

New oligothiényl-phenanthroline ligands: precursors for polymers consisting of conjugated links entwined around transition metal

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RÉSUMÉ

Une nouvelle famille de complexes à ligands encastrés, $\text{Cu}(\text{T}_1)_2^-$ et $\text{Cu}(\text{T}_2)_2^+$, a été synthétisée respectivement à partir de la 2,9-di-(2-thiényl)-1,10-phénanthroline (T_1) et de la 2,9-di-(2-bithiényl)-1,10-phénanthroline (T_2). Leurs propriétés spectroscopiques et électrochimiques sont étudiées. L'électropolymérisation sur électrode de platine des ligands et des complexes est décrite. $\text{Cu}(\text{T}_1)_2^-$ conduit à des monocouches ne contenant plus de centres métalliques. En revanche, le film obtenu à partir de $\text{Cu}(\text{T}_2)_2^+$ présente à la fois une électroactivité du centre métallique et de la matrice polythiophène.

mots-clés : Oligothiényl-phénanthroline, Cuivre I, Electropolymérisation, Electrode modifiée, Complexe à ligands encastrés, Polythiophène.

ABSTRACT

A new class of complexes of entwined ligands, $\text{Cu}(\text{T}_1)_2^-$ et $\text{Cu}(\text{T}_2)_2^+$, has been synthesized respectively from the 2,9-di-(2-thienyl)-1,10-phenanthroline (T_1) and the 2,9-di-(2-bithienyl)-1,10-phenanthroline (T_2). Their spectroscopic and electrochemical properties have been studied. Electropolymerization of these ligands and complexes on platinum electrode is depicted. $\text{Cu}(\text{T}_1)_2^-$ leads to a monolayer which doesn't contain metallic center. On the other hand, the film obtained from $\text{Cu}(\text{T}_2)_2^+$ shows an electroactivity of both the metallic center and the polymer matrix.

key words : Oligothiényl-phenanthroline, Copper I, Electropolymerization, Modified electrode, Entwined ligands complex, Polythiophene.

INTRODUCTION

The functionalization of electronic conducting polymers (PCE) has turned out to be a powerful tool for the modification of electrode surfaces [1]. We have recently developed electroactive films containing complexing cavities performed by entwining around a metallic center two 2,9-diphenyl-1,10-phenanthroline units linked to two

pyrrole nuclei by an alkyl spacer arm [2]. We are now developing the elaboration of aromatic polyimine ligands conjugated with oligothieryl wires (Fig. 1).

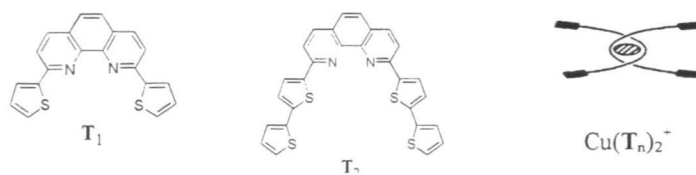


Figure 1 : Ligands T_n precursors of entwined complexes $Cu(T_n)_2^+$ ($n=1, 2$).

In the present article, we describe the spectroscopic and electrochemical properties of their corresponding copper complexes, $Cu(T_1)_2^+$ and $Cu(T_2)_2^+$ (Fig.1). The electropolymerization on platinum electrode of the ligands T_n and of their copper complexes is also depicted.

EXPERIMENTAL

All electrochemical experiments were performed in a glove box filled with an argon atmosphere. Acetonitrile (BDH, Hiper Solv.) and dichloromethane (Carlo Erba, RPE) were distilled over P_2O_5 . Tetraethylammonium tetrafluoroborate (FLUKA) (nEt_4NBF_4) was dried under vacuum at $100^\circ C$ for one day before use. Tetrabutylammonium hexafluorophosphate (FLUKA) (nBu_4NPF_6) was used as received. The electrochemical and UV-visible absorption apparatus have already been described [2].

RESULTS AND DISCUSSION

The synthesis of ligands T_n is similar to those described for the preparation of 2,9-diaryl-1,10-phenanthroline [3] and will be reported elsewhere [4].

Electrochemical and spectroscopic properties of $Cu(T_n)_2^+$ in solution

Formation of $Cu(T_n)_2^+$ according to the classical procedure [2] was instantaneous. The red complex $Cu(T_1)_2^+$ shows in CH_2Cl_2 intense electronic adsorption bands between 400 and 600 nm with a shoulder at 490 nm ($\log \epsilon = 3.361$) typical of a metal-

to-ligand charge transfer (MLCT) process, whereas the orange complex $\text{Cu}(\text{T}_2)_2^+$ shows broader and less resolved absorption bands, due to a stronger absorption of the bithienyl substituents between 350 and 450 nm. $\text{Cu}(\text{T}_n)^+$ exhibit in $\text{CH}_3\text{CN}/\text{nEt}_4\text{NBF}_4$ 0.1 M reversible monoelectronic transfers at +300 mV and +280 mV respectively for $\text{Cu}(\text{T}_1)_2^+$ and for $\text{Cu}(\text{T}_2)_2^+$ corresponding to the $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ redox process.

Electropolymerization of the ligands T_n and of $\text{Cu}(\text{T}_n)_2^+$

Both ligands T_1 and T_2 show by CV an irreversible oxydation peak, and a markedly cathodic shift was observed for T_2 (0.65V) compared with T_1 (1.15V). Poly(T_1) and poly(T_2) obtained by electropolymerization (Fig.2) exhibit typical CV of conjugated organic materials[5].

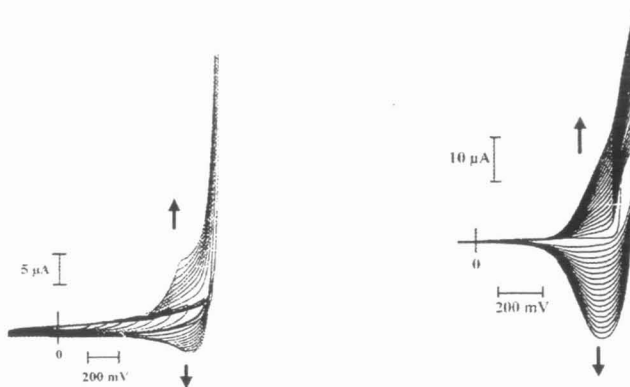


Figure 2 : Successive cyclic voltammograms recorded at 50 mV/s for the electropolymerization of $1.6 \cdot 10^{-2} \text{M}$ T_1 (left) and 10^{-2}M T_2 (right) in 0.1M nEt_4NBF_4 in CH_3CN . Synthesis of films performed by passing 20 mC cm^{-2} (left) and 28 mC cm^{-2} (right). Ref : Ag^+ (10^{-2}M)/ Ag .

Multisweep CV measurements on $\text{Cu}(\text{T}_1)_2^+$ in CH_2Cl_2 or CH_3CN show a slight increase of the matrix polymer electrochemical response while copper ion electroactivity is vanishing (Fig.3). The thus-modified electrode exhibits the same CV than poly(T_1), suggesting the loss of the copper ion during electropolymerization and the formation of very few layers. In the case of $\text{Cu}(\text{T}_2)_2^+$, the simultaneous growth of both the metallic center and the polymer matrix response was observed (Fig.3). The ratio of metallic center vs matrix electroactivities is 1 : 2 in the corresponding CV.

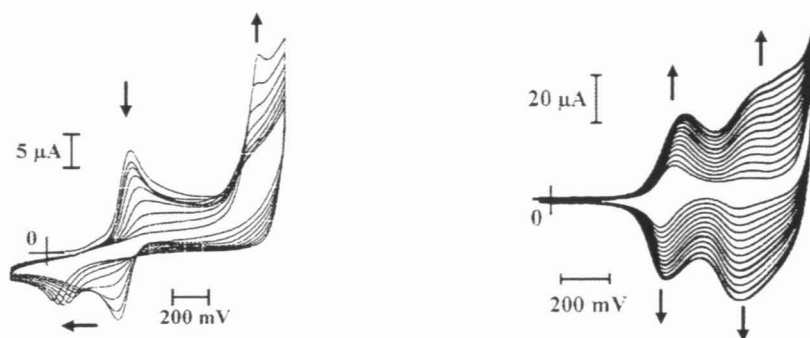


Figure 3 : Cyclic voltammograms recorded at 50 mV/s for the electropolymerization of $10^{-3}M$ $Cu(T_1)_2^+$ in $0.1M$ nEt_4NBF_4 in CH_3CN (left) and $10^{-3}M$ $Cu(T_2)_2^+$ in $0.3M$ nBu_4NPF_6 in CH_2Cl_2 (right). Synthesis performed by passing 15 mC/cm^2 (left) and 23 mC/cm^2 (right). Ref : Ag^+ ($10^{-2}M$)/ Ag .

In summary, 2,9-oligothienyl-1,10-phenanthroline ligands and their corresponding entwined complexes have been synthesized and electropolymerized. The lengthening of the oligoethienyl chain allows conservation of the complexing cavity inside the polymer. Further studies are in progress in order to determine the electronic interactions between the metal centres and the oligoethienyl wires.

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