Electroactive Films of $[Cu(dpp)_2]^+$ Covalently Attached to Polypyrrole (dpp = 2,9-Diphenyl-1,10-phenanthroline)

Gérard Bidan,[a] Bernadette Divisia-Blohorn,[a] Jean-Marc Kern,[b] and Jean-Pierre Sauvage[b]

[a] *Equipe d'Electrochimie Moléculaire, Laboratoires de Chimie, Département de Recherche Fondamentale, Centre d'Etudes Nucléaires de Grenoble, 85X, F-38041 Grenoble Cedex, France*

[b] *Institut de Chimie, Université Louis Pasteur, 1 rue Blaise Pascal, F-67000 Strasbourg Cedex, France*

A copper(I) complex containing two entwined dpp ligands (dpp = 2,9-diphenyl-1,10-phenanthroline), each covalently linked to a pyrrole sub-unit, has been synthesized; electropolymerization of the complex generates a conductive film on platinum or glassy carbon, which can be reversibly de- and re-metallated.

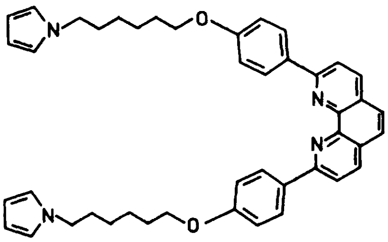
Incorporation of redox centres in conductive polypyrrole films can be conveniently achieved by covalently linking the molecular electroactive species to pyrrole *via* its nitrogen atom prior to electropolymerization. Several examples of such conducting materials have recently been described,[1] with particular emphasis on transition metal complexes containing π-accepting ligands like 2,2′-bipyridine.[2] In view of the remarkable ability of catenands or 2,9-diphenyl-1,10-phenanthroline (dpp) derivatives to stabilize low oxidation state transition metal complexes,[3] and to allow their use in redox photocatalysis,[4] we have synthesized the ligand (**1**), which contains both a dpp co-ordinating site and a pyrrole subunit.

Compound (**1**) was prepared in 70% yield by condensing 2,9-bis(*p*-hydroxyphenyl)-1,10-phenanthroline[5] with the tosylate of 6-(pyrrol-1-yl)hexan-1-ol[6] in dimethylformamide, at 60 °C, in the presence of Na_2CO_3.

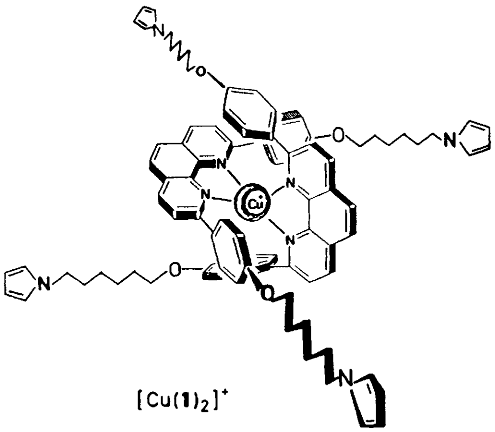
Electropolymerization of (**1**) was performed by electrolysis on Pt or glassy carbon in MeCN–CH_2Cl_2 (75 : 25 v/v; applied potential +0.8 V *vs.* Ag^+/Ag; $[Ag^+] = 10^{-2}$ mol l^{-1} in MeCN). Film growth was monitored by cyclic voltammetry as shown in Figure 1(a). Figure 1(b) shows a cyclic voltammogram of the film itself, the electrode being immersed in MeCN. The behaviour is as expected for an *N*-substituted polypyrrole film, with an oxidation peak at +0.4 V.

Polymerization of the copper complex $[Cu(\mathbf{1})_2]^+$ was expected to lead to some cross-linking and possibly interlocking of rings. Anodic electropolymerization of $[Cu(\mathbf{1})_2]^+$ was carried out on Pt or glassy carbon, either at a fixed potential (+0.85 V *vs.* Ag^+/Ag) or by repeated scanning. The reversible Cu^{II}/Cu^{I} couple is clearly observed in Figure 2(a) (+0.4 V) whereas the irreversible oxidation of the pyrrole fragment is seen at 0.9 V (first scan). The Cu^{II}/Cu^{I} redox potential is slightly shifted towards anodic potentials by polymerization.

The $[Cu(dpp)_2]^+$-modified polypyrrole film (Cu^+–PP) displays electrochemical properties close to those of analogous complexes[3a] in solution. However, whereas redox processes involving the Cu^{II}/Cu^{I} couple can be repeated many times without significant modification of the film, reduction of Cu^+–PP to a formally copper(0) species is irreversible: partial demetallation occurs in the zero-valent state. The copper centre plays a catalytic role in the polymerization process. Since the $[Cu(\mathbf{1})_2]^{2+}/[Cu(\mathbf{1})_2]^+$ couple has a redox potential similar to the oxidation potential of the polypyrrole subunit but markedly less anodic than that of the pyrrole, the copper complex could act as an electron relay during pyrrole oxidation.



(**1**)



$[Cu(\mathbf{1})_2]^+$

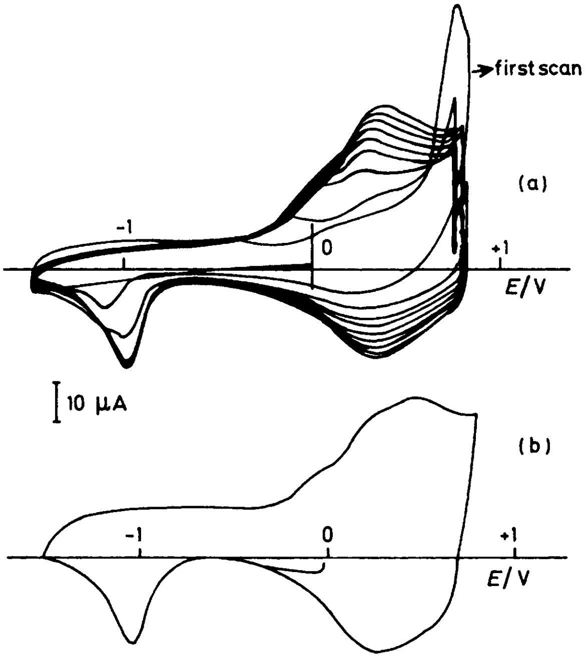


Figure 1. (a) Cyclic voltammograms showing deposition of (**1**) onto a platinum electrode in MeCN–0.1 M Et_4NClO_4 (scan rate 100 mV s^{-1}) by electrolysis at 0.8 V (*vs.* Ag^+/Ag); $Q = 2 \times 10^{-4}$ C between two successive scans. Proton reduction is observed around −1 V; (b) cyclic voltammogram of (**1**)–PP-modified electrode in MeCN–0.1 M NEt_4ClO_4 (scan rate 10 mV s^{-1}).

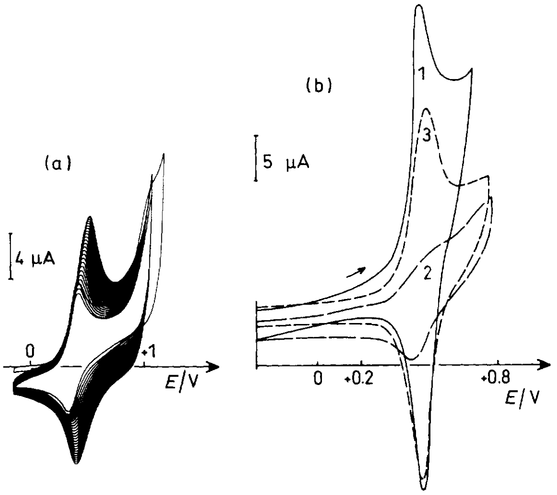


Figure 2. (a) Electrodeposition of $[Cu(\mathbf{1})_2]^+$ onto platinum in MeCN–0.1 M Et_4NClO_4 by sweeping the potential between −0.2 and +1 V; (b) cyclic voltammograms (MeCN–0.1 M Et_4NClO_4) of the Cu^+–PP-modified electrode (de- and re-metallation reactions): curve 1, Cu^+–PP; curve 2, after immersion (30 min) of the film in KCN solution and rinsing; curve 3, after immersion (30 min) of the preceding electrode in 0.2 M $[Cu(MeCN)_4][BF_4]$ solution in MeCN and rinsing.

Conductivity measurements with a four-probe system led to a value of $\sigma \simeq 2.7 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$ for Cu^+–PP, consistent with an *N*-substituted polypyrrole. The presence of copper(I) complexes does not seem to increase the film conductivity significantly.

Demetallation of Cu^+–PP was performed by dipping the modified electrode into KCN solution in MeCN–H_2O (20 : 1). The decomplexation was easily monitored by voltammetric measurements carried out in the course of the demetallation reaction [Figure 2(b)]. As expected, removal of the copper(I) centre is accompanied by loss of electroactivity around +0.4 V (*cf.* curves 1 and 2). It was considered that the rigidity of the polymer matrix might help the formation of predisposed co-ordination sites, favouring pseudo-tetrahedral complexes. Indeed, the film obtained after CN^- treatment can be readily re-metallated in the presence of $[(Cu(MeCN)_4]^+[BF_4]^-$, as demonstrated by the reappearance of the Cu^{II}/Cu^{I} couple [curve 3, Figure 2(b)].

The behaviour of the film obtained by demetallating Cu^+–PP is surprisingly different from that of dpp–PP. Whereas the former can easily be remetallated, the dpp–PP film obtained from (**1**) does not seem to display co-ordinating ability for transition metals.

We thank the C.N.R.S. for financial support (A.R.C. 'Electrodes Modifiées par des Polymères Organiques Conducteurs Fonctionnalisés').

Received, 7th December 1987; Com. 1759

References

1 (a) M. V. Rosenthal, T. Skotheim, and J. Warren, *J. Chem. Soc., Chem. Commun.*, 1985, 342; (b) A. Haimerl and A. Merz, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 180; (c) G. Bidan, A. Deronzier, and J. C. Moutet, *J. Chem. Soc., Chem. Commun.*, 1984, 1185; (d) P. Audebert, G. Bidan, and M. Lapkowski, *ibid.*, 1986, 887; (e) J. G. Eaves, H. S. Munro, and D. Parker, *Synth. Methods*, 1986, **16**, 123.

2 (a) G. Bidan, A. Deronzier, and J. C. Moutet, *Nouv. J. Chim.*, 1984, **8**, 501; (b) S. Cosnier, A. Deronzier, and J. C. Moutet, *J. Electroanal. Chem.*, 1986, **198**, 187; (c) J. G. Eaves, H. S. Munro, and D. Parker, *J. Chem. Soc., Chem. Commun.*, 1985, 684; (d) J. G. Eaves, H. S. Munro, and D. Parker, *Inorg. Chem.*, 1987, **26**, 644; (e) S. Cosnier, A. Deronzier, and J. C. Moutet, *J. Electroanal. Chem.*, 1986, **207**, 315; (f) F. Daire, F. Bedioui, J. Devynck, and C. Bied-Charreton, *J. Electroanal. Chem.*, 1986, **205**, 309.

3 (a) C. O. Dietrich-Buchecker, J. P. Sauvage, and J. M. Kern, *J. Am. Chem. Soc.*, 1984, **106**, 3043; (b) C. O. Dietrich-Buchecker, J. M. Kern, and J. P. Sauvage, *J. Chem. Soc., Chem. Commun.*, 1985, 760.

4 (a) A. Edel, P. A. Marnot, and J. P. Sauvage, *Nouv. J. Chim.*, 1984, **8**, 495; (b) J. M. Kern and J. P. Sauvage, *J. Chem. Soc., Chem. Commun.*, 1987, 546.

5 C. O. Dietrich-Buchecker and J. P. Sauvage, *Tetrahedron Lett.*, 1983, **46**, 5091.

6 G. Bidan and M. Guglielmi, *Synth. Methods*, 1986, **15**, 49.