

Supramolecular architecture consisting in Π -conjugated polymetallorotaxane.

P.-L. Vidal¹, C. Borel, V. Lamy, B. Divisia-Blohorn¹, G. Bidan¹, F. Genoud¹, J.-M. Kern² and J.-P. Sauvage²

¹ UMR 5819 CEA/CNRS/Univ- J. Fourier, CEA Grenoble, F-38054 Grenoble cedex 9, France.

² UMR 7513 CNRS, Institut Le Bel, Université Louis Pasteur, F-67000 Strasbourg cedex, France.

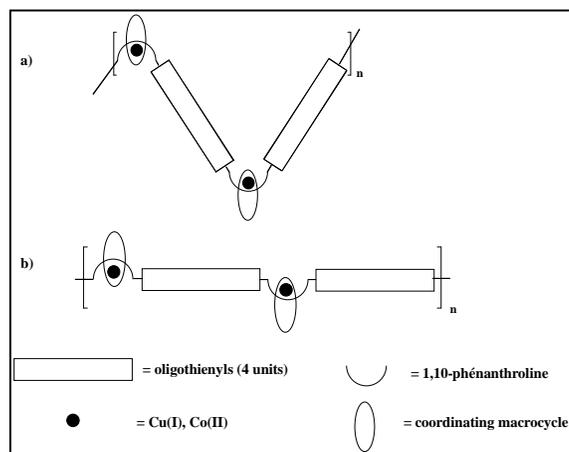
In the past few years, many efforts have been devoted to the elaboration of **hybrid materials containing transition metal centers directly connected to the conjugated polymer backbone** in the aim to mix the classical properties of organic conjugated polymers (extended electronic transport) with those of transition metal complexes (catalytic properties, magnetism, redox properties or photoactivity) and this resulted in some **new properties for the hybrid system**. Indeed, metal centres have been shown to enhance photoconductivity, photorefractivity or contribute in some cases to the conductivity of the conjugated architecture (**cooperative effect**).

On the other hand, rotaxanes-cyclic molecules threaded by linear fragments-have been intensively studied, especially in terms of photoinduced electron transfer and electro- or photochemically driven molecular motions.

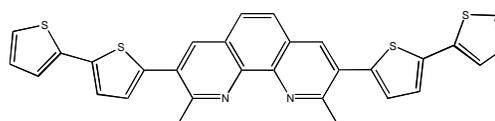
Electropolymerisation of a pseudo rotaxane precursor is a elegant way to elaborate films of conducting polymetallorotaxanes.¹ In this communication, we relate works with U-shaped or linear 1,10-phenanthroline directly connected to electro-polymerizable thienyl derivatives, in an effort to control better the structure and to improve electronic coupling between the rotaxane coordinating site and the conjugated backbone. Supramolecular architectures that consist of conjugated polymer wires, which have alternating oligothiényl moieties with well-defined lengths and phenanthroline complexing sites are obtained using a three-dimensional assembling and templating effect of copper (I) and this is followed by electropolymerisation of the assembled precursor. By this way two types of structures of polymetallorotaxane are obtained when the acyclic U-shaped or linear fragments thread through the coordinating ring (**scheme 1**).

The U-shaped polymetallorotaxanes include only Cu (I). Copper (I) binding was reversible only if lithium cation was present during copper removal, as a labile scaffolding, maintaining the topography of the free coordinating sites and of the organic matrix. In the other hand, the linear polymetallorotaxanes can incorporate new metallic centres such as cobalt (II) or zinc (II) leading to new hybrid materials (**scheme 2**). Similarly to U-shaped ligands, in situ conductivity measurements performed on these new linear ligands show clearly that copper contributes to the conductivity of the structure.

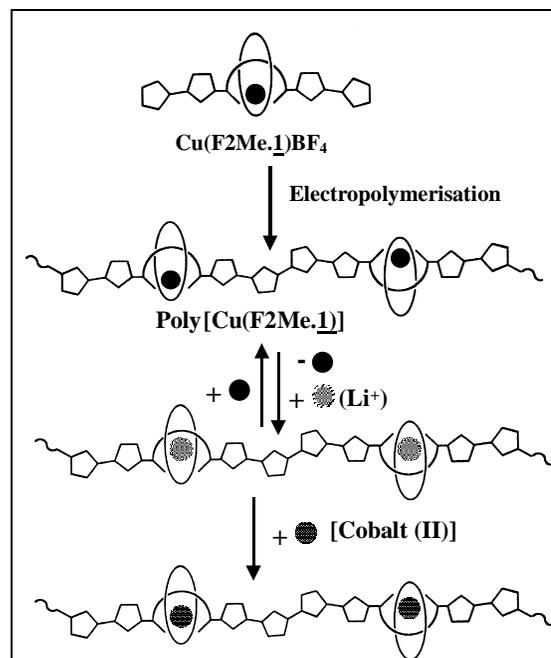
In the case of $\text{Cu}(\text{F2Me.1})\text{BF}_4$, the different states responsible of its conductive properties have been characterise by in situ ESR spectroelectrochemistry.



Scheme 1 : design of the U-shaped or linear shaped polymetallorotaxanes .



F2Me



Scheme 2. Reversible complexation into the linear polyrotaxane with exchange of Cu(I) centres with Co(II) centres. The successive steps are the assembling of the precursor $\text{Cu}(\text{F2Me.1})$ then electrodeposition of the polymer film $\text{poly}[\text{Cu}(\text{F2Me.1})]$ and exchange of Cu(I) by Co(II) through the intermediate Li^+ scaffolded complex.

¹ Vidal, P. L.; Divisia-Blohorn, B.; Bidan, G.; Hazemann, J. L.; Kern, J. M.; Sauvage, J. P. *Inorg. Chem.* **1999**, *38*, 4203.