMF by potential sweep or controlled potential electrolysis (CPE). The GC electrode was inserted into the preparation cell containing **L** solution in the supporting electrolyte and was biased to a defined potential which was maintained until a defined electrical charge was reached. The resulting CME was removed from the preparation solution, blotted with fine paper and rinsed with CH₃CN. It was then introduced and conditioned in the transfer cell (containing 0.1 M acetate buffer solution, pH = 4.5), equilibrated (15 CV cycles at 0.1 V/s between -0.89 V and 0.6 V) and superoxidized (15 CV cycles at 0.1 V/s between -0.19 V and 1.85 V). Then, the conditioned CME was introduced into the HMs mixture containing 5.10⁻⁵ M of each cation (Cd²⁺, Pb²⁺, Cu²⁺, and Hg²⁺) in deionized water under controlled stirring. After 15 min, the electrode was removed and placed in 0.1 M acetate buffer solution (pH = 4.5) and held for 3 min at -1 V, then a DPV scan (0.01 V/s) from -1 V to 0.6 V was initiated. The resulting DPV curve was recorded and the current for each peak was measured relative to baseline. This procedure was applied for each studied ligand.

The UV-Vis studies were performed on a JASCO V-670 spectrometer in 1 cm optical path quartz cuvettes. For each ligand study, the spectra of different concentrations of ligand in acetonitrile were recorded vs. acetonitrile. For the study of HM ions complexation, the HM ions were added from the stock solutions as aliquots in demineralized water in the cuvette containing the ligand solved in acetonitrile under stirring. The spectra recorded after 1, 5, 10, 15 minutes were recorded to see the stability. The spectra after a time of 1 minute were finally kept and compared for all solutions. The determination of the complexation ratio was done by the method of continuous variations (Job) [26, 27] and Mollard method [28].

All experiments were conducted at 25°C.

Density functional theory (DFT) investigation was conducted using the B3LYP/6-31(d,p) method to determine reactivity-related properties for the ligands at the equilibrium geometry, in the ground state. For property computations, it was used Spartan Software (Wavefunction Inc.) using B3LYP/6-31(d,p) methodology, like in previous studies on different azulene derivative structures [24, 25].



Fig. 1.2. AUTOLAB 302N potentiostat (a) and NOVA interface (a) used for conducting electrochemical experiments

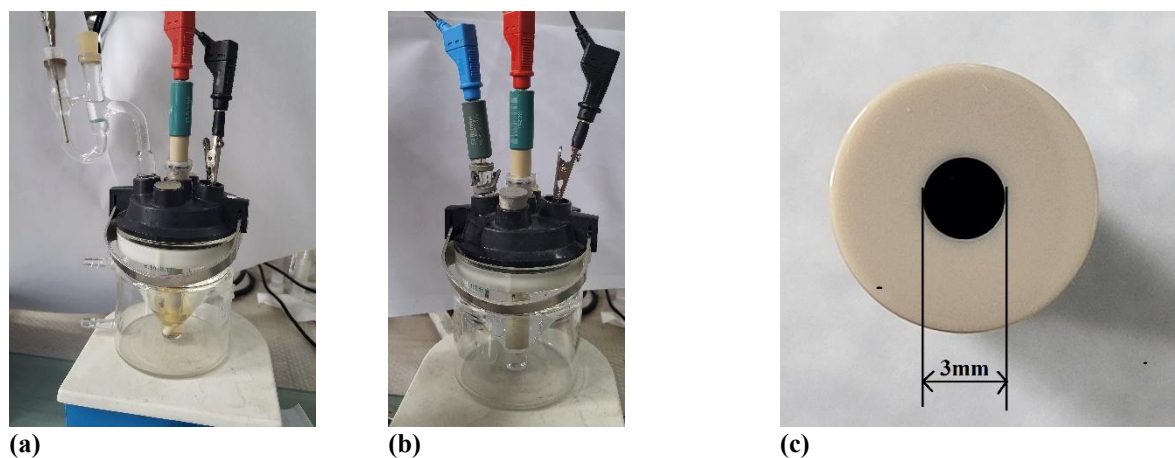
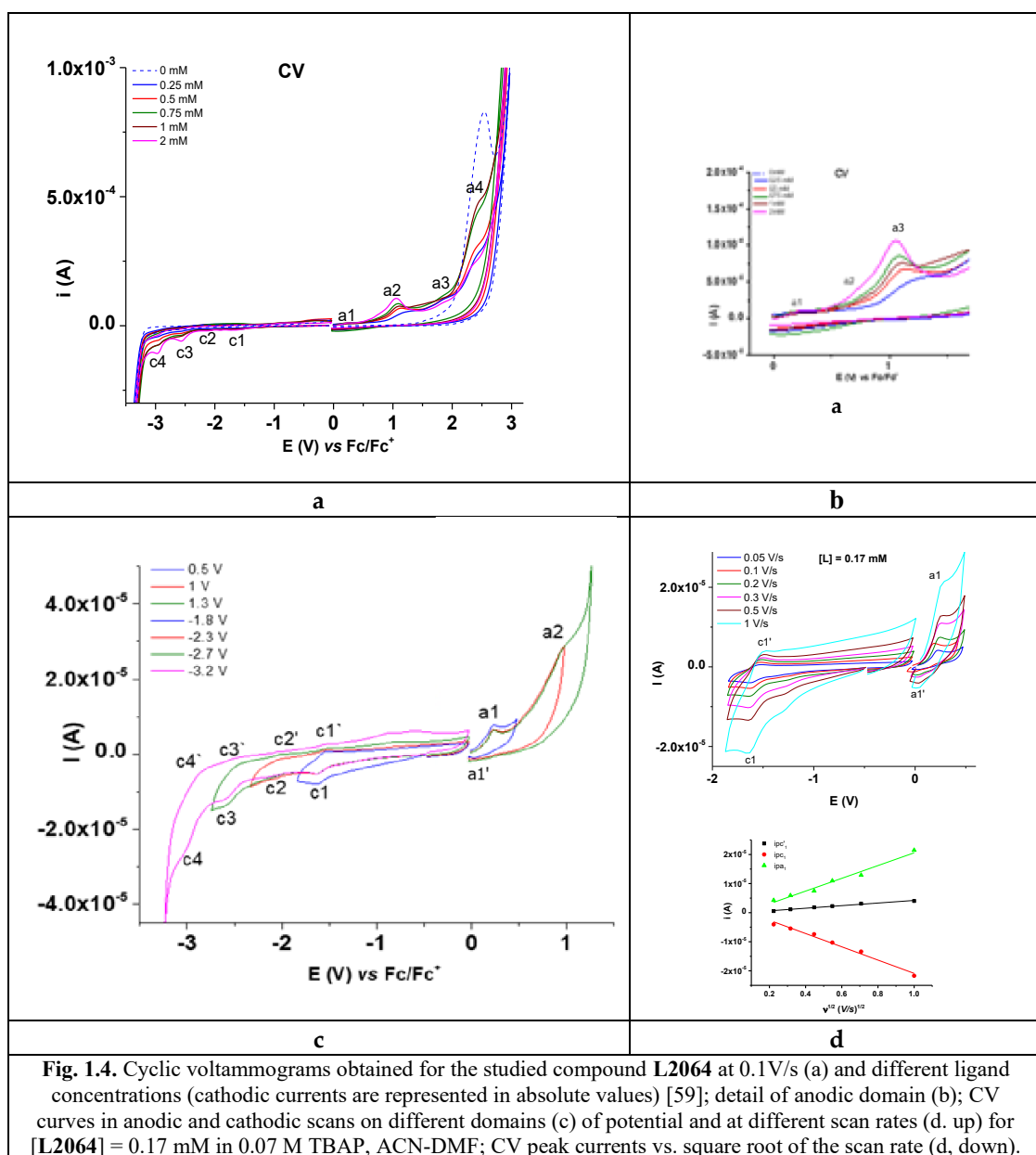


Fig. 1.3. The electrochemical cells used to carry out the electrochemical experiments for organic medium (a), for aqueous medium (b) and a detail of the GC electrode used (c).

1.2.1.1. Cyclic voltammetry (CV) investigations

One of the most used electrochemical techniques was CV, due to its simplicity and ease of measurement. With the help of this technique, we can form a perspective on the reactions that take place near the active surface of the electrode, as well as the reactivity of the electrochemically active species. Therefore, CV is used to study and understand the electrochemical processes of frontier systems, reaction monitoring and electrode characterization [60].

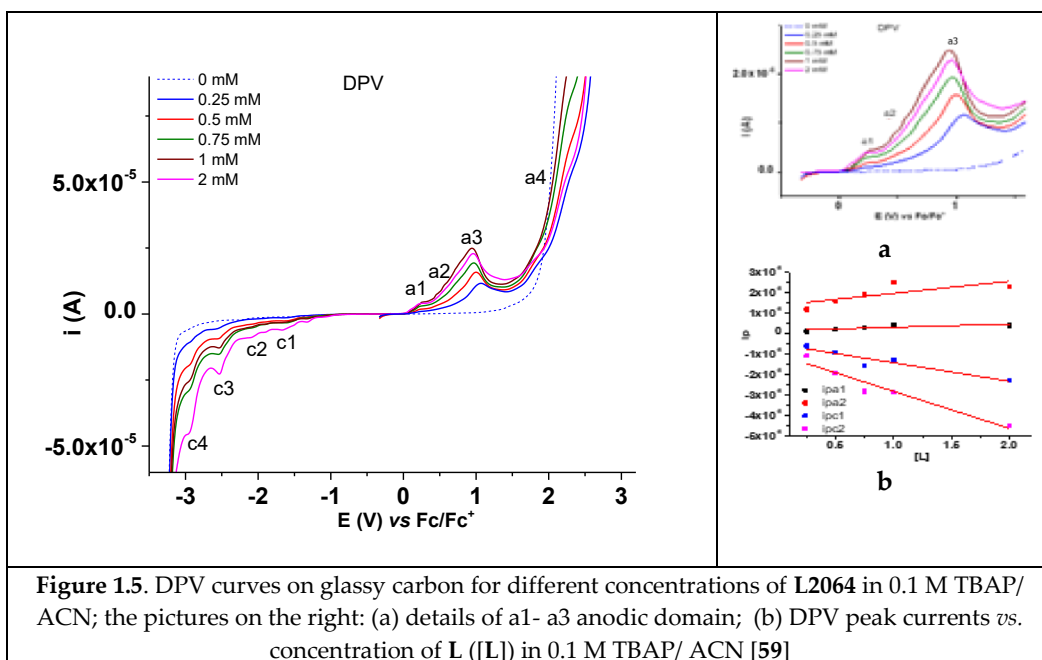
The characterization of the ligands by cyclic voltammetry (CV) was carried out in repeated experiments at different scan rates, on different potential domains using variable concentrations of ligand solutions in $\text{CH}_3\text{CN} + 0.1 \text{ M TBAP}$. The voltammograms were recorded on glassy carbon (GC) electrode, freshly clean and polished on electrode velvet, initially in the supporting electrolyte, and then in the ligand solution. They were conducted starting from the stationary potential towards positive potentials for the evidence of oxidation (anodic) processes (denoted in the order of their apparition a1, a2, a3, a4), and back to the negative potentials, to see if the processes evidenced in the direct scan have responses on the reverse scan. If they have such correspondent processes, they are denoted with the same name, but with ' (in the order of their apparition a1'). After cleaning the electrode, the GC electrode was polarized towards negative potentials for the characterization of reduction processes (cathodic), denoted in the order of their apparition c1, c2, c3, c4), and back again to put in evidence the corresponding processes (denoted c1', c2', c3', c4'). If it was not specified otherwise, the scan rate was 0.1 V/s as in Figure 1.4 in which the voltammograms obtained for one of the studied compounds, for different ligand concentrations are presented [59, 61-67].



1.2.1.2. Differential pulse voltammetry (DPV) investigations

DPV is a pulsed technique that is designed to minimize background currents. The waveform in DPV is a sequence of pulses in which a baseline potential is held for a specified period before a potential pulse is applied [68].

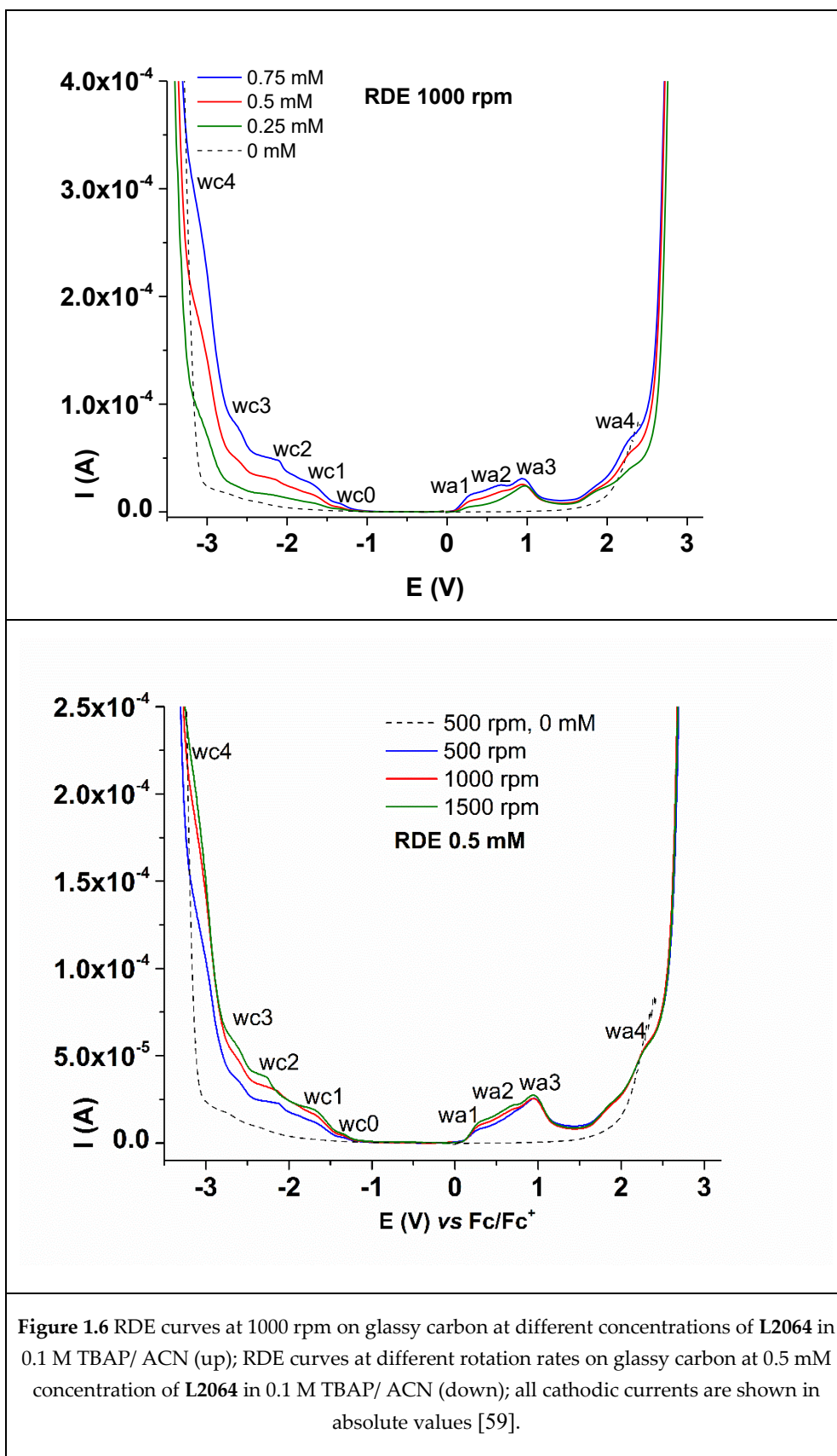
The characterization of the ligands by DPV was carried out at 0.01 V/s scan rate, with the pulse amplitude of 0.025 V and the step of 0.2 s using their millimolar solutions in $CH_3CN + 0.1$ M TBAP. The experiments were carried out at room temperature (25°C) under argon atmosphere. The voltammograms were recorded on freshly clean GC electrode polished by electrode diamond paste on electrode velvet starting from the stationary potential towards the positive potentials for the evidence of oxidation (anodic) processes. After cleaning the electrode, it was also polarized towards negative potentials for the evidence of reduction processes (cathodic). In Figure 1.5. are shown several DPV curves obtained for the studied compound **L2064** [59, 61-67].



1.2.1.3. Voltammetry with rotating disk electrode (RDE) investigations

In the method of voltammetry with rotating disk electrode (RDE) the electrode is rotated in the solution with a controlled rate. The rotating disk draws the fluid to its surface and, due to centrifugal force, throws the solution outwards from the centre in a radial direction. The fluid at the surface of the disk is replenished by a flow normal to the surface. Convection occurs near the surface of the disc. Since there is a thin layer that rotates with the disc electrode, the convection velocity of the solution from the surface of the disc is increased with the rotation rate. As result, the diffusion layer becomes thinner as the diffusion rate increases. It means that the diffusion rate of the substrate is regulated by controlling the rotation rate of the electrode [69].

The characterization of the ligands by RDE was carried out at 0.01 V/s scan rate, and different rotation speeds (500, 1000 and 1500 rpm) using their millimolar solutions in CH₃CN + 0.1 M TBAP. The experiments were carried out at room temperature (25°C) under argon atmosphere. The voltammograms were recorded starting from the stationary potential towards positive potentials for the evidence of oxidation (anodic) waves (wa1, wa2, wa3 and wa4). After cleaning the electrode, it was also polarized towards negative potentials for the evidence of reduction (cathodic) waves (wc1, wc2, wc3 and wc4). In Figure 1.6 are shown the RDE voltammograms obtained for the compound **L2064** [59, 61-67].



1.2.2. Optical methods for investigation of the ligands

The optical properties of the ligands were examined by UV-Vis spectroscopy of micromolar solutions of each of the ligands in acetonitrile. UV-Vis spectrometry studies were performed on a JASCO V-670 spectrometer (Figure 1.7a) in quartz cuvettes with an optical path of 10 mm and a volume of about 3.5 mL (Figure 1.7b) in freshly dried acetonitrile. Input of experimental parameters and acquisition of experimental data were performed via the Spectra Manager interface (Figure 1.7c).

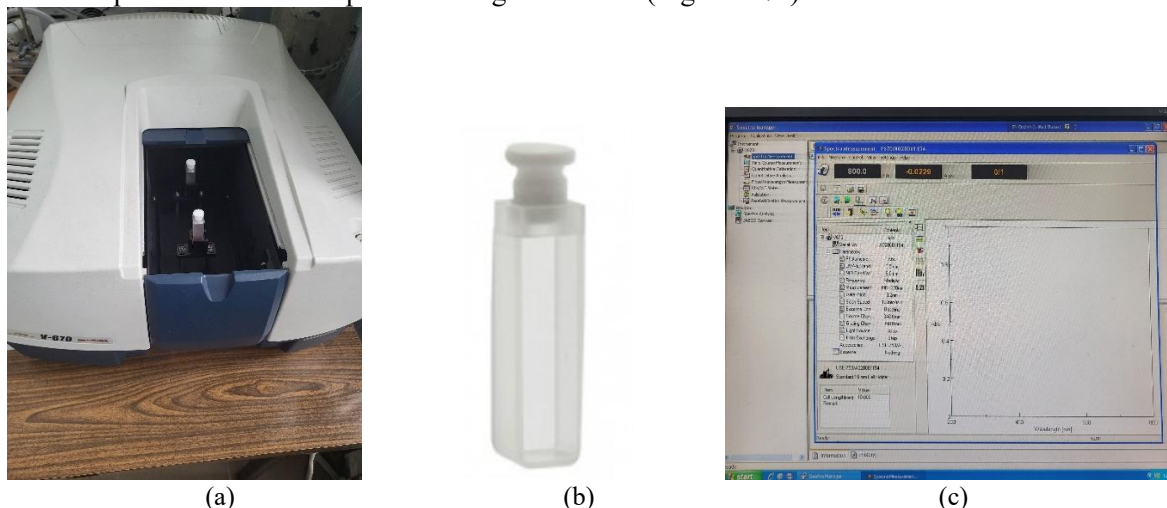


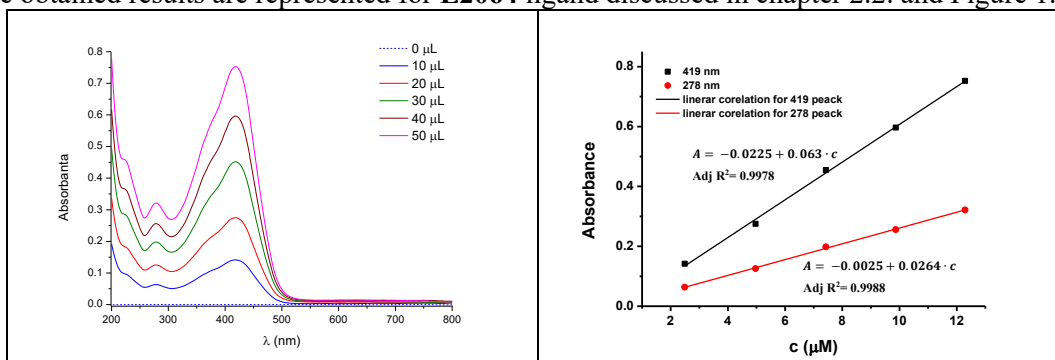
Figure 1.7. JASCO V-670 bi-beam spectrometer (a), 10mm optical path quartz cuvette (b) and Spectra Manager interface (c) used to run UV-Vis spectrometry experiments

1.2.2.1 Characterization of studied ligands properties by UV-Vis spectrometry

UV-Vis study the optical properties of the ligands consisted of recording the absorbance at different wavelengths from the UV-Vis domain. From plotting the UV-Vis peaks heights at different concentrations of the compound the calibration curves for each ligand are obtained following the following steps [1–3]:

1. 3 mL of CH_3CN were introduced into the two cuvettes of the spectrophotometer.
2. the baseline was recorded for wavelengths in the 800-200 nm range.
3. the background (without ligand solution), the UV-Vis spectrum was recorded at 0 ligand concentration in the 800-200 nm range, with CH_3CN in both tanks.
4. 5 μL of the ligand solution in CH_3CN (2mM) was added to the tank for sample equipped with a stirrer, the solution inside was stirred for 1 minute, after which the spectrum was recorded.
5. The operation from point 4 was repeated by adding an additional 5 μL of ligand solution (2 mM) in CH_3CN , followed by shaking the solution in the cuvette for one minute and recording the spectrum, after each addition, until a total amount of 25 μL was added from the ligand solution (2 mM) in CH_3CN .
6. The wavelengths at which maxima were obtained were identified and the calibration lines (Absorbance vs. ligand concentration) were drawn for each of them.

The obtained results are represented for **L2064** ligand discussed in chapter 2.2. and Figure 1.8. [59]



A	B
Figure 1.8. (A)—UV-Vis spectra obtained for different concentrations of L2064 and (B)—dependence of absorbances on L concentration ([L]).	

1.3. DFT CALCULATION METHODS FOR INVESTIGATION OF ORGANIC LIGANDS

Density functional theory (DFT) calculation methods were applied to calculate the structural parameters and properties of studied molecules. This has developed a wide variety of different procedures or models, divided into two categories, quantum chemistry models and molecular mechanics models. Quantum chemical models derive from the Schrödinger equation, which treats molecules as collections of nuclei and electrons, without any reference to "chemical bonds" [70]. The Schrödinger equation can only be solved for a one-electron system (the hydrogen atom) and approximations must be done for the other atoms. Quantum models differ in these approximations.

1.3.1. Principles and algorithms of DFT calculation

DFT theory provides us with a computational quantum mechanical modelling method used in physics, chemistry, and materials science to investigate the ground-state electronic structure (or nuclear structure) of many-body systems, especially atoms, molecules, and condensed phases. The papers of interest published for this thesis used Spartan'18 software from Wavefunction, Inc. Irvine, USA Property calculations were performed using density functional theory (DFT) and hybrid functional B3LYP [71] with the 6-31G (d, p) polarization basis set for the ground state equilibrium geometry [72].

1.3.2 Examples of properties calculated by DFT

DFT calculations were performed for the lowest energy conformer of the investigated compound. Regarding the predicted energy levels of the HOMO (E_{HOMO}) and LUMO (E_{LUMO}) frontier molecular orbitals. Global chemical reactivity parameters (ionization potential, electron affinity, electronegativity, global hardness, softness and electrophilicity index), as well as local reactivity descriptors (Mulliken and electrostatic charges, potential electrostatic and local ionization potential), using the following relations [74, 75]:

- Ionization potential, I (eV): $I = -E_{\text{HOMO}}$
- Electron affinity, A (eV): $I = -E_{\text{LUMO}}$
- Frontier molecular orbitals energy gap, ΔE (eV): $\Delta E = E_{\text{HOMO}} - E_{\text{LUMO}}$
- Electronegativity, χ (eV): $\chi = (I + A)/2$
- Global hardness, η (eV): $\eta = (I - A)/2$
- Local softness, σ (eV^{-1}): $\sigma = 1/\eta$
- Chemical potential, μ (eV): $\mu = (E_{\text{HOMO}} + E_{\text{LUMO}})/2$
- Global electrophilicity index, ω (eV): $\omega = \mu^2/(2\eta)$.

The obtained results can be found in chapter 2.2 and 2.3 and, in other works [59, 61-67] published during the doctoral stage.

1.4. PREPARATION OF CHEMICALLY MODIFIED ELECTRODES (CMEs) BASED ON INVESTIGATED LIGANDS

A chemically modified electrode (CME) is an electrode covered by a conductive or semiconductor material that has been coated with a monomolecular, multimolecular, ionic or polymeric film that changes the interface properties (Figure 1.9) [76]. CMEs prepared within PESO Laboratory consisted of producing a polymer film on a glassy carbon electrode (GC) by electropolymerization of each studied ligand. The electropolymerization was done either by controlled potential electrolysis (CPE) or by successive scanning of potential in specified domains by CV (CVS).

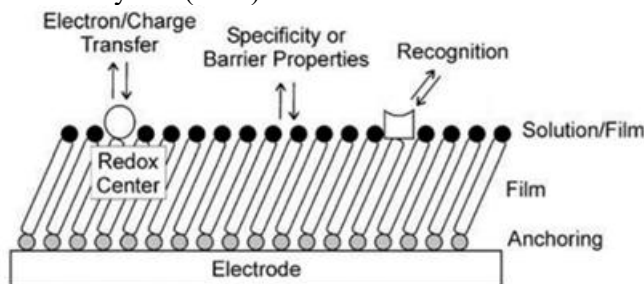


Fig. 1.9 General representation for a CME interface and its reactions [76].

1.4.1. Preparations of CMEs based on investigated ligands by CV scanning (CVS)

Preparations of CMEs by CVS was carried out at 0.1 V/s scan rate, and different domains on a glassy carbon electrode (GC) with a diameter of 3 mm, using a 2 mM solution of each ligands in $\text{CH}_3\text{CN} + 0.1 \text{ M TBAP}$. The experiments were carried out at room temperature (25°C). The deposition was done by successively making a number of cycles, as discussed in chapter 2.1 [59] for **L2064**. After preparation, the modified electrodes were cleaned with acetonitrile.

1.4.2. Preparations of CMEs based on investigated ligands by controlled potential electrolysis (CPE)

Preparation of CMEs by controlled potential electrolysis (CPE) was performed at different electrodeposition potentials on 3 mm diameter glassy carbon (GC) electrode using millimolar solutions of each ligand in $\text{CH}_3\text{CN} + 0.1 \text{ M TBAP}$.

For the immobilization of each ligand on the GC surface by CPE, different electrical charges and different potentials were checked like in Table 1 taken from chapter 2.3 [62].

Table 1. CMEs characterization methods by ferrocene redox probe (Fc), chronoamperometry, SEM, AFM, and HMs detection for several modified electrodes prepared by CPE on GC electrodes from **L** solutions in 0.1 M TBAP/ACN in different conditions: **L** concentration ([**L2548**]), potential, electric charge. The working electrodes were GC disks with either 3 mm diameter (GC3) or 6 mm diameter (GC6).

CME	[L] (mM)	Preparation Potential/ Electrode	Electric Charge (mC)	CME's Characterization
1	1.3	1.3 V/GC3	0.5	Fc^{*a}
2	1.3	1.3 V/GC3	1	Fc^{*a}
3	1.3	1.6 V/GC3	0.5	Fc^{*a}
4	1.3	1.6 V/GC3	1	Fc^{*a}
5	1.3	1.6 V/GC3	1.3	Fc^{*a}
6	1	1.3 V/GC3	1	Chronoamperometry, Fc^{*b}
7	1	1.3 V/GC3	1.2	
8	1	0.9 V/GC6	4	SEM, AFM, Raman
9	1	1.3 V/GC6	4	SEM, AFM, Raman
10	1	1.3 V/GC6	14	SEM, AFM, Raman

^{*a} Transfer of CME in Fc solution in 0.1 M TBAP/ACN; ^{*b} HMs detection.

1.5..CHARACTERIZATION OF CMEs BASED ON INVESTIGATED LIGANDS

The characterization of the obtained CMEs was done either by transferring the CMEs in the supporting electrolyte without ligand and comparing the signal obtained on CME with that on the bare electrode, or by studying their interaction with solutions of known concentration of ferrocene in $\text{CH}_3\text{CN} + 0.1 \text{ M TBAP}$ (redox probe). Separately, they were tested for analytical purposes. In this thesis the new prepared CMEs were tested for the recognition of heavy metal ions from aqueous solutions of known concentrations of heavy metal HMs ions: Cd(II) , Pb(II) , Cu(II) , Hg(II) .

1.5.1. Characterization of CMEs based of investigated ligands by CV in the supporting electrolyte

A system of two cells with three electrodes was used, as described in chapter 1.2. In one of the cells there is a solution of known concentration of ligand in $\text{CH}_3\text{CN} + 0.1 \text{ M TBAP}$, and in the other a solution of supporting electrolyte ($\text{CH}_3\text{CN} + 0.1 \text{ M TBAP}$). After preparation of the CME in the preparation cell, it was washed with solvent, then it was introduced in the second cell containing the supporting electrolyte, and CME was polarized in anodic/cathodic scans to see the new signals which appear in comparison with those on bare electrode. The CV or DPV recorded voltammograms were compared with those of GC. The obtained results can be found in chapters 2.2, and 2.3 [59, 62]. An example is given in Figure 1.10a for a CME obtained from the ligand **L2064** [59].

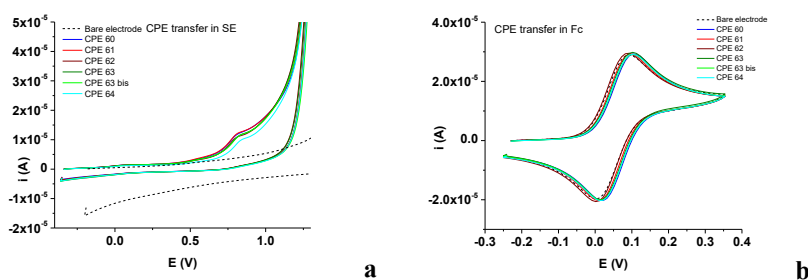


Figure 1.10 CV curves recorded on **L**-CMEs prepared by CPE at 0.7 V and using different electropolymerization charges (0.5 mC - 5 mC) in 0.1 M TBAP in DMF (**a**) and in 3 mM solution of ferrocene in 0.1 M TBAP in DMF (**b**).

1.5.2. Characterization of CMEs based on investigated ligands by redox probe

A system of two cells with three electrodes as described in chapter 1.2 was used. In one of the cells there is a solution of known concentration of ligand in $\text{CH}_3\text{CN} + 0.1 \text{ M TBAP}$, and in the other a solution of ferrocene in $\text{CH}_3\text{CN} + 0.1 \text{ M TBAP}$. CME obtained as described in chapter 1.4. were washed with acetonitrile. After that, it was transferred to the cell with ferrocene solution in $\text{CH}_3\text{CN} + 0.1 \text{ M TBAP}$ of known concentration. The CV or DPV recorded voltammograms were compared with those of GC. The obtained results can be found in chapters 2.2 and 2.3 [59, 62]. Un example is shown in Figure 1.10b for CMEs obtained from **L2064**. Another example is given in Figure 1.11, for CMEs based on **L2548** prepared in different conditions [62].

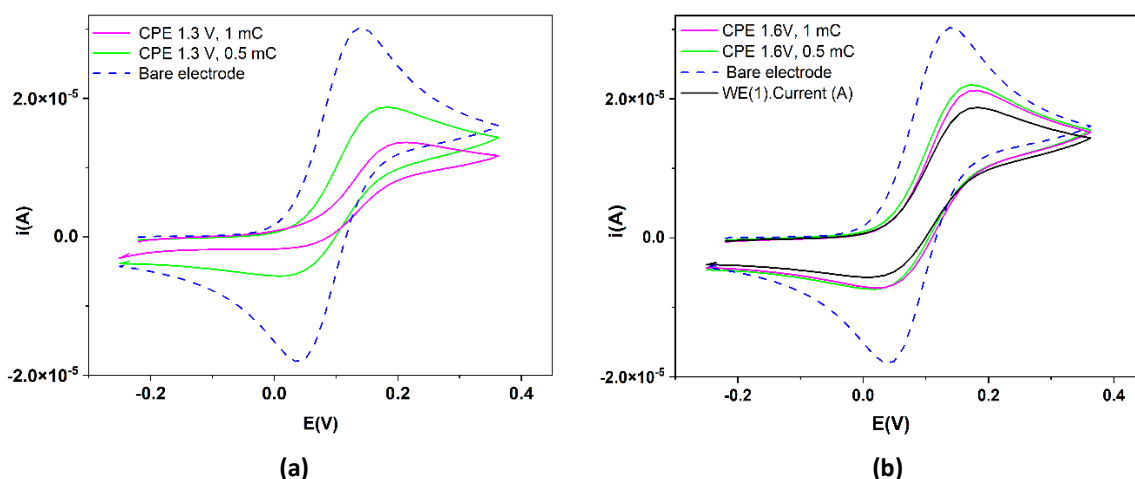


Figure 1.11 CV curves ($0.1 \text{ V} \cdot \text{s}^{-1}$) recorded in 1 mM ferrocene solution in 0.1 M TBAP/ACN for CMEs prepared by CPE in L solution (1.3 mM in 0.1 M TBAP/ACN) at different potentials: (a) 1.3 V and (b) 1.6 V, using various electropolymerization charges (solid lines) vs bare electrode (dashed lines).

1.5.3. Characterization of CMEs based on investigated ligands by SEM

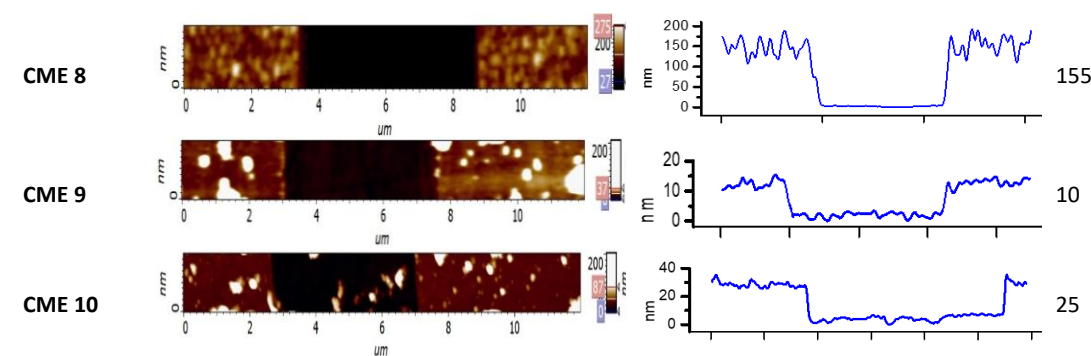
The surfaces of CMEs based on **L2548** (**L2548**-CMEs) were investigated using SEM to determine the characteristics of the films deposited on GC6 discs (diameter 6 mm) obtained at different potentials and electropolymerization charges. Several SEM micrographs are shown in Figure 1.12 for different charges and potentials.

1.5.4. Characterization of CMEs based on investigated ligands by AFM

The surfaces of CMEs based on **L** (**L**-CMEs) were investigated using AFM for the films deposited on GC6 discs (diameter 6 mm). Several AFM images are shown in Table 2 for different electropolymerization potentials and charges. The thickness of the films deposited by CPE was measured using a technique involving scraping (mechanical removal) the film with the AFM tip, followed by scanning across an area that includes both the scraped region and the adjacent intact surface. The results obtained for three films (CME 8, CME 9 and CME 10) are depicted in Table 2.

Table 2. AFM topography images and lines profiles indentation acquired for CMEs obtained by CPE prepared at different potentials and charges: +0.9 V, 4 mC (CME 8), +1.3 V, 4 mC (CME 9), and +1.3 V, 14 mC (CME 10).

AFM topography	Line profile across indentation	Thickness (nm)
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1.6. INTERACTION BETWEEN ORGANIC LIGANDS AND HM IONS

1.6.1 Homogeneous interaction of organic ligands with HMs in solution

The first way tasted for determination the r/m complexation ratio is the molar ratio method [29, 30], which consists in the graphical representation of the maximum intensity peak absorbance, for a specific wavelength, as a function of $[Pb(II)] / [R]$, and observing the change in the slope. The value of the ratio at the point where the slope of the line changes is equal to the ratio r/m.

The second way for determination the r/m complexation ratio is the method of continuous variations (Job) [29,30], and consisted in measuring the absorbance, for a specific wavelength, of a series of solutions, in which the molar fraction ($X = [Me]/([Me] + [R])$) of the metal varied between 0 and 1. The molar fraction (X) at which there is a minimum or maximum absorbance is related to the stoichiometric ratio in the complex, through the relationship: $r/m = (1 - X)/X$. If the dissociation of the complex is significant then the minimum or maximum absorbance points were determined by extrapolating the linear domains.

The third way for determination the r/m complexation ratio was the Molland method [29, 31] concerned in measuring the absorbance for two solutions, one containing the metal ion in concentration C_M and the ligand in large excess, for which the absorbance is A_M , and one in which the metal ion is in excess vs. the ligand concentration C_R for which the absorbance is A_R . The value of r/m was given by the relationship (1)

$$r/m = C_M A_R / (C_R A_M) \quad (1)$$

Spectrophotometric methods allowed the evaluation of the concentration of some species, without removing them from the system. For this reason, they could be used to study the equilibria and stoichiometry of chemical complexation reactions between ligands and HMs ions introduced into ligand solutions [77].

For the study of the stoichiometry of chemical reactions, a particular application of spectrophotometric titration was carried out, which led to the determination of the complexation ratio of metals with different ligands. In this thesis, the complexation studies were performed one by one, in relation to Cd(II), Cu(II) and Hg(II) ions. Since the electrochemical studies indicated a preferential complexation of Pb(II) in relation to Cd(II), Cu(II) and Hg(II), complexation testing was performed in solution with Pb(II) ions in certain cases. UV-Vis spectra were recorded for ligand solutions with increasing concentrations of Pb(II) ions, and the variations of absorbances at the main wavelengths with respect to the amount of Pb(II) ions added were plotted.

To observe the effect of complexation with HM(II) ions, the following steps were performed for each of the analysed ligands:

1. 3 mL of CH_3CN were introduced into the two cuvettes of the spectrophotometer.
2. the baseline was recorded for wavelengths in the 800-200 nm range.
3. the background (without ligand solution), the UV-Vis spectrum was recorded at 0 ligand concentration in the 800-200 nm range, with CH_3CN in both tanks.
4. 10 μL of 2mM ligand solution (in 0.1 M TBAP, CH_3CN , sampling from the electrolysis cell) was added to the working vessel, equipped with a stirrer, stirred for 1 minute and the spectrum was recorded in the 800-200 nm range.

- the concentration of the ligand in the working tank was determined (based on the previously determined calibration curve), and the amount of 10^{-3}M metal ions solution in water necessary to be introduced into the tank was calculated to obtain the following molar ratios $[\text{HM(II)}]/[\text{L}]$: 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.2, 1.5, 1.8, 2.0, 2.5 and 3.0, as well as the quantities needed to be added to change from one ratio to the next one.
- The amount of metal ion solution calculated in point 6 to obtain the molar ratio $[\text{Hg(II)}]/[\text{L}] = 0.1$ was added over the ligand solution in the tank, of known concentration, and stirred for one minute
- The UV-Vis spectrum was recorded at the known $[\text{HM(II)}]/[\text{L}]$ ratio in the 800-200nm range.
- The working vessel was removed from the spectrophotometer and stirred for 30 seconds on the magnetic stirrer, after which the UV-Vis spectrum was recorded in the 800-200nm range. (the spectrum corresponds to a complexation time of $1+7 = 8$ minutes)
- The operation was repeated from point 8 of the spectrum (corresponds to a complexation time of $8+7 = 15$ minutes)
- To obtain the mixture corresponding to the following ratio, over the solution from point 8 was added the amount of metal ion solution, concentration 10^{-3}M calculated at point 6 and it was stirred for one minute.
- The UV-Vis spectrum was recorded at the known $[\text{HM(II)}]/[\text{L}]$ ratio in the 800-200nm range
- The operations from points 10 and 11 were repeated for all $[\text{HM(II)}]/[\text{L}]$ ratios.

The obtained titration curves are represented for **T1 – T3 ligands** in chapter 2.1. An example is given in Figure 1.13 for **T1** ligand complexation with Pb(II) ions in solution [61].

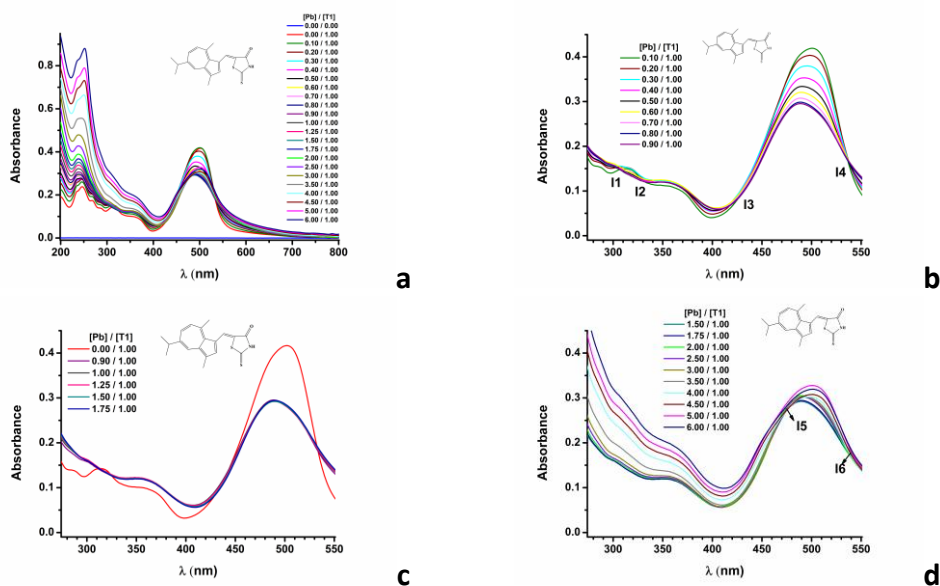


Figure 1.13 UV-Vis spectra for $[\text{T1}] = 8.75 \mu\text{M}$ in solutions for different $[\text{Pb(II)}]/[\text{T1}]$ ratios between: 0-6 (a), 0.1- 0.9 (b); 0.9- 1.75 (c) and 1.5- 6 (d)

1.6.2. Heterogeneous interaction of investigated ligands with HMs on CMEs

A system of two electrochemical cells was used to study the interaction of heavy metal ions with CMEs. In the first there is a solution of known concentration of rhodanine derivatives in $\text{CH}_3\text{CN} + 0.1 \text{ M TBAP}$, and in the other an aqueous acetate buffer solution (0.1M) of $\text{pH} = 4.5$.

CME obtained by CPE, rinsed with CH_3CN , as in the procedure described in chapter 1.4 is conditioned. The CME conditioning procedure consists in transferring it to the cell with acetate buffer (0.1M) of $\text{pH} 4.5$ and carrying out the equilibration operations (by performing a number of 15 successive scans in the $-0.6 \text{ V} - 0.9 \text{ V}$ range) and superoxidation (by performing a number of 15 successive scans in the range $-0.2 \text{ V} - 1.85 \text{ V}$) By conditioning the CME is stabilized in order to ensure a better reproducibility.

Conditioned CME was introduced into a container in which a known volume of synthetic solution of heavy metal ions of known concentration is under gentle agitation for a period of 15 minutes, unless otherwise specified. After the CME accumulation stage with HMs, it is washed with ultrapure water and introduced into the cell with acetate buffer. Here the electrode is polarized at -1.0 V for 180 s after which the DPV is recorded. The procedure followed and the results obtained for each investigated ligand can be found in chapters 2.1, 2.2 and 2.3 [59, 61, 62].

After carrying out the procedure described above, the presence of heavy metals in the synthetic solution can be observed on the representations obtained. The amount of metal ion absorbed by the CME is directly proportional to the area of the peak. Results obtained for each investigated ligand can be found in chapters 2.2 and 2.3 [59, 62].

A CME prepared with the same electrical charge and potential of the EPC is used to create the calibration curves. The conditioning is done under the same conditions for all determinations, the absorption of heavy metal ions of different concentrations is done. The electrodes are polarized under the same conditions, followed by recording the DPV curves during CPE (Figure 12) applied for **L2548** solutions [62]. For the detection of HM(II) in aqueous solutions with different concentrations of HMs the modified electrodes were conditioned and then immersed in these solutions.

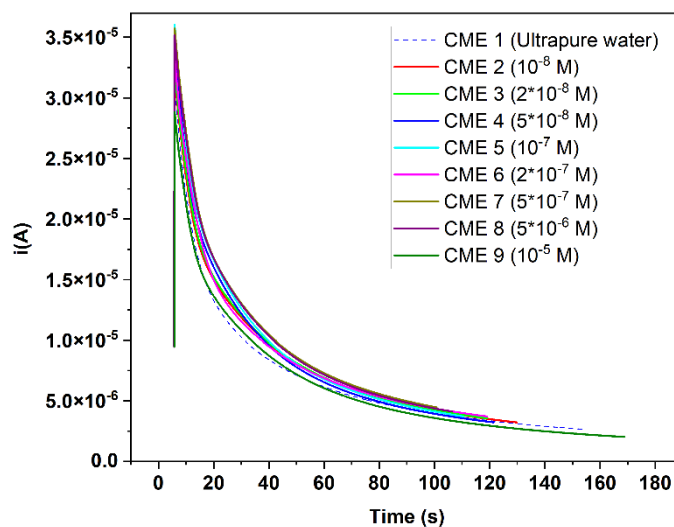


Figure 1.14 Reproducibility test: chronoamperograms for the individual experiments of CMEs based on **L2548** preparation by CPE using a 1mC charge at a potential of 1.3 V; these CMEs were used for metal (M) detection in water solutions with different concentrations (M = Pb) [62].

Electrodes modifications was performed via controlled potential electrolysis (CPE) in acetonitrile solutions containing millimolar concentrations of ligand L and 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. The working electrodes were GC disks with either 3 mm diameter (GC3) or 6 mm diameter (GC6).

Chemically modified electrodes (CMEs) were evaluated for their sensitivity to heavy metal ions in a 0.1 M acetate buffer solution (pH 4.5), following the methodology outlined in references [78]. The working electrode was the CMEs based on **L2548**, the counter electrode was platinum, and the reference electrode was Ag/AgCl in 3 M KCl (for aqueous systems). Stock solutions of HMs were prepared, followed by successive dilution with deionized water to get the desired concentration of each HM.

The CMEs were conditioned [79] in 15 CV scans from -0.9 V to +0.6 V (0.1 V/s) and was followed by overoxidation through 15 CV cycles from -0.2 V to +1.5 V (0.1 V/s). To accumulate the HMs ions in the film deposited on CMEs each conditioned CME was rinsed with ultrapure water and immersed in an aqueous solution containing HM ions in given concentration (starting from the lowest concentrations we would like to achieve using a sensor based on chemically modified electrodes cu **L2548**) under magnetic stirring for 15 minutes. Then the modified electrode which has accumulated the HM ions was rinsed again with ultrapure water to eliminate the HMs solution on its surface. The amount of each metal ion complexed

within the film was quantified using anodic stripping voltammetry (ASV), employing differential pulse voltammetry (DPV) via potentiostat software. After a 3-minute pre-concentration step in 0.1 M acetate buffer at -1.2 V, applied to reduce all heavy metal ions, DPV stripping was performed from -1.2 V to $+0.5$ V (scan rate: 0.01 V/s, pulse height: 0.025 V, step time: 0.2 s). The DPV curves were superposed as in Figure 13a, to see better the difference between the peak heights obtained after the immersion in solutions with different concentrations. The peak currents were represented vs. the HMs concentration to get the calibration curves, like in Figure 13b [62]. This curve has an initial linear domain, from which the detection limit can be evaluated, and a plateau for higher concentrations, where the saturation of the CME occurs. The linear range was determined for CMEs modified with the investigated ligands, as mentioned in chapter 2.3 and shown in Figure 12b for CMEs prepared from **L2548** [62].

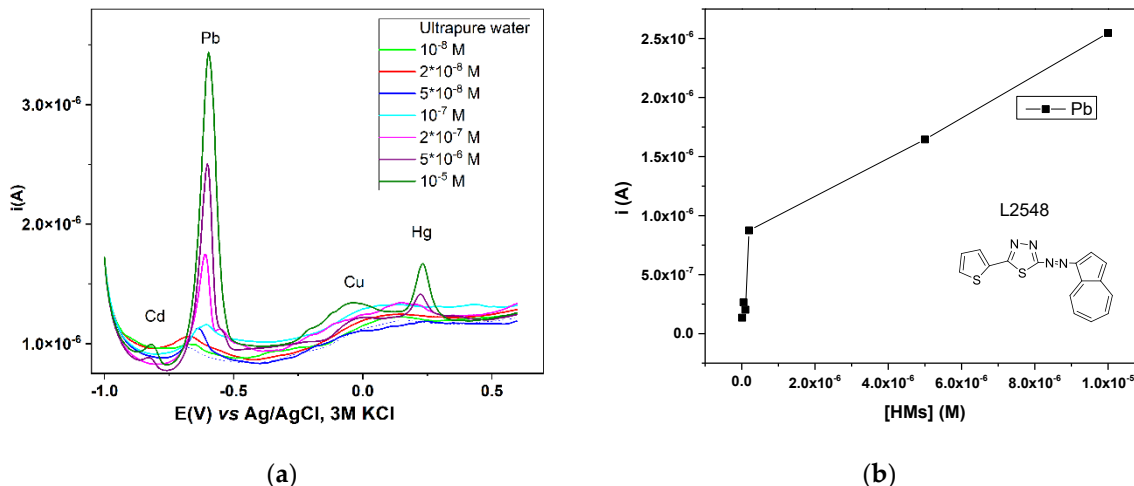


Figure 15. Stripping curves (0.01 V/s) recorded in 0.1 M acetate buffer (pH 4.5) after 15 minutes of accumulation in solutions containing equal concentrations of Cd(II), Pb(II), Cu(II) and Hg(II) in water (a); calibration curves for Pb(II) on CMEs according to Figure 18a (b); the modified electrodes obtained by CPE at $+1.3$ V using an electrical charge of 1 mC in 1 mM **L2548** solution in 0.1 M TBAP/ACN [62].

2. ARTICLES PUBLISHED IN EXTENSO WITH THE MAIN SCIENTIFIC RESULTS OF THE DOCTORAL THESIS

2.1. STUDIES ON AZULENE-RHODANINE DERIVATIVES COMPLEXATION WITH Pb(II) BY UV-Vis

. *Cornelia Elena Mușină (Borșaru), Ovidiu-Teodor Matica, Eleonora-Mihaela Ungureanu, Studies on azulene-rhodanine derivatives complexation with Pb(II) by UV-Vis, UPB Scientific Bulletin, Series B, Vol. 87, Iss. 3, 2025, ISSN 1454-2331, 47.3.*

Results and Discussion

a. UV-Vis studies for ligands

Figs. 2 and 3 show the spectra obtained for different concentrations of ligand **T1** and **T2**, respectively in ACN. The maxima were examined as wavelengths and absorbance. The absorbance was plotted vs. each ligand concentration, and their linear dependences were examined.

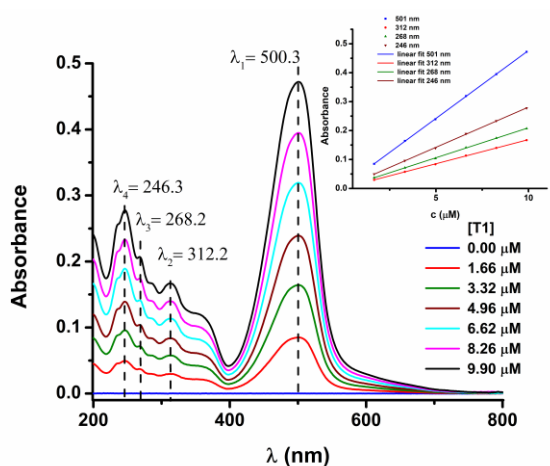


Fig. 2. UV-Vis spectra for different concentrations of T1 and the dependence of absorbances on the concentration of T1 (in set)

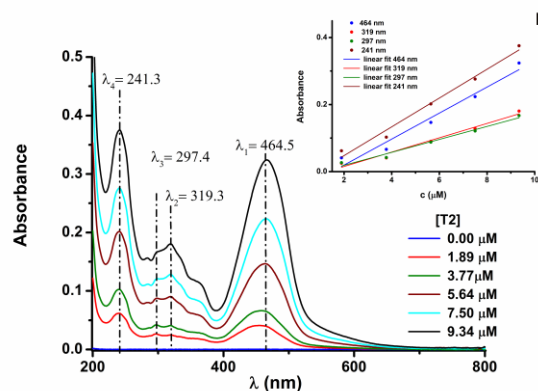
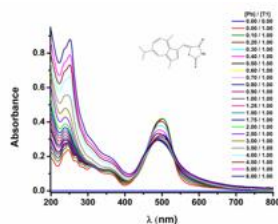
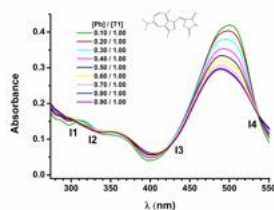


Fig. 3. UV-Vis spectra for different concentrations of T2 and the dependence of absorbances on the concentration of T2 (inset)

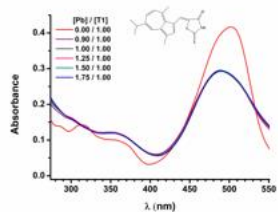
Evoluțiile spectrelor au fost examinate ca absorbantă și lungimi de undă în funcție de raportul dintre concentrația de Pb(II) și concentrația de ligand ($[Pb(II)]/[R]$) sau fracția molară de Pb(II) în soluție ($[Pb(II)]/[R] + [Pb(II)]$), în conformitate cu toate metodele pentru fiecare ligand, după cum se observă pentru T1 în figura 4., Figura 5 și Tabelul 5.



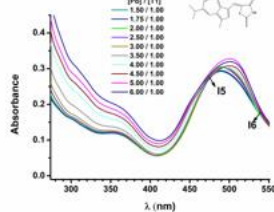
a



b



c



d

Fig. 4. UV-Vis spectra for $[T1] = 8.75 \mu\text{M}$ in solutions for different $[\text{Pb(II)}]/[\text{T1}]$ ratios between: 0-6 (a), 0.1-0.9 (b); 0.9-1.75 (c) and 1.5-6 (d)

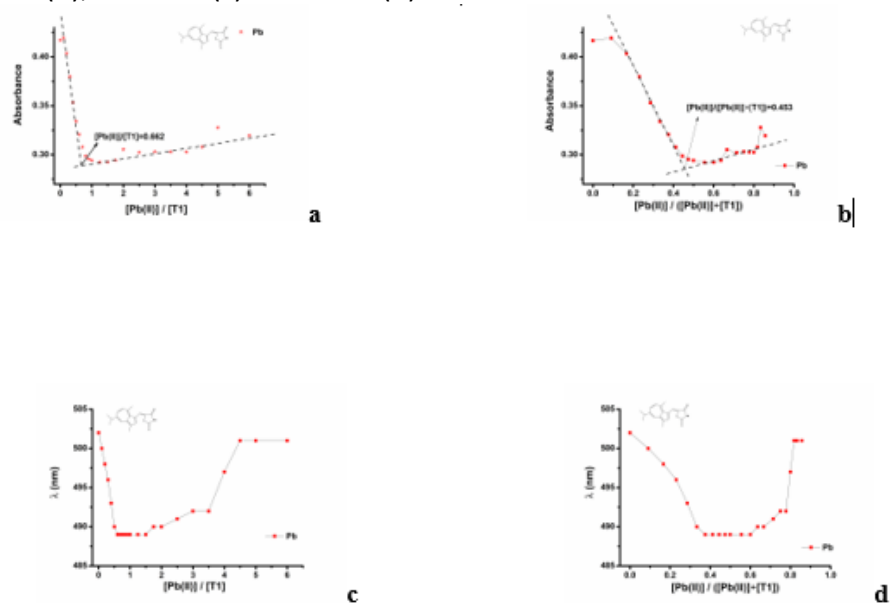


Fig. 5. Variations in absorbance (a, b) and wavelength (c, d) as a function of the $[\text{Pb(II)}]/[\text{T1}]$ ratio (a, c) and the $[\text{Pb(II)}]/([\text{Pb(II)}]+[\text{T1}])$ ratio (b, d)

Raporturile r/m pentru $(Pb)_m(Tl)_r$ în conformitate cu metoda Mollard pentru absorbanta (A)

Crt. No.	Excess de Pb			Excess de Ligand			r/m	m	r	Formula complex ului
	[Pb]/[Tl]	[Tl] μM	A	[Pb]/[Tl]]	[Pb] μM	A				
1a	6/1	8.32	0.319	0.2/1	1.76	0.403	5.98	1	5.98	PbTl ₆
2a	5/1	8.39	0.328	0.2/1	1.76	0.403	5.88	1	5.88	PbTl ₆
3a	4/1	8.46	0.303	0.2/1	1.76	0.403	6.31	1	6.31	PbTl ₆
4a	3.5/1	8.50	0.303	0.2/1	1.76	0.403	6.45	1	6.45	PbTl ₆
5a	3/1	8.53	0.328	0.2/1	1.76	0.403	6.47	1	6.47	PbTl ₆
1b	6/1	8.32	0.319	0.3/1	2.63	0.380	3.76	1	3.76	PbTl ₄
2b	5/1	8.39	0.328	0.3/1	2.63	0.380	3.69	1	3.69	PbTl ₄
3b	4/1	8.46	0.303	0.3/1	2.63	0.380	3.97	1	3.97	PbTl ₄
4b	3.5/1	8.50	0.303	0.3/1	2.63	0.380	4.05	1	4.05	PbTl ₄
5b	3/1	8.53	0.323	0.3/1	2.63	0.380	4.06	1	4.06	PbTl ₄
1c	6/1	8.32	0.319	0.4/1	3.51	0.353	2.62	1	2.62	PbTl ₃
2c	5/1	8.39	0.328	0.4/1	3.51	0.353	2.58	1	2.58	PbTl ₃
3c	4/1	8.46	0.303	0.4/1	3.51	0.353	2.77	1	2.77	PbTl ₃
4c	3.5/1	8.50	0.303	0.4/1	3.51	0.353	2.83	1	2.83	PbTl ₃
5c	3/1	8.53	0.323	0.4/1	3.51	0.353	2.84	1	2.84	PbTl ₃
1d	6/1	8.32	0.319	0.5/1	4.38	0.334	1.99	1	1.99	PbTl ₂
2d	5/1	8.39	0.328	0.5/1	4.38	0.334	1.95	1	1.95	PbTl ₂
3d	4/1	8.46	0.303	0.5/1	4.38	0.334	2.10	1	2.10	PbTl ₂
4d	3.5/1	8.50	0.303	0.5/1	4.38	0.334	2.14	1	2.14	PbTl ₂
5d	3/1	8.53	0.323	0.5/1	4.38	0.334	2.15	1	2.15	PbTl ₂
1e	6/1	8.32	0.319	0.6/1	5.25	0.321	1.59	1	1.59	Pb ₂ Tl ₃
2e	5/1	8.39	0.328	0.6/1	5.25	0.321	1.56	1	1.56	Pb ₂ Tl ₃
3e	4/1	8.46	0.303	0.6/1	5.25	0.321	1.68	1	1.68	Pb ₂ Tl ₃
4e	3.5/1	8.50	0.303	0.6/1	5.25	0.321	1.71	1	1.71	Pb ₂ Tl ₃
5e	3/1	8.53	0.323	0.6/1	5.25	0.321	1.72	1	1.72	Pb ₂ Tl ₃

2.2 ELECTROCHEMICAL AND OPTICAL EXPERIMENTS AND DFT CALCULATIONS OF 1,4,6,8-TETRAKIS((E)-2-(THIOPHEN-2-YL)VINYLAZULENE +

Cornelia Musina (Borsaru), A.-G. Brotea, O.-T. Matica, M. Cristea, A. Stefaniu, E.-M. Ungureanu, Electrochemical and optical experiments and DFT calculations for an allyl-thiophene substituted azulene, *Molecules* 2025, 30(18), 3762. <https://doi.org/10.3390/molecules30183762>

This paper demonstrates that (L) has high potential for nonlinear optics and coloring. This compound was studied electrochemically using cyclic voltammetry, differential pulse voltammetry, and rotating disk voltammetry in organic electrolytes. The main processes that took place during the oxidation and reduction scans were highlighted and characterized. Calculations based on density functional theory (DFT) were performed to evaluate the chemical reactivity of this compound. UV-Vis studies of L in acetonitrile were performed to establish the optical parameters in this solvent and its complexing power towards heavy metal (HM) ions.

2.1. Electrochemistry on L

Ligand L was examined by differential pulse voltammetry (DPV), cyclic voltammetry (CV), and rotating disk electrode (RDE) voltammetry in millimolar solutions of L in organic electrolytes. Typically, tetrabutylammonium perchlorate (TBAP) dissolved in acetonitrile (ACN) at a concentration of 0.1 M (0.1 M TBAP/ACN) was used. However, in the case of this L ligand, which is not very soluble in ACN, dimethylformamide (DMF) was added as a solvent, and the study was carried out in 2:1 ACN-DMF mixtures (0.1 M TBAP in ACN-DMF). These voltammetric methods were used to highlight the main oxidation and reduction processes that occur with this molecule when the potential is scanned at anodic or cathodic potentials. The curves were initially recorded separately on the GC electrode (freshly cleaned) in the usual supporting electrolyte for organic substrates (0.1 M TBAP, ACN). The working electrode was polarized starting from the steady-state potential to a positive potential of approximately 3 V, and then the potential was returned to its steady-state value. After cleaning the electrode, a similar procedure was applied for the cathodic scan potential up to approximately -3 V, and then reversed to positive values to detect all anodic processes corresponding to those generated in the cathodic scan. All DPV, CV, and RDE curves were recorded for decreasing millimolar concentrations of L solutions in the electrolyte after adding L to the electrolytic cell.

2.2.1. L studies by UV-Vis

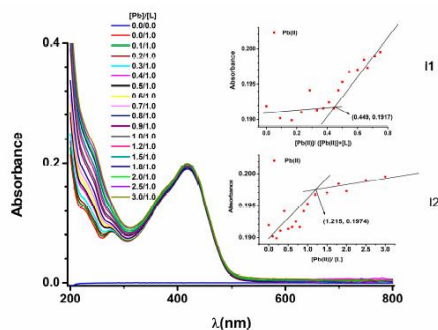


Figure 10. UV-Vis spectra at $t = 1$ min for different $[Pb]/[L]$ ratios; in set: variation of absorbance for the peak at 419 nm versus the molar fraction $[Pb]/([Pb] + [L])$ (in set 11) and versus the ratio $[Pb]/[L]$ (in set 12).

2.2.2 DFT calculation for quantum parameters of chemical reactivity

Figure 12 illustrates the variation of charge distribution on surface L, indicating regions with positive (blue) and negative (red to orange) electrostatic potential, as well as neutral regions (green).

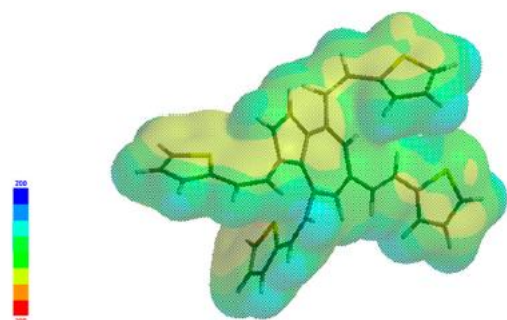


Figure 12. Electrostatic potential map of L.

POLYMER FILMS OF 2-(AZULENE-1-YL DIAZENYL)-5-(THIOPHENE-2-YL)1,3,4-THIADIAZOLE: SURFACE CHARACTERIZATION AND ELECTROCHEMICAL DETECTION OF HEAVY METALS

Cornelia Musina (Borsaru), Mihaela Cristea, Raluca Gavrilă, Oana Brîncoveanu, Florin Comănescu, Veronica Anăstăsoaie, Gabriela Stanciu, Eleonora-Mihaela Ungureanu, Polymer films of 2-(azulen-1-yldiazenyl)-5-(thiophen-2-yl)-1,3,4-thiadiazole: surface characterization and electrochemical sensing of heavy metals, Molecules 2025, in press.

This article presents the ligand 2-(azulen-1-yldiazenyl)-5-(thiophen-2-yl)-1,3,4-thiadiazole (L) as a functional monomer capable of forming stable, redox-active films with high affinity for lead in aqueous solutions.

Table 1. Methods for characterizing CMEs using ferrocen (Fc) redox probe, chronoamperometry, SEM, AFM, and heavy metal detection for several modified electrodes prepared by controlled potential electrolysis (CPE) on GC electrodes from L solutions in 0.1 M TBAP/ACN under different conditions: L concentration ([L]), potential, electric charge. The working electrodes were GC discs with a diameter of 3 mm (GC3) or 6 mm (GC6).

CME	[L] (mM)	Preparation Potential/ Electrode	Electric Charge (mC)	CME's Characterization
1	1.3	1.3 V/GC3	0.5	Fc ^{*a}
2	1.3	1.3 V/GC3	1	Fc ^{*a}
3	1.3	1.6 V/GC3	0.5	Fc ^{*a}
4	1.3	1.6 V/GC3	1	Fc ^{*a}
5	1.3	1.6 V/GC3	1.3	Fc ^{*a}
6	1	1.3 V/GC3	1	Chronoamperometry, Fc ^{*b}
7	1	1.3 V/GC3	1.2	
8	1	0.9 V/GC6	4	SEM, AFM, Raman
9	1	1.3 V/GC6	4	SEM, AFM, Raman
10	1	1.3 V/GC6	14	SEM, AFM, Raman

^{*a} Transfer of CMEs in Fc solution in TBAP/ACN 0.1 M; ^{*b} Detection of HMs.

Figure 2 shows some comparative CV curves recorded in ferrocene solution for CMEs prepared by CPE in L solution at two potentials using different electropolymerization loads. The solid lines

represent the CV curves for CME, and the dashed line corresponds to the signal given by ferrocene on the bare electrode, without film.

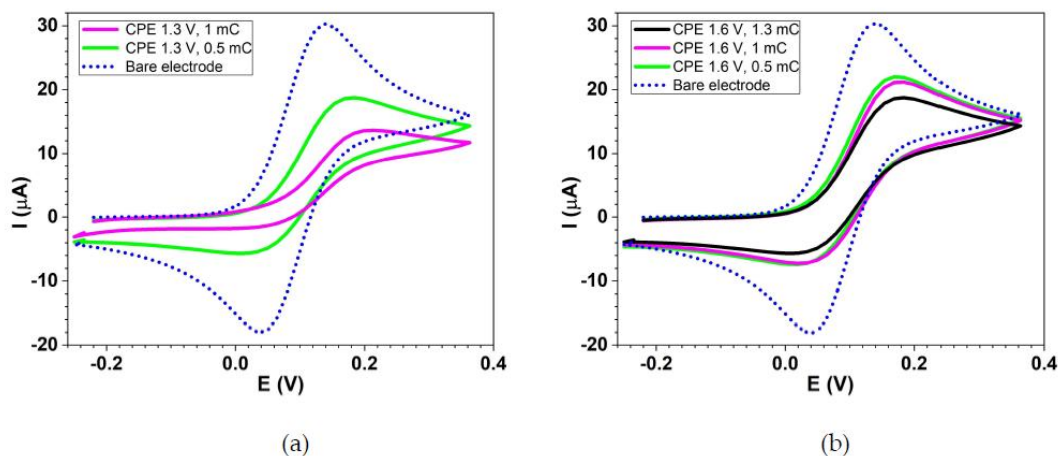


Figure 2. CV curves ($0.1 \text{ V}\cdot\text{s}^{-1}$) recorded in 1 mM ferrocene solution in 0.1 M TBAP/ACN for CMEs prepared by CPE in solution L (1.3 mM in 0.1 M TBAP/ACN) at different potentials: (a) 1.3 V and (b) 1.6 V, using various electropolymerization loads (solid lines) vs. empty electrode (dotted lines).

Characterization of CMEs by scanning electron microscopy

Scanning electron microscopy (SEM) is a non-destructive analysis technique that uses an electron beam probe to analyze surface details down to the nanometer scale.

L-based CMEs (L-CMEs) were investigated using SEM to determine the characteristics of the films deposited on GC6 discs (6 mm diameter) obtained at different potentials and electropolymerization loads. Several SEM micrographs are shown in Figure 3 for different loads and potentials.

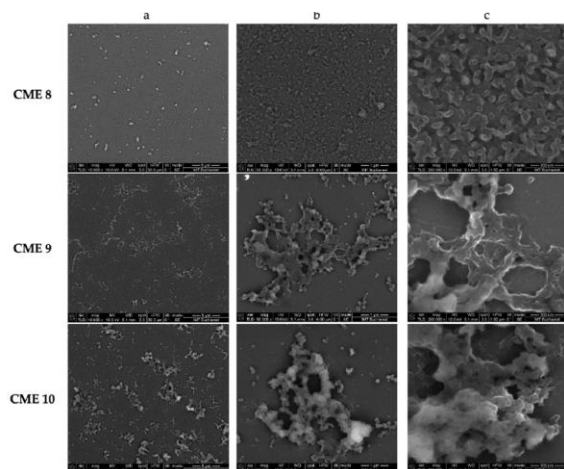


Figure 3. SEM images at different magnifications: 10,000 (a), 50,000 (b), and 100,000 (c) for CME (CPE at +0.9 V, 4 mC), CME 9 (CPE at +1.3 V, 4 mC), and CME 10 (CPE at +1.3 V, 14 mC).

2.4. Characterization of CMEs by Raman spectroscopy

Figure 4 shows the Raman spectra for films obtained at different potentials and loads on CMEs 8, CMEs 9, and CMEs 10.

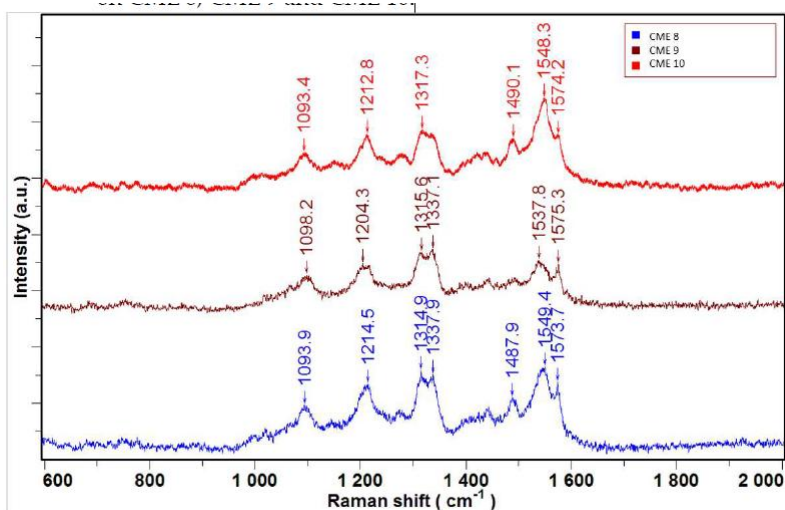


Figure 4. Raman spectra acquired for CMEs obtained at different potentials and charges; the films were prepared by CPE at: +0.9 V, 4 mC (CME 8), +1.3 V, 4 mC (CME 9), and +1.3 V, 14 mC (CME 10)

3. GENERAL CONCLUSIONS

1. This thesis explored several optical and electrochemical properties of azulene derivatives of rhodanine, thiophen and thiazole. The main investigated compounds were: 5-(5-isopropyl-3,8-dimethyl-azulen-1-ylmethylene)-2-thioxo-thiazolidin-4-one (T1) and 2-thioxo-5-(4,6,8-trimethyl-azulen-1-ylmethylene)-thiazolidin-4-one (T2) in comparison with those of unsubstituted compound, (Z)-5-(azulen-1-ylmethylene)-2-thioxo-thiazolidin-4-one (T3), 1,4,6,8-tetrakis((E)-2-(thiophen-2-yl)vinyl) (L2064) and 2-(azulen-1-yl-diazenyl)-5-(thiophen-2-yl)-1,3,4-thiadiazole (L2548).

2. The three thioxo-thiazolidin-4-one (T1-T3) studied by UV-Vis spectra recorded in acetonitrile and methanol, exhibit solvatochromism. In methanol, compounds T1-T3 show absorption maxima at longer wavelengths than in acetonitrile, and the molar extinction coefficients are slightly lower than those obtained in acetonitrile. This observation shows that UV-Vis transitions are easier to achieve in methanol and can be useful in applications that can be carried out in different solvents.

3. The UV-Vis study of their complexation against Pb(II) in acetonitrile solution put in evidence the formation of main soluble complexes for [Pb(II)]/[ligand] molar ratio less the unity, corresponding to the formula Pb(ligand)₂, but also the formation of other complexes. The three ligands have also complexed with different stoichiometries Pb₂(ligand)₃, Pb(ligand)₃, Pb(ligand)₆. The stoichiometric ratios in the main complexes were established by three methods with similar results.

4. The molar ratio method and the method of continuous variations (Job) allowed to highlight the formation of several complexes with different stoichiometries evidenced by the absorbance inflection peaks and by the variation of the wavelength with increasing Pb amount.
5. The Molland method led to the calculation of the stoichiometries of complexes formed during complexation. The most stable complexes appear to be those formed by T2, since the wavelength is practically constant for the range of molar ratios $[Pb(II)]/[T2]$ between 2.5 and 10.
6. The electron-withdrawing groups on the azulene core of T1 and T2, which increase the complexing power of the rhodanine ring, make these ligands better complex the Pb(II) ion. The best complexing agent seemed to be T2.
7. The obtained results confirm that grafting onto azulene substituents with electron-repelling effects, such as methyl and i-propyl, leads to optical properties that vary with the polar solvent and to specific complexing properties with respect to the Pb(II) ion in solution.
8. Comprehensive electrochemical investigations of 1,4,6,8-tetrakis((E)-2-(thiophen-2-yl)vinyl)azulene (L2064) demonstrated its pronounced electropolymerization capacity, which was experimentally confirmed through the successful preparation of chemically modified electrodes (CMEs). These CMEs exhibited selective recognition properties toward Pb(II) and Cd(II), with their analytical responses strongly influenced by the electrode preparation conditions. In contrast, UV-Vis optical studies revealed a different complexation order, indicating selective homogeneous complexation with Pb(II) and Hg(II) ions.
9. Theoretical insights obtained by DFT calculations were consistent with the experimental electrochemical and spectroscopic findings, confirming the moderate reactivity of L and highlighting the role of its conjugated thiophen-2-yl)vinyl-azulene framework in dictating redox and binding behaviour. This correlation between theory and experiment provides a robust foundation for understanding the structure–function relationships of such ligands.
10. Taken together, these results establish L2064 as a promising functional material for electrode surface modification and as a versatile platform for the development of advanced electrochemical sensors. Its combined optical, electrochemical, and theoretical properties recommend it for further exploration in heavy metal ion detection and potential optoelectronic applications.
11. This thesis introduces also L2548 as a functional monomer capable of forming stable, redoxactive films with high affinity for Pb(II) ion. The electrochemical characterization of the monomer L2548 was performed in acetonitrile solutions in presence of tetrabutylammonium perchlorate on GC electrodes using CV, DPV, and RDE methods. All methods revealed pronounced asymmetry between the oxidation and reduction curves, indicating mainly reversible electrochemical processes occurring at cathodic potentials and irreversible processes with films formation at anodic potentials. The three methods lead to concordant results regarding the formation of films by electropolymerization of the ligand L2548.
12. The conclusions drawn from examining the films obtained under different electropolymerization conditions from L2548 through surface analyses performed using SEM, AFM, and Raman spectroscopy allowed for the evaluation of the porosity, aggregation, and adhesion of the films obtained through electropolymerization, which is particularly useful for specific applications of these films (optical or electrochemical).
13. The morphological differences observed by SEM and subsequently investigated using AFM confirm that in case of L2548 higher deposition rates at high potentials favour the formation of nanostructured surfaces with increased roughness. These were tested for the detection of heavy metals (Cd (II), Pb (II), Cu(II), and Hg (II)) for analytical applications based on modified electrodes. Among the monitored metals, the best signal on the unoptimized modified electrodes was obtained for Pb, whose detection limit was below 10^{-8} M, which proves an electrochemical

performance that can be improved. The resulting CMEs show promise for deployment in portable environmental monitoring systems, with implications for public health protection and environmental safety. Other experiments are in progress to determine the influence of preparation conditions on sensor response in terms of sensitivity and selectivity.

14. DFT calculations done for all investigated ligands aimed to evaluate several quantum parameters useful for electrochemical applications' in the recognition of HMs ions. Quantitatively approximated electrophilic and nucleophilic sites using DFT theory enhanced our strategy efforts in designing better ligands.

15. Other ligands were also partially studied and calculated within the doctoral program.

4. ORIGINAL CONTRIBUTIONS

1. The study of investigated azulene ligands enlarged the data disponibile pentru compusii azuleni care sunt cunoscuti ca fiind greu de sintetizat si analizat datorita ractivitatii lor.
2. Studiul lor prin by electrochemistry allowed the elucidation of the main processes occurring at different potentials. This is very important aspect in view of building new materials for the electrochemical sensors. These compounds apartin unor clase diferite azulene-rhodanines, azulene-thiazoles, and azulene-tiofeni, cu proprietati deosebit de interesante din punct de vedere al opticii nelineare si al polimerizarii.
3. Complex characterisation of each ligand by UV-Vis and electrochemical methods such as cyclic voltammetry (CV), differential pulse voltammetry (DPV), and rotating disk electrode voltammetry (RDE) allowed to identify the anodic potentials favourable for film deposition, as confirmed by all these electrochemical methods which gave concordant results.
4. The comparative study of several similar structures by UV-Vis and electrochemistry allowed the elucidation of structure role in the main processes occurring at different potentials.
5. By this thesis the oxidation and reduction processes of were first revealed.
6. Preparation of chemically modified electrodes based on these ligands was achieved either by scanning or by controlled potential electrolysis (CPE).
7. The chemically modified electrodes were used to build analytical devices for the detection of Cd(II), Pb(II), Cu(II), Hg(II) ions from synthetic aqueous solutions. The most intense response was obtained for Pb(II) ion with an estimated detection limit of 5×10^{-8} M, but the research was not optimised.
8. The ability of these ligands to form complexes with Pb(II) ion was tested also by UV-Vis spectrophotometry, which indicated the formation of Pb(II)L₂ as the most stable complexes.
9. The characterization of ligands by electrochemical (CV, DPV, RDE) and UV-Vis methods showed that these compounds have potentiality to build electrochemical sensors for the analysis of HMs by using chemically modified electrodes (CMEs) based on these ligands.
10. The study of the influence of the film thickness and of the potential of their formation to have a lower detection limit for HMs.
11. The comparison of the binding capacity of the ligands studied by UV-Vis showed similar stoichiometric ratios in complexes for all structures.
12. DFT calculations were done to evaluate several quantum parameters useful for electrochemical applications in the recognition of HMs ions. Quantitatively approximated electrophilic and nucleophilic sites using DFT theory enhance our strategy efforts in designing better ligands.
13. The CMEs were characterized through performant surface analyses using SEM, AFM, and Raman spectroscopy which allowed for the evaluation of the porosity, aggregation, and adhesion of the films obtained through electropolymerization, which is particularly useful for specific applications of these films (optical or electrochemical). The conclusions drawn from examining the films through all these methods were concordant. The morphological differences observed by SEM and subsequently

investigated using AFM confirm that in particular conditions higher deposition rates at high potentials favour the formation of nanostructured surfaces with increased roughness.

14. The testing of such CMEs for the detection of heavy metals (Cd (II), Pb (II), Cu(II), and Hg (II)) for analytical applications is original and full of perspectives. Among the monitored metals, the best signal on the unoptimized modified electrodes was obtained for Pb, whose detection limit was below 10^{-8} M, which proves a remarkable electrochemical performance that can be also improved.
15. The resulting CMEs show promise for deployment in portable environmental monitoring systems, with implications for public health protection and environmental safety.
16. Other experiments are in progress to determine the influence of preparation conditions on sensor response in terms of sensitivity and selectivity.

5. DISSEMINATION OF RESULTS

5.1. PUBLISHED PAPERS (ARTICLES)

A1. A.-G. Brotea, O. T. Matica, **C.-E. Musina (Borsaru)**, E.-M. Ungureanu, *Polyazulene-Based Materials based on 4-(azulene-1-yl)-2,6-bis((E)-2-(thiophene-2-yl)vinyl)pyridine for Heavy Metals Ions Detection*, UPB Scientific Bulletin, Series B, Vol. 84, Iss. 3, 2022, ISSN 1454-2331, 117.

FI = 0,5, SRI = 0, AIS= 0,044;

A2. A.-G. Brotea, O.-T. Matica, **C.-E. Musina (Borsaru)**, M. Cristea, A. Stefaniu, A.-M. Pandele, E.-M. Ungureanu. *Advanced Materials Based on Azulenyl-Phenyloxazolone*, Symmetry 2023, 15,540. <https://doi.org/10.3390/sym15020540>.

FI = 2,700, SRI = 0,096 (0,670/7), AIS= 0,406;

A3. O.- T. Matica, A.-G. Brotea, **C.-E. Musina (Borsaru)**, E.-M. Ungureanu, M. Cristea, R. Isopescu, G. O. Buica, A. Razus. *Electrochemistry of rhodanine derivatives as model for new colorimetric and electrochemical sensors based on azulene for the detection of heavy metal ions*, Symmetry 2023, 15, (3), doi: 10.3390/SYM15030752.

FI = 2,700, SRI = 0,084 (0,670/8), AIS= 0,406;

A4. A.-G. Brotea, O.-T. Matica, **C.-E. Musina (Borsaru)**, A. M. Pandele, R. Trusca, E.-M. Ungureanu, *Chemically Modified Electrodes Based on 4-((5-Isopropyl-3,8-dimethylazulen-1-yl)methylene)-2-phenyloxazol-5(4H)-one*, Symmetry 2024, 16, (2), doi: 10.3390/sym16020245.

FI = 2,700, SRI = 0,112 (0,670/6), AIS= 0,406;

A5. Eleonora-Mihaela Ungureanu, **Cornelia Elena Musina (Borsaru)**, Ovidiu-Teodor Matica, Raluca Isopescu, Gabriela Stanciu, Amalia Stefaniu, *Studies on rhodanine derivatives for estimation of chemical reactivity parameters by DFT*, Symmetry 2025, 17, 444. <https://doi.org/10.3390/sym17030444>.

FI = 2,200, SRI = 0,125 (0,750/6), AIS= 0,393;

A6. **Cornelia Elena Mușină (Borșaru)**, Ovidiu-Teodor Matica, Eleonora-Mihaela Ungureanu, *Studies on azulene-rhodanine derivatives complexation with Pb(II) by UV-Vis*, UPB Scientific Bulletin, Series B, Vol. 87, Iss. 3, 2025, ISSN 1454-2331, 47.

FI = 0,5, SRI = 0,032 (0,098/3), AIS= 0,041

A7. **Cornelia Musina (Borsaru)**, Mihaela Cristea, Raluca Gavrilă, Oana Brîncoveanu, Florin Comănescu, Veronica Anăstăsoaie, Gabriela Stanciu, Eleonora-Mihaela Ungureanu, *Polymer films of 2-(azulen-1-yl)diazanyl-5-(thiophen-2-yl)-1,3,4-thiadiazole: surface characterization and electrochemical sensing of heavy metals*, Molecules 2025, in press.

FI = 4,600, SRI = 0,222 (1,777/8), AIS= 0,740

A8. **Cornelia Musina (Borsaru)**, A.-G. Brotea, M. Cristea, G. Stanciu, A. Stefaniu, E.-M. Ungureanu, *Electrochemical and optical experiments and DFT calculations for an alyl-thiophene substituted azulene*, Molecules 2025, 30(18), 3762. <https://doi.org/10.3390/molecules30183762>

FI = 4,600, SRI = 0,296 (1,777/6), AIS= 0,740

FI cumulat (poz. 6+7+8) = 9.7

SRI cumulat (poz. 6+7+8) = 0.55

AIS cumulat (poz. 6+7+8) = 1.521

5.2. INTERNATIONAL CONFERENCES

- C1. A.-G. Brotea, **C.-E. Musina (Borsaru)**, O.-T. Matica, M. Cristea, E.-M. Ungureanu, A. Stefaniu, *Advanced materials based on azulene-phenyloxazolone*, Global Advanced Materials & Surfaces International Conference (GAMS 2022), Paris, France, 15 - 17 June 2022, poster 28.
- C2. **C.-E. Musina (Borsaru)**, A.-G. Brotea, O. T. Matica, R. Isopescu, E.-M. Ungureanu, A. Stefaniu, *DFT analysis of quantum chemical reactivity parameters for electro-chemical applications of an azulene-phenyloxazolone based ligand*, 8th Regional Symposium on Electrochemistry for South-East Europe, Graz, Austria, 11-15 July 2022.
- C3. A.-G. Brotea, O.-T. Matica, **C.-E. Musina (Borsaru)**, M. R. Bujduveanu E.-M. Ungureanu, *Chemical modified electrodes based on new azulene-thiophen-vinylpyridine*, 22nd Romanian International Conference on Chemistry and Chemical Engineering, Sinaia, Romania - September 7 – 9, 2022, Poster S7- 107.
- C4. E.-M. Ungureanu, O.-T. Matica, **C.-E. Musina (Borsaru)**, A.-G. Brotea, R. Isopescu, A. C. Razus, *Rhodanine derivatives as model for new electrochemical and colorimetric sensors based on azulene*, The 4th International Conference on Symmetry, Barcelona, Spain, 21–23 Jun 2023.
- C5. A. Stefaniu, A.-G. Brotea, O.-T. Matica, **C.-E. Musina (Borsaru)**, E.-M. Ungureanu, *In silico approaches for rational design of new electrochemical sensors based on azulene-phenyloxazolone*, The 4th International Conference on Symmetry, Barcelona, Spain, 21–23 June 2023, Poster P10.
- C6. **C.-E. Musina (Borsaru)**, A.-G. Brotea, O.-T. Matica, O.I. Enache, A. Stefaniu, E.-M. Ungureanu, *Electrochemical and DFT analysis of quantum chemical reactivity parameters for electrochemical applications of an azulene-phenyloxazolone*, New Trends on Sensing-Monitoring-Telediagnosis for Life Sciences, September 8-10, 2022, Braşov, Romania, Poster.
- C7. **C.-E. Musina (Borsaru)**, A.-G. Brotea, M.R. Bujduveanu, E.-M. Ungureanu, A. Ştefaniu, *Modified electrodes based on ethene-2,1-diyltetrathiophene azulene derivative for electroanalytical applications*, XIXth edition of the International Symposium "Priorities of Chemistry for a Sustainable Development", PRIOCHEM 2023, 11-13 October 2023, INCDCP-ICECHIM, Bucharest, Romania, Poster.
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