**Electronic Supporting Information:**

Bis(tetraethylthiophosphoramidoyl)methylamine as an electrochemical ligand for simultaneous detection of iron and copper bivalent cations

Bis(tétraéthylthiophosphoramidoyl)méthylamine comme ligand électrochimique pour la détection simultanée des cations bivalents du fer et du cuivre

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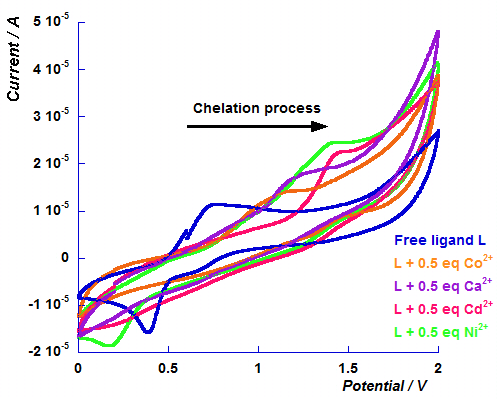
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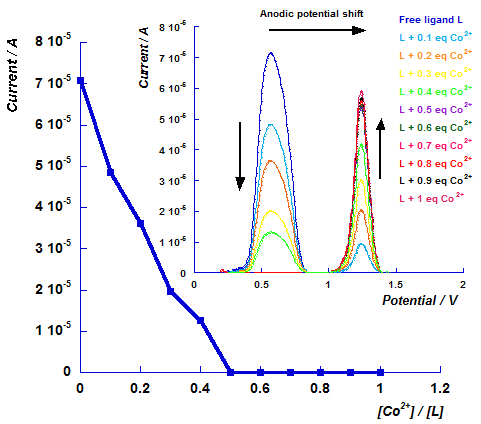
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**Abstract :** A new thiophosphoramide-based electrochemical ligand was synthesized and used as a bivalent metallic cation sensor. The electrochemical studies reveal a sensitive detection process toward various cations such as Fe2+, Co2+, Ni2+, Cd2+, Cu2+ and Ca2+. The chelation process was accompanied by dramatic changes in the redox properties of free ligand. Interestingly, the ligand shows a simultaneous sensing behavior towards iron and copper cations. The oxidation peak potentials of the two complexes can be well separated allowing the sensitive detection. Furthermore, UV-Visible spectra showed red-shifts of absorbance bands of free ligand in the presence of cations due to the coordination of the thiophosphoryl groups. Electrochemical and UV-Visible studies confirmed that the metal-ligand complexes have 1:2 stoichiometry.

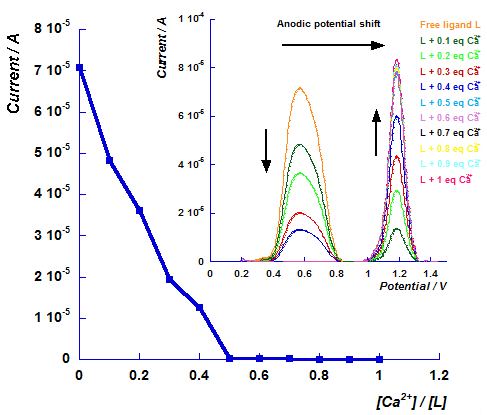
**Résumé** : Dans ce travail, un nouveau ligand électrochimique à base de thiophosphoramide a été synthétisé pour la détection des cations métalliques bivalents. Les études électrochimiques ont montré que la présence des différents cations métalliques tels que Fe2+, Co2+, Ni2+, Cd2+, Cu2+ et Ca2+ provoque un changement considérable au niveau des propriétés électrochimiques du ligand libre. Par ailleurs, le ligand a montré la possibilité de détecter d’une manière simultanée les ions Fe2+ et Cu2+. En outre, les investigations UV-Visible montrent un déplacement considérable des bandes d’absorption du ligand vers les longueurs d’onde infrarouge. Ceci est dû à la coordination des groupements thiophosphoryles présents dans la structure du ligand. Les études électrochimiques et par UV-Visible confirment que les complexes formés ont une steochiométrie 1 :2.



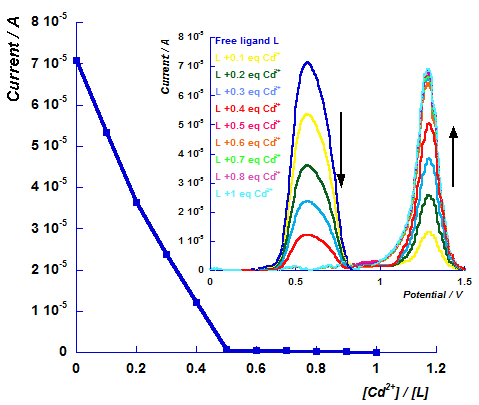
**Figure.S.1.** Cyclic voltammograms of 1.0 mM solution of free ligand **L** and in presence of 0.5 equivalent of cobalt perchlorate, calcium perchlorate, cadmium perchlorate and nickel perchlorate cations in 0.1M TBAClO4 acetonitrile solution. Scan rate: 0.1 Vs-1.



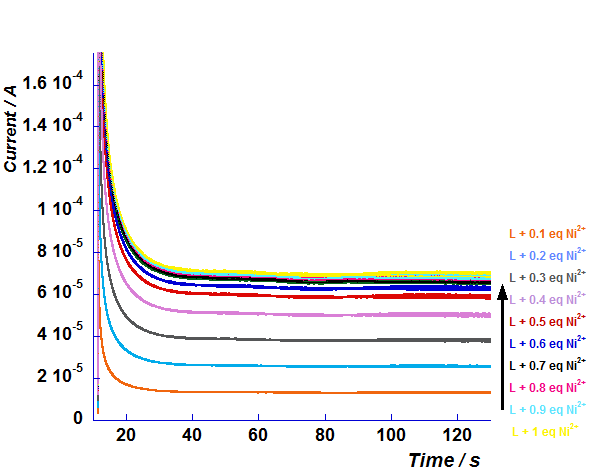
**Figure.S.2.** Variation of peak current Ipa of free ligand **L** depending on relative Co2+ concentration. Inset: Differential pulse voltammograms of the successive addition of the cobalt perchlorate cation (from 0.1 to 1 equivalent) to the free ligand **L** solution (1 mM).



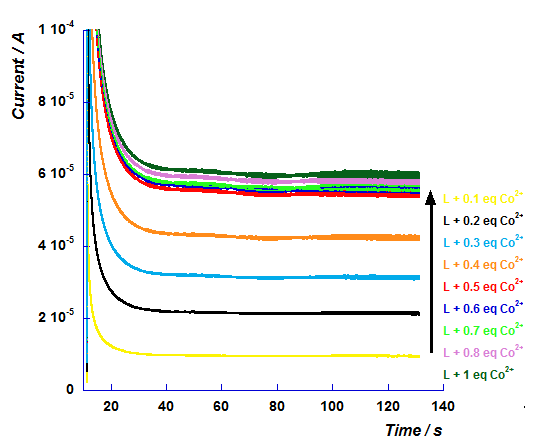
**Figure.S.3.** Variation of peak current Ipa of free ligand **L** depending on relative Ca2+ concentration. Inset: Differential pulse voltammograms of the successive addition of the calcium perchlorate cation (from 0.1 to 1 equivalent) to the free ligand **L** solution (1 mM).



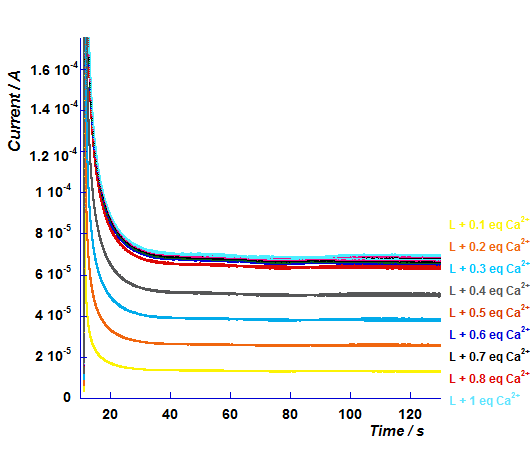
**Figure.S.4.** Variation of peak current Ipa of free ligand **L** depending on relative Cd2+ concentration. Inset: Differential pulse voltammograms of the successive addition of the cadmium perchlorate cation (from 0.1 to 1 equivalent) to the free ligand **L** solution (1 mM).

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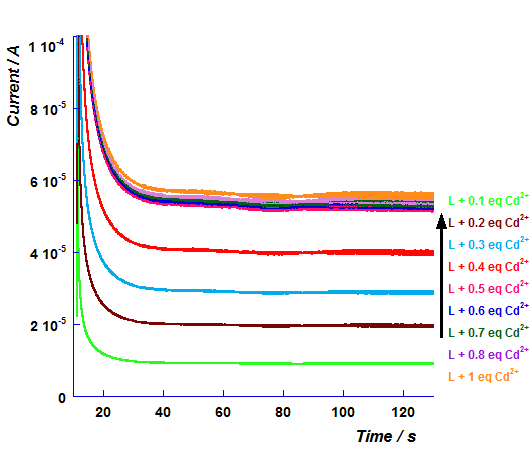
**Figure.S.5.** Chronoamperograms of the successive additions of the nickel perchlorate cation equivalents on the **L** solution (1 mM) performed on the potential of the oxidation of the nickel complex.



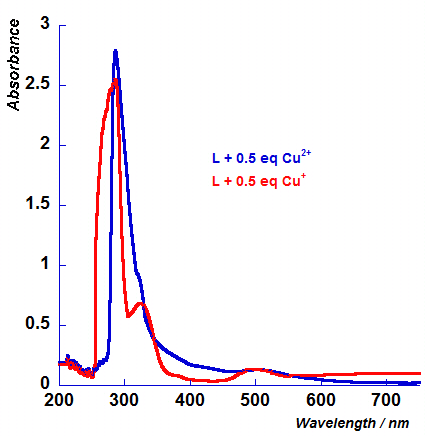
**Figure.S.6.**Chronoamperograms of the successive additions of the cobalt perchlorate cation equivalents on the L solution (1 mM) performed on the potential of the oxidation of the cobalt complex.



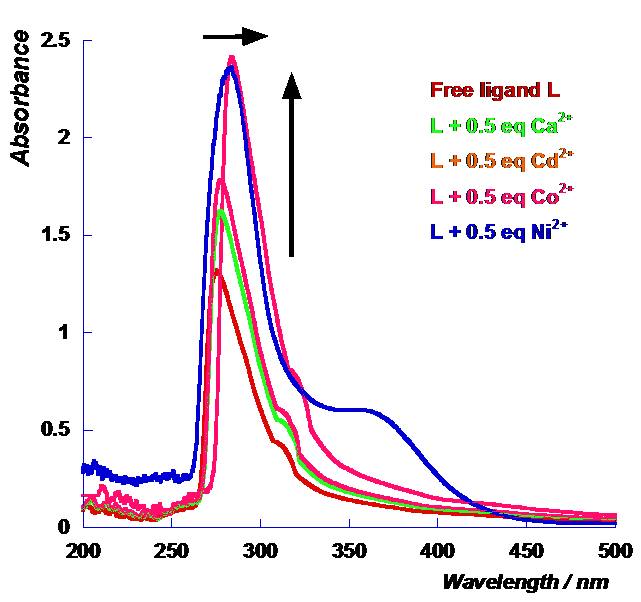
**Figure.S.7.** Chronoamperograms of the successive additions of the calcium perchlorate cation equivalents on the **L** solution (1 mM) performed on the potential of the oxidation of the calcium complex.



**Figure.S.8.** Chronoamperograms of the successive additions of the cadmium perchlorate cation equivalents on the **L** solution (1 mM) performed on the potential of the oxidation of the cadmium complex.



**Figure S.9.** UV-Visible absorption spectra after addition of 0.5 equivalent of Cu[ClO4]2.6H2O (blue curve) and Cu[MeCN]4.BF4 (red curve) to an acetonitrile solution of **L** .



**Figure S.10.** UV-Visible absorption spectra before and after addition of 0.5 equivalent of Ca2+, Cd2+, Ni2+and Co2+ to an acetonitrile solution of **L** .