Conjugated polyrotaxanes containing coordinating units: reversible copper(I) metallation–demetallation using lithium as intermediate scaffolding

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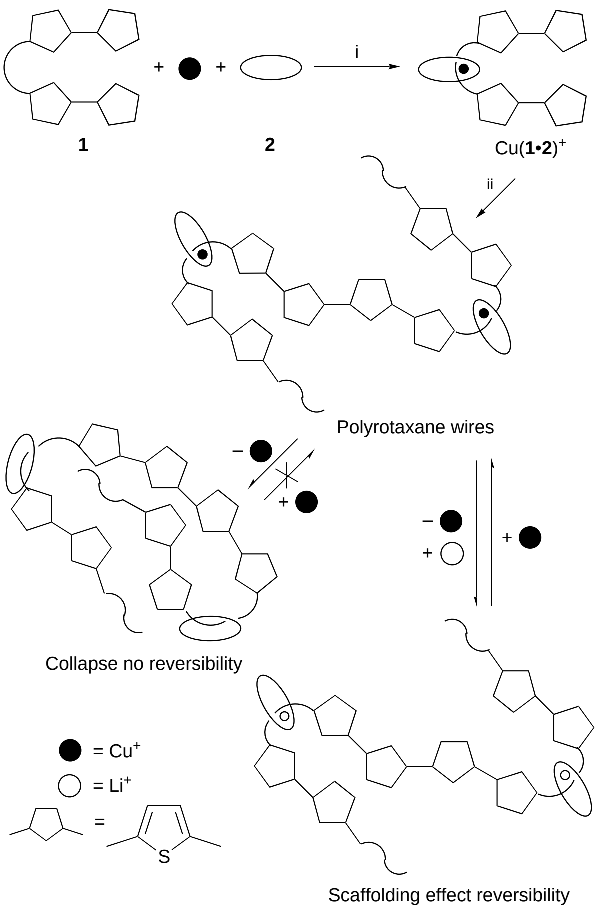
A new polyrotaxane containing a conjugated backbone has been synthesized *via* a copper(I) template and electropolymerisation; after decomplexation of Cu^I, remetallation is only possible if lithium is present during copper removal, as labile scaffolding able to prevent collapse of the free coordination sites and of the organic matrix.

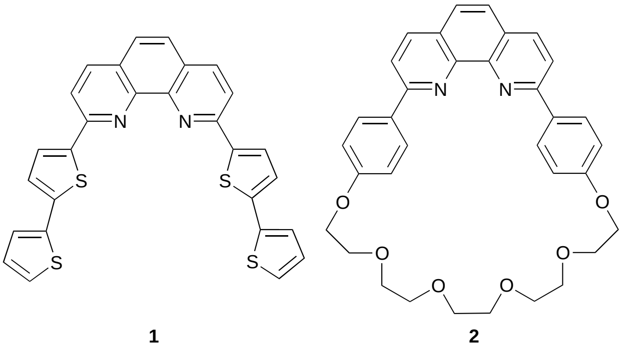
Functionalised conducting polymers obtained by electropolymerisation of pyrrole or thiophene derivatives represent an important family of organic materials.[1] In parallel, rotaxanes have attracted much attention, in relation with photoinduced electron transfer[2] and electro- or photo-chemically driven molecular motions.[3–5]

Recently, the synthesis of a polymetallorotaxane[6] with a conjugated rod threaded through coordinating 30-membered rings has been reported, following a strategy similar to previous works from one of our groups.[7] This report prompts us to disclose our own results and we would like to describe a new coordinating polyrotaxane, with a conjugated $-(\text{phen–tph})-_n$ backbone (phen = 1,10-phenanthroline, tph = thiophene) and its demetallation–remetallation behaviour.

As indicated in Scheme 1, the Cu^I template used to assemble the fragments of the precursor could be removed but, interestingly, subsequent remetallation was only possible if lithium was present during demetallation. The function of lithium is assumed to be that of an ionic scaffolding, maintaining the topography of the coordination site after copper removal, though forming a labile complex.



Scheme 1 i, Threading step; ii, electropolymerisation



Scheme 2

The molecules used are depicted in Scheme 2. The bithienyl-2,9 disubstituted compound **1**† was chosen as the key ligand and the dpphen-containing macrocycle **2**[8] (dpphen = 2,9-diphenyl-1,10-phenanthroline) as its partner for complexation (Scheme 1). The reaction between **2** and a slight deficit of $[Cu(MeCN)_4]BF_4$ followed by addition of **1** in CH_2Cl_2–MeCN at room temperature led to the intertwined heteroleptic copper complex $[Cu(\mathbf{1}\cdot\mathbf{2})]BF_4$ in 95% yield after purification by column chromatography. Analytical and spectroscopic data of this dark red, stable complex confirmed its structure.‡ Cyclic voltammetry (CV) of a 2×10^{-3} mol dm^{-3} complex solution in CH_2Cl_2–0.3 mol dm^{-3} $NBu^n{}_4PF_6$ showed a one electron reversible wave ($E_{1/2}$ = 0.51 V *vs.* 0.01 mol dm^{-3} Ag^+/Ag) corresponding to the redox reaction Cu^{II}–Cu^I.§

Electropolymerisation on a platinum electrode (S = 0.07 cm^2, Q = 26 mC cm^{-2}) by continuous cycling of this solution between −0.2 and +1.4 V led to the deposition of a thin red–orange film, characterized by CV measurements [Fig. 1(*a*)]. The presence of the Cu^I template is evidenced by the unchanged potential value compared to the monomer. A partial loss of reversibility was observed for this response, but at a slower potential sweep rate (10 mV s^{-1}), the ΔE_p value observed (20 mV) is typical of immobilized electroactive systems. The response between 0.8 and 1.4 V consists of two well defined waves, in agreement with the electrochemical behaviour of end-capped tetrathienylenes,[9] which confirms the electrochemical coupling of the terminal bithienyl units.

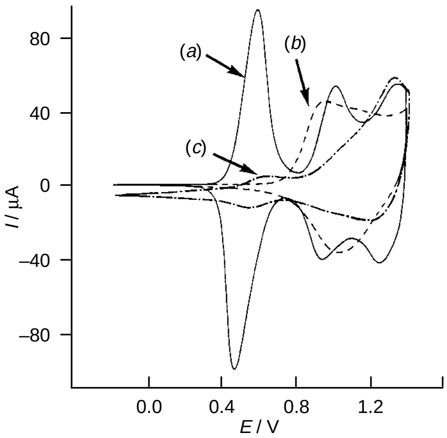


Fig. 1 Cyclic voltammetry in CH_2Cl_2 + 0.3 mol dm^{-3} $NBu^n{}_4PF_6$ (v = 50 mV s^{-1}) of (*a*) a freshly prepared poly[Cu(**1**·**2**)$^+$] film (solid line), (*b*) after dipping (20 min) in a 0.1 mol dm^{-3} $NBu^n{}_4CN$ MeCN solution (dashed line) and (*c*) after dipping (4 h) in a 0.1 mol dm^{-3} $[Cu(MeCN)_4]BF_4$ MeCN solution (dot–dashed line)

On treating this film with the strong copper complexing agent CN^-, the signal due to the metallic centre disappeared, whereas those due to the oligothienyl wires dramatically changed with total loss of resolution [Fig. 1(*b*)]. The collapse of the polyrotaxane network was confirmed by the non-reincorporation of Cu^I [Fig. 1(*c*)] or other metallic centers.

Dipping another film freshly prepared under the same conditions in a 0.1 mol dm^{-3} Li^+ + 0.1 mol dm^{-3} CN^- MeCN solution resulted again in complete loss of the copper response but in this case a partial conservation of resolution of the oligothienyl response was observed [Fig. 2(*b*)], which could be attributed to the scaffolding effect induced by Li^+ complexation. Conservation of the topography of the network was spectacularly evidenced by the nearly quantitative reincorporation of Cu^I species [Fig. 2(*c*)] (shown by determination of the ratio of current quantities corresponding respectively to the metallic and the oligothienyl redox systems), probably due to a Li^+/Cu^+ exchange. The strong anodic shift (140 mV) of the electrochemical response of the wire when copper centres are present could be attributed to copper–phenanthroline interactions which induce an electroattracting effect onto the oligothienyl moiety.

Reversibility of this demetallation–remetallation process is strongly dependent on the ratio $r = [Li^+]/[CN^-]$ (with $[CN^-]$ = 0.1 mol dm^{-3}) during the demetallation process: for r = 0.1, reincorporation of Cu^I is slower and of 80% compared to the case r = 1, with a loss of reversibility for both the metallic center and the oligothienyl wires, whereas for r = 0.01, collapse of the structure was observed.

In situ conductivity measurements are underway to evaluate the electronic properties of our conjugated structure.

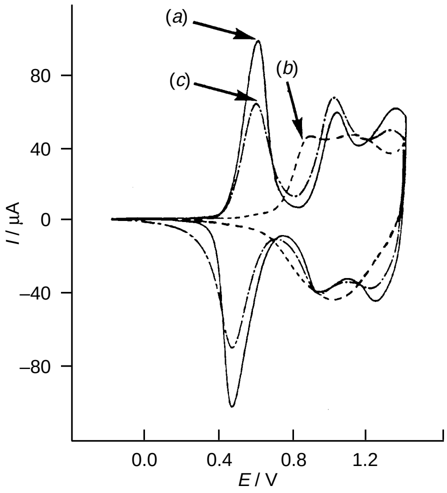


Fig. 2 Cyclic voltammetry in CH_2Cl_2 + 0.3 mol dm^{-3} $NBu^n{}_4PF_6$ (v = 50 mV s^{-1}) of: (*a*) a freshly prepared poly[Cu(**1**·**2**)$^+$] film (solid line), (*b*) after dipping (20 min) in a 0.1 mol dm^{-3} $LiClO_4$ + 0.1 mol dm^{-3} $NBu^n{}_4CN$ MeCN solution (dashed line) and (*c*) after dipping (3 h) in a 0.1 mol dm^{-3} $[Cu(MeCN)_4]BF_4$ MeCN solutionn (dot–dashed line)

Notes and References

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† **1** was prepared in two successive additions of a cold solution (0 °C) of 5-lithio-2,2′-bithiophene: first, onto a THF solution of 1,10-phenanthroline maintained at room temp. and then on the resulting 2-[5-(-2,2′bithienyl)]-1,10-phenanthroline. Each step was followed by hydrolysis and reoxidation with MnO_2.[8] 5-Lithio-2,2′-bithiophene itself was prepared by reacting at −78 °C 1 equiv. of LDA with bithiophene dissolved in THF. After addition of the base, the solution was raised to 0 °C. Overall yield: 18%. Attempts to obtain **1** in a single step were unsuccessful. ^1H NMR (CD_2Cl_2, 400 MHz): δ 8.20 (d, 2 H), 7.95 (d, 2 H), 7.74 (d, 2 H), 7.70 (s, 2 H), 7.42 (dd, 2 H), 7.29 (dd, 2 H), 7.27 (d, 2 H), 7.09 (dd, 2 H).

‡ ^1H NMR (CD_2Cl_2, 400 MHz): δ 8.54 (d, 2 H), 8.42 (d, 2 H), 8.17 (s, 2 H), 7.91 (s, 2 H), 7.89 (d, 2 H), 7.86 (d, 2 H), 7.32 (d, 4 H), 7.24 (d, 2 H), 7.10 (dd, 2 H), 6.78 (dd, 2 H), 6.65 (d, 2 H), 6.17 (dd, 2 H), 5.96 (d, 4 H), 3.85–3.40 (m, 20 H). FABMS: *m/z* 1137.2 ($[M - BF_4]^+$), 629.2 ([M − **1** − $BF_4]^+$), 570.9 ([M − **2** − $BF_4]^+$), 509.0 ([**1**H]$^+$).

§ $E_{1/2}$ (ferrocene) = 0.18 V *vs.* our reference electrode Ag^+/Ag. $E_{1/2}$ = 0.48 V for a 10^{-3} mol dm^{-3} solution of $Cu(dap)_2{}^+$ in the same supporting electrolyte [dap = 2,9-di(*p*-anisyl)-1,10-phenanthroline].

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