

# **A Novel Copper (II) Complex of Tetradentate NNOO Schiff Base Containing Pyrrol Ring: Synthesis, Spectral Characterization, Electrochemical Study, Morphological and Electrocatalytical Properties on Cu(II) Modified Glassy Carbon Electrode**

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## **Abstract**

New copper (II) complex of general formula Cu(II)-L containing N<sub>2</sub>O<sub>2</sub> donor atoms have been prepared from 6-[3'-(N-pyrrol)propoxy]-2-hydroxyacetophenone and diaminoethane in the presence of copper acetate dihydrate, it was characterized by elemental and spectral analysis such as FT-IR, UV–Vis, mass spectra and cyclic voltammetry. The electronic spectra of the copper complex show the d–d transition in the range 505–602 nm. The electrochemical behavior of copper (II) complex with Schiff-base ligand containing pyrrole groups has been investigated in acetonitrile solvent by cyclic voltammetry containing tetrabutylammonium perchlorate(TBAP). Electrochemical oxidation of copper (II) complexes in acetonitrile produces conducting polymeric films at the electrode surface. The modified electrodes were electrochemically and morphologically characterized and their electrocatalytical properties have been examined. The catalytic reactivity proved this complex to be efficient catalyst toward electro-oxidation of several organic molecules especially isopropanol alcohol than the other kinds of alcohols (ethanol, benzyl alcohol and methanol) and for the reduction of carbon dioxide.

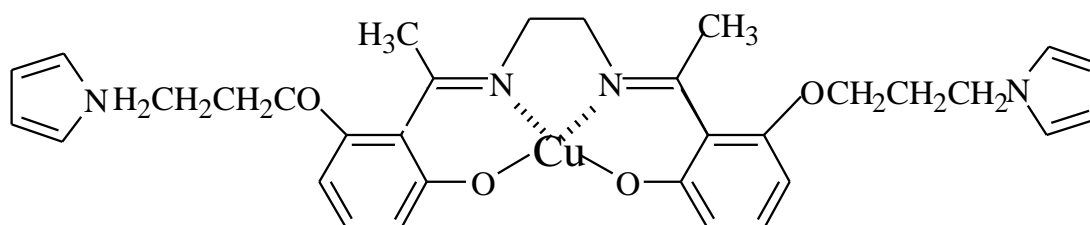
**Key Words:** *copper(II) complex, mass spectra, modified electrodes, oxidation of alcohols.*

## **1. Introduction**

During recent years, Schiff base ligands were found to be an important class of chelating agents in coordination chemistry [1,2]. These compounds have also played a considerable role in the development of this chemistry. A large number of these Schiff base ligands and their complexes have been studied in the past because of their wide application, for their interesting properties as in electrocatalysis [3], corrosion protection [4], and biosensors [5]. So, a particular interest was paid to the complexes obtained from tetradentate ligands (OONN) containing oxygen and nitrogen as heteroatom donors. However, these complexes have extensively been used as catalysts for a wide variety of reactions, including olefins polymerization [6], oxygen activation [7] and carbon dioxide [8].

In continuation of our recent papers [9], we have undertaken a covalent grafting of electropolymerizable units as pyrrole, aniline and thiophene on Schiff base ligands in order to elaborate their modified electrodes for application essentially in heterogeneous catalysis and electrocatalysis. In this context, the transition metal complexes anchored on the polymer matrices is an active area of research due to their structural, magnetic properties and potential catalytic models of several biological systems [10] as, for example, cytochrome P450

reactions. The oxidative electropolymerization of various metal–salen complexes has been investigated [11] and the electrochemical design of modified electrodes by electrodeposition of polymer films has also been widely developed while those of conductor polymers are little studied. For this reason, this work aims the elaboration of new materials such as coordination compounds bearing pyrrol units which have been found to be very useful for catalytic applications in various fields of organic, inorganic and bioorganic synthesis [12]. Thus, a copper(II)-Schiff base complex (**1b**) was synthesized and characterized by routine spectroscopic methods as the elemental analysis, UV-vis, FTIR and mass spectrometry. Finally, an electrochemical behavior of this complex was investigated by cyclic voltammetry in diverse experimental conditions such as those of its electropolymerization and its catalytic activities towards some small molecules as carbon dioxide and molecular oxygen. The synthesis of our new copper(II)-Schiff base complex was illustrated by the following scheme 1.



**Scheme 1**

## 2. Experimental

### 2.1. Synthesis of complex Cu(II)-L

In a 50-ml three necked flask, equipped with a reflux condenser and magnetic stirrer, 518 mg (2 mmol) of 6-(3'-N-pyrrolpropoxy)-2-hydroxyacetophenone [13] and 60 mg (1 mmol) of ethylenediamine were dissolved in 15 ml of absolute ethanol. This mixture was refluxed for about 1 hour until completion of the reaction. To this solution, 199 mg (1 mmol) of copper acetate monohydrated ( $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ ) dissolved in 10 ml of absolute ethanol were immediately added in one portion. The mixture was heated to reflux under nitrogen atmosphere for two other hours again and then abandoned overnight in the refrigerator. The complex was precipitated by diethyl oxide and the solid was recovered by filtration, yielding 85 mg (61 %).

### 2.2. Physical characteristics of the complex Cu(II)-L

**Complex (Cu (II)-L): UV-vis** ( $\lambda$  max / nm - $\epsilon$  ( $\text{M} \cdot \text{cm}^{-1}$ , DO)):  $\lambda_1$  =288 nm (34730, 1.88),  $\lambda_2$  =351 nm (42326, 0.67),  $\lambda_3$  =550nm (66323, 0.05) .**FTIR:**  $\nu_{\text{x-y}}$  ( $\text{cm}^{-1}$ ):  $\nu_{\text{C-H}}$  = 2905;  $\nu_{\text{C=N}}$  = 1602;  $\nu_{\text{C-O-C}}$  = 1096;  $\nu_{\text{C-H(arm.)}}$  = 740;  $\nu_{\text{M-N(arm.)}}$  = 625;  $\nu_{\text{M-O(arm.)}}$  = 570. **Microanalysis** (Calc. (found)): **C:** 63.62 (63.54); **H:** 5.96 (6.36); **N:** 9.27 (9.70).

### 3. Results and discussion

#### 3.1. Infrared Spectra

The IR spectrum of the complex is consistent with the structural data presented in this work. The strong absorption band at  $1602\text{ cm}^{-1}$  may be due to the coordination of the copper (II) ion by the azomethine (C=N) nitrogen atom [14]. The formation of the M–O and M–N bonds was further supported by the appearance of the  $\nu$  (M–O) and  $\nu$  (M–N) bands in the regions  $570$  and  $625\text{ cm}^{-1}$ , respectively, in the spectra of the chelate [14]. The IR spectra of the copper (II) complex shows strong bands at  $1096\text{ cm}^{-1}$  assigned to coordinated phenolic C–O–C stretching mode, however, the band in  $1249\text{ cm}^{-1}$  is assigned to the C–N stretching.

#### 3.2. Electronic Spectra

The formation of the copper (II) complexes was also confirmed by UV–Vis spectra. The electronic spectra of Cu (II)-L in DMF display main features at 288, 351 and 550 nm. The intense absorption band at short wavelength is attributed to  $\pi$ – $\pi^*$  transition of the heterocyclic moiety and phenyl rings [15]. The broad absorption band at 351 nm is arising from a transition involving electron migration along the entire conjugate system of the ligand associated with the C = N linkages ( $n$ – $\pi^*$ ) [15]. The transition observed in the visible region at 550 nm is attributed to weak d–d transitions [16].

#### 3.3. Mass spectroscopy

The FAB-mass spectra suggested that the complex has a binuclear nature. This complex shows molecular ion peak in good agreement with the empirical formula suggested by elemental analyses.

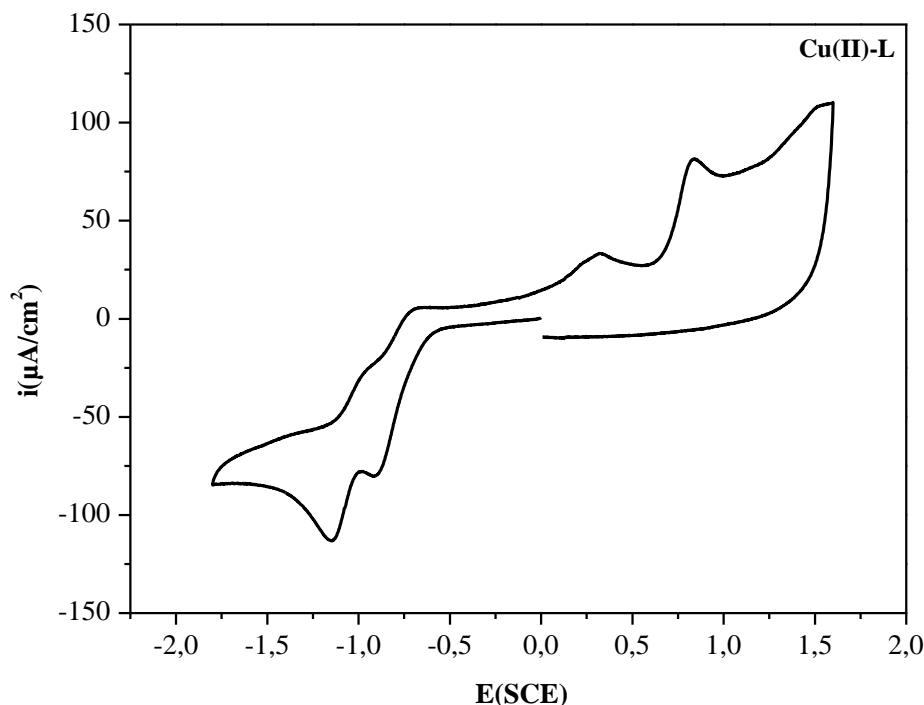
The Cu(II)-L complex exhibit a strong peak at  $543.7\text{ m/z}$  (100%), which is indicative of the  $[L+H]^+$  ion. Also, the FAB-mass spectrum of the [Cu(II)-L] complex shows a peak at  $m/z = 606.6$  (20%), which corresponds to the weight of the complex for a mononuclear structure. The mass spectrum shows multiple peaks representing successive degradation of the complex molecule by the formation of different fragments, the series of peak at  $145.1$  (3.07%),  $272.6$  (13.46%),  $330.6$  (17.30%),  $344.4$  (9.23),  $367.6$  (3.07%),  $384.6$  (3.84%) and  $436.4$  (3.07%) corresponding to these various fragments. The  $m/z$  value  $1209.9$  (11.53%) corresponds to the binuclear structure of the [Cu(II)-L].

#### 3.4. Electrochemical Study of Cu(II)-L

##### 3.4.1. Cyclic voltammetry

The monomer Cu(II)-L was studied by cyclic voltammetry in acetonitrile solution and at scan rate  $100\text{ mVs}^{-1}$  investigating the potentials ranging from  $-1.800\text{ V}$  to  $+1.600\text{ V}$ . So, the voltammogram obtained, given below in the figure 1, shows five oxidation waves observed at  $E_{pa1} = -0.975$ ,  $E_{pa1} = -0.697$ ,  $E_{pa3} = +0.323$ ,  $E_{pa4} = +0.841$  and  $E_{pa5} = +1.525\text{ V/SCE}$  respectively. The first is ascribed to the reoxidation of Cu(I)/Cu(O), the second for the reoxidation of Cu(II)/Cu(I) while the third ones may be attributed to the oxidation of Cu(III)/Cu(II) [17], the waves located at  $+0.841\text{ V/SCE}$  correspond to the pyrrole moieties leading to the formation of poly (pyrrole), and the last ones, it may be assigned to the oxidation of the Schiff base ligand. Regarding the return sweep, only two reduction waves was observed at  $E_{pc1} = -0.904$  and  $E_{pc2} = -1.143\text{ V/SCE}$ , the first is attributable to the

reduction of the Cu(II)/Cu(I) species and the second for the reduction of Cu(I)/Cu(0) couple. To prior, it seems that the oxidation wave of pyrrole group is an irreversible system [18].



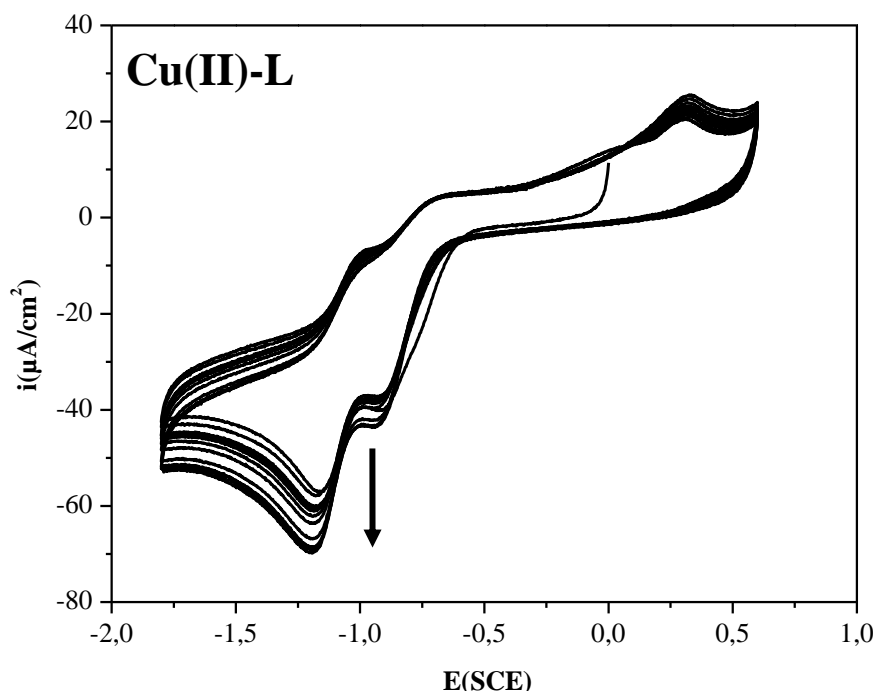
**Fig.1.** Cyclic voltammogram of 1 mM Cu(II)-L at a GC electrode in acetonitrile solution, 0.1 M, TBAP. Scan rate: 100 mV s<sup>-1</sup>.

Cyclic voltammograms, recorded in the range between +1 and 0.0 V, show a redox couple exhibiting two ox/red waves Cu(III) at 0.48 V and Cu(II) at 0.36 V. The peak-to-peak separation ( $\Delta E_p$ ) was found to be 120 mV. On the other hand, the  $\Delta E_p$  data though being larger than the theoretical value for an electrochemically reversible one-electron process, at least suggest that the oxidation of copper(II) in the complex under study should correspond to a one-electron charge transfer. The exceedingly large  $\Delta E_p$  value for the electrochemical oxidation of copper (II) in this complex would be due to a quasi-reversible behavior of the couple  $[\text{Cu(III)L}] + e^- = [\text{Cu(II)L}]^-$ . This fact implies that these electrochemical processes are mainly diffusion-controlled. In addition, in the range 0.0 to -1.5V, it is observed that the binuclear copper (II) complex show two irreversible reduction waves in the cathodic potential region. The first reduction potential ranges from -0.60 to -1.00 V which can be assigned to Cu(II)/ Cu(I) and the second reduction potential lies in the range -0.94 to -1.26 V that can be assigned to Cu(I)/Cu(0) processes.[19]

#### 3.4.2. Modified electrode poly-(Cu(II)-L)/GC

During the repeated potential scans between -0.1 and 1.1 V, the oxidation of monomer is only observed during the first positive scans since the subsequent scans show an obvious decreasing in the peak current expressing, probably, an electrocatalytic effect of copper leading to an overoxidation of the poly(pyrrole) films. On the figure 2, the

electropolymerization of Cu(II)-L was achieved by repetitive cycling of the potential of the vitreous carbon electrode between +0.6 and -1.8 V at 100 mV s<sup>-1</sup>. The buildup of the electropolymerized poly-Cu(II)-L can be followed by the increase in the voltammetric currents and repeated cycling result the deposition of an electroactive polymer on the electrode surface. Thus, different polymer thickness can be obtained by controlling the number of the electropolymerizing scans. These experiments were performed in acetonitrile solutions 10<sup>-1</sup> M TBAP using 10<sup>-3</sup> M of complex (Cu(II)-L) on indium tin oxide electrodes.



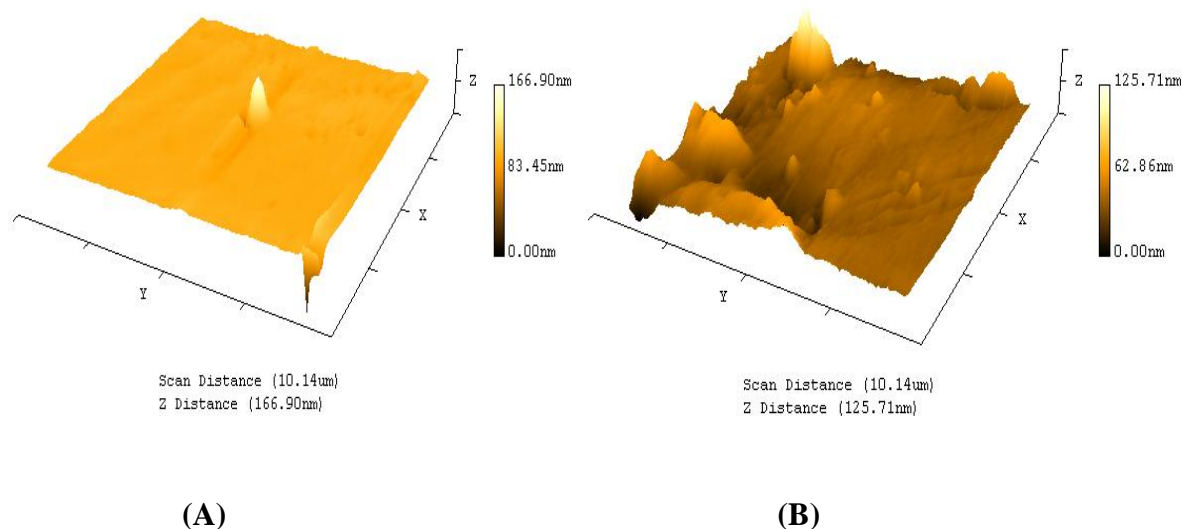
**Fig.2.** Cyclic voltammogram showing deposition of poly-[Cu(II)-L] onto a glassy-carbon electrode in acetonitrile 0.1 M in TBAP, scan rate: 100 mVs<sup>-1</sup>.

The growing of the poly-Cu(II)-L films on indium tin oxide as  $\pi$ -conjugated conductor polymer, which is evidenced by the continuous increasing of the currents  $i_{pa}$  and  $i_{pc}$  of poly-(Cu(II)-L) films has been also investigated. When the modification of this electrode poly-(Cu(II)-L)/ITO are accomplished, it copiously rinsed with bi-distilled water, then with acetonitrile and immediately transferred to another fresh CH<sub>3</sub>CN solution no containing monomer. Thus, the ME (poly-Cu(II)-L /ITO) was identified by an electrochemical technique using cyclic voltammetry giving a characteristic poly (Cu(II)-L) system, attesting the presence of electrodeposited poly (pyrrole) films. So, the amount of the electrodeposited poly-(Cu(II)-L) films was estimated using the Faraday equation,  $Q_{\text{poly-Cu (II)-L}} = 1.747 \text{ mC}$ .

#### 4. Atomic force microscopy

Atomic force microscopy was used to explore the morphology of the poly-[Cu(II)-L] films, electrodeposited onto ITO-substrates. On these images, it is clearly observed that there is a

significant increase in roughness and film thickness values with the number of voltammetric scans. A typical 3-D AFM image is shown in figure 3. From the observation of the AFM image, it is clear that nuclei are formed in large number and different sizes

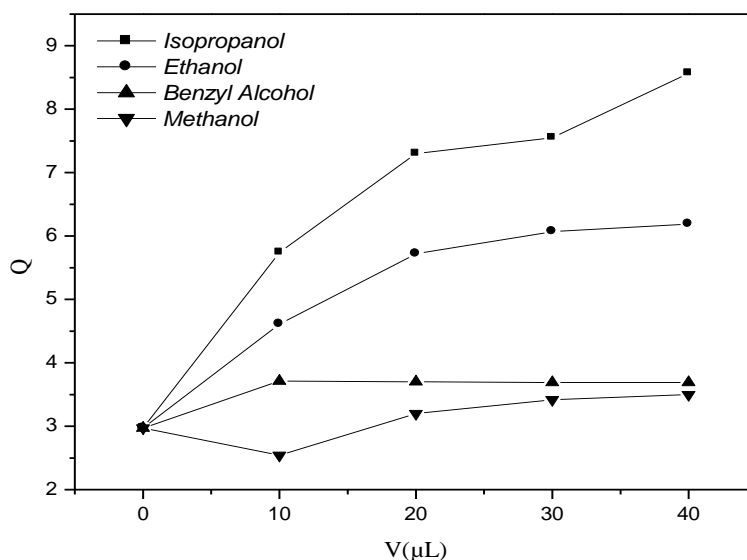


**Fig.3.** AFM images obtained for the polymerized films of Cu (II)-L at several cyclical scans; (A): 1 cycle; (B): 10 cycles; on ITO electrodes.

## 5. Catalysis studies

### 5.1. Alcohols oxidation

The oxidation of benzyl alcohol, ethanol, isopropanol and methanol was attested using copper(II) complex as catalyst in aqueous media. These electrochemical experiments were confirmed the presence of electrocatalytic behavior for the different alcohols above indicated as it can be observed on the following figure 4.

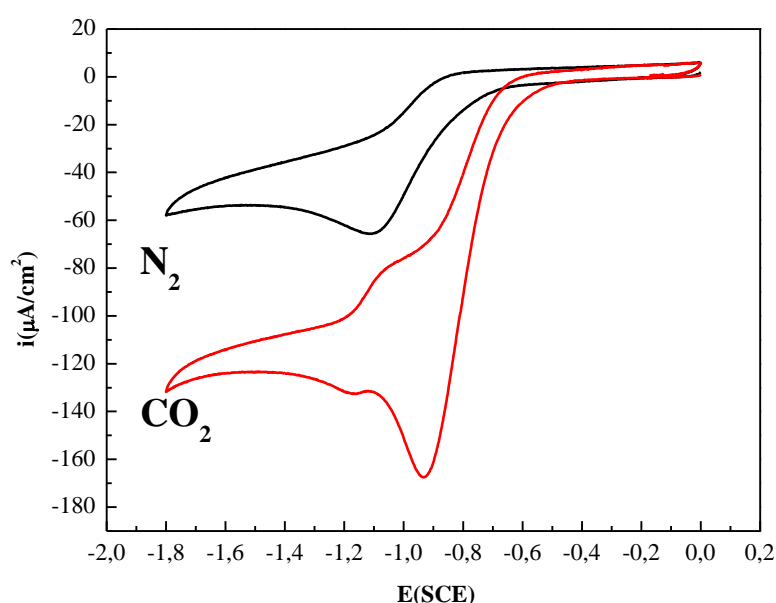


**Fig. 4.** Plots of the anodic oxidation charge ( $Q_{ox}$ ), recorded for various volumes ( $\mu$ l) of each one of studied alcohols.



### 5.2. Activation of carbon dioxide (CO<sub>2</sub>)

The reduction of carbon dioxide (CO<sub>2</sub>) has also been investigated. Cyclic voltammograms of GC-electrode modified with electrodeposition of poly-[Cu(II)-L] films in acetonitrile (AN) solutions are shown in figure 5. Under CO<sub>2</sub> atmosphere, the  $E_{pc}$  of the redox system Cu(II)/Cu(I) appears at -0.940 V instead -1.100 V/SSCE under dinitrogen (N<sub>2</sub>) atmosphere. The shifting of the reduction wave potential of carbon dioxide to the potentials less cathodic is consistent with the presence of an electrocatalytic process, suggesting 160 mV as gain of potential associated to an electrocatalytic current, represented by the ratio  $i_{pc}(CO_2)/i_{pc}(N_2)$  which is equal to 3.28. The importance of this ratio permits to judge the efficiency of the electrocatalytic reaction studied. By way of consequence, a large enhancement of this current augurs a good efficiency for the considered electrocatalytic reaction. [20]



**Fig. 5.** Voltammograms of the electrocatalytic reduction of CO<sub>2</sub> of Cu (II)-L on GC: with N<sub>2</sub> (—, full line); with CO<sub>2</sub> (—, dotted line).

### 6. Conclusion

This work allowed us to establish some conclusions that we can present as following: (i) proposition of a simple and efficient method for the synthesis of new dinuclear copper(II)-Schiff base complex clearly evidenced by cyclic voltammetry and mass spectrometry analysis, (ii) copper(II)-complex obtained was easily electropolymerized by anodic oxidation to its poly-(Cu(II)-L) films yielding modified electrodes containing catalytic sites (Cu<sup>II</sup>) in their poly(pyrrole) matrices to oxidize some alcohols, (iii) These new modified electrodes have also been showed their ability to use them as sensors for detection of small molecules such as carbon dioxide. Finally, we can again conclude that the materials of electrode as GC is more adapted for working in electrocatalysis while ITO surfaces are rather better for morphology studies.

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