# Conjugated polyrotaxanes: improvement of the polymer properties by using sterically hindered coordinating units

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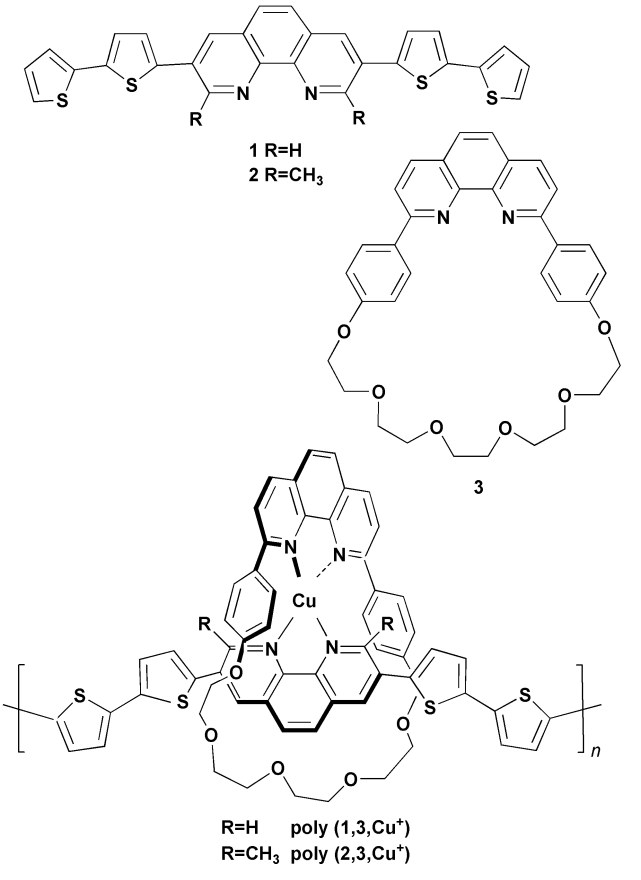
A new conjugated copper-complexed polyrotaxane has been prepared by electropolymerization of a thiophene derivative; the rings are threaded onto a multi-1,10-phenanthroline (phen) axle, copper(I) acting as a template. The presence of $CH_3$ groups *ortho* to the nitrogen atoms of the phen nuclei belonging to the conjugated backbone has a profound effect on the stability of the polymer, on its electrochemical properties and on its ability to be remetallated once the template metal centre (copper(I)) has been removed.

Polyrotaxanes represent a new class of macromoleclar systems, whose synthesis has been greatly facilitated by the introduction of templated strategies based on organic[1] or inorganic[2,3] cores used as templates. Among the numerous materials elaborated and studied, conjugated polyrotaxanes are particularly promising. They represent a subclass of conjugated polymers[4] and they may find applications in relation to sensors,[5] conducting and light-emitting materials,[6] and electrocatalysis.[7]

In recent work, Swager *et al.*[2] as well as our groups[8] have shown that copper(I)-complexed rotaxanes functionalized by appropriate electropolymerizable groups are convenient precursors. We would now like to describe a new system for which (i) the conjugated backbone is linear (connections at the 3 and 8 positions of the phen unit) and (ii) the chelating unit is functionalized by methyl groups located at the *ortho* positions to the N atoms. The first parameter (i) endows the polymer with better conjugation than the U-shaped chelates originally used by us (2,9-disubstituted 1,10-phenanthroline) and the second one (ii) ensures very high stability of the tetrahedral complexes and reversibility of demetallation/remetallation. For the sake of comparison, the materials containing 1,10-phenanthroline with no substituents on the 2 and 9 positions have also been made and investigated (see Scheme 1).

Compound **1** was prepared in 74% yield from 3,8-dibromo-1,10-phenanthroline[9] and 5-trimethylstannyl-2,2′-bithiophene[10] in DMF at 120 °C, using *in situ* generated $Pd(0)(PPh_3)_2$ as catalyst. **1** was converted to **2** using MeLi in THF, following a procedure derived from that of a recently reported reaction.[11] **2** was obtained in 54% yield from **1** as an orange solid. The macrocyclic ligand **3** was prepared according to a classical procedure.[12] The synthesis of the copper(I) complexes used as precursors was carried out in the usual way by adding $Cu(CH_3CN)_4BF_4$ to the stoichiometric amount of **3**, followed by addition of one equivalent of the linearly substituted phen, **1** or **2**. A deep red solution was obtained which contains essentially pure $(\mathbf{1}, \mathbf{3}, Cu)^+$ or $(\mathbf{2}, \mathbf{3}, Cu)^+ \cdot BF_4^-$ respectively. The copper complexes were chromatographed (silica) to afford light and air stable solids. These two precursors have been characterized by ESMS, UV-vis spectroscopy and $^1H$ NMR. The latter method is particularly informative and




**Scheme 1** Threads **1** and **2**, and ring **3**, constitutive elements of the polyrotaxanes poly$(\mathbf{1}, \mathbf{3}, Cu)^+$ and poly$(\mathbf{2}, \mathbf{3}, Cu)^+$.

demonstrated in a non-ambiguous fashion the threaded nature of the complexes. Indeed, a strong upfield shift of the doublets corresponding to the $H_m$ protons (Scheme 1) of the macrocycle **3** ($\Delta\delta = -1.29$ ppm for $(\mathbf{1}, \mathbf{3}, Cu)^+ \cdot BF_4^-$ and $\Delta\delta = -1.24$ ppm for $(\mathbf{2}, \mathbf{3}, Cu)^+ \cdot BF_4^-$) is observed. This shielding effect is

characteristic of entwined 2,9-diaryl-1,10-phenanthroline complexes[13] and is due here to the spatial proximity of the phenyl group of the coordinating macrocyclic subunit **3** to the phenanthroline core of the thread **1**.

Electropolymerization of (**1**, **3**, Cu)$^+$ or (**2**, **3**, Cu)$^+$ was performed following a previously described experimental protocol.[8,14] The films were grown on a Pt disk, by scanning the potential between −0.1 V or −0.2 V and 1.05 or 1.20 V *vs* a $Ag^+/Ag$ reference electrode[14] for (**1**, **3**, Cu)$^+$ or (**2**, **3**, Cu)$^+$ respectively. From the first scan, the difference between both species is obvious. Whereas the non-methylated species (**1**, **3**, Cu)$^+$ leads to an irreversible peak at 0.28 V corresponding to the Cu(II)/Cu(I) couple, the more hindered complex (**2**, **3**, Cu)$^+$ results in a perfectly reversible peak centered at 0.52 V, also associated to the Cu(II)/Cu(I) couple. The various voltammograms obtained for (**2**, **3**, Cu)$^+$ are shown in Fig. 1.

The successive scans (−0.2 to 1.1 V) show, Fig. 1a, the simultaneous and continuous growth of the intensity of the anodic and cathodic peaks. The response of the copper centre (around 0.52 V) is accompanied by two other reversible peaks, evidencing the deposition of an electroactive material on the Pt electrode. The same experiment conducted with (**1**, **3**, Cu)$^+$ (not shown) leads to a similar growth of the peaks associated with the polymer matrix (around 0.82 and 1.02 V) but the intensity of the Cu(II)/Cu(I) peak first decreases and then levels off after a few scans, indicating that substantial decomplexation occurs. Once deposited onto the electrode surface, the orange film of poly-(**2**, **3**, Cu)$^+$ was copiously washed ($CH_3CN$–$CH_2Cl_2$) and subjected to cyclic voltammetry (0.3 M $Bu_4NPF_6$ in $CH_2Cl_2$). As shown in Fig. 1b, the electrochemical response is clean, with three peaks corresponding to Cu(II)/Cu(I) (0.52 V; $\Delta Ep = 20$ mV at 10 mV $s^{-1}$) and to the polymer matrix (0.80 V and 1.04 V) respectively. The two matrix-localized electrochemical processes are assigned to the conjugated system generated by oxidative coupling of the bithiophene units during the electropolymerization processes. The ratio of the charge associated to the conjugated organic backbone over that corresponding to the copper centre is in agreement with a structure consisting of alternating copper(I) complex units and quaterthiophene fragments (1.25 electrons exchanged by oxidized quaterthiophene). Interestingly, this electrochemical response is significantly shifted towards cathodic potentials as compared to the analogous polymer for which the phen units of the backbone are substituted at the 2 and 9 position (0.96 V and 1,28 V). This observation points to an enhanced electronic delocalisation of the linear backbone in poly-(**2**, **3**, Cu)$^+$ *versus* that in the polymer containing U-shaped motifs.[8,14]

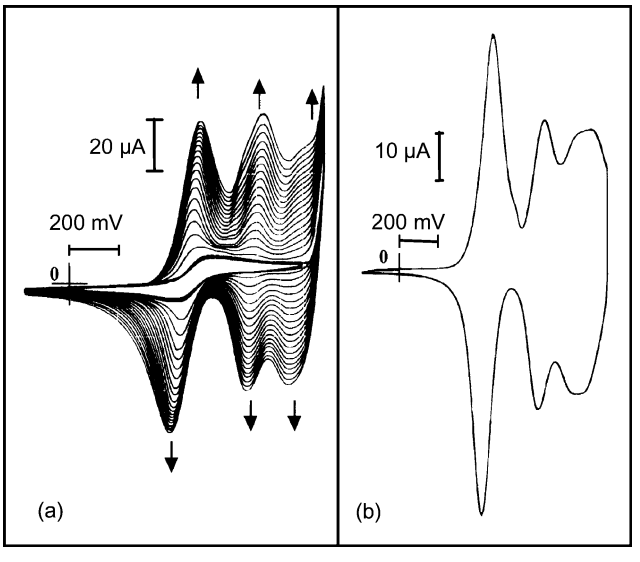



**Fig. 1** (a) Electropolymerization of (**2**, **3**, Cu)$^+$: evolution of the cyclic voltammetry curves by scanning repetitively (100 mV $s^{-1}$) the working electrode potential between −0.2 and 1.1 V in $CH_2Cl_2$–$Bu_4NPF_6$ (0.3 mol $L^{-1}$), Pt electrode, $Ag^+/Ag$ reference. (b) Cyclic voltammetry response of the film (50 mV $s^{-1}$) prepared in (a), after rinsing and dipping in a fresh electrolytic solution (same conditions as above).

An interesting feature of coordination conjugated polymers is their propensity to be reversibly demetallated and subsequently recomplexed to an appropriate metal. These reactions can easily be monitored by electrochemical measurements on the film. We have recently observed that the presence of $Li^+$ is indispensable for the process to be reversible with the U-shaped system.[15] $Li^+$ acts as a transitory scaffold, preventing the organic backbone (rings and macromolecular axle) from collapsing. The behaviour of poly-(**2**, **3**, Cu)$^+$ is particularly interesting in this respect. Even without $Li^+$, partial recoordination is observed after the copper(I) centres have been abstracted from their coordination sites, contrary to previously reported examples. Moreover, perfect reversibility is observed for the copper(I) decoordination/recoordination process in the presence of $Li^+$, as indicated in Fig. 2a. The coordination sites seem thus to be remarkably preserved from any deterioration thanks to the dual effect of the $CH_3$ groups and of $Li^+$.

The film in its uncomplexed form is obtained by dipping in an acetonitrile solution of $Bu_4NCN$ and $LiClO_4$. It can also be remetallated using another metal centre such as $Co^{2+}$. By immersing the film-bearing electrode obtained in a $Co(ClO_4)_2$ solution (0.1 mol $L^{-1}$; $CH_3CN$), clean incorporation of $Co^{2+}$ in the coordination sites is observed (Fig. 2b) as testified by the peak at −0.74 V, ascribed to the Co(II)/Co(I) couple.[3] On the other hand, the response of the polymer matrix (0.81 and 1.02 V) occurs at the same potentials as that of the copper-complexed film, evidencing the very weak electronic interaction between the quaterthiophene fragments of the backbone and the metal complex. In other words, the overall polymer chain is better conjugated in the present linear system than in the material containing U-shaped chelating units[8] but the communication between the metal complex core itself and the conjugated backbone is less pronounced. This in accordance with the limited coupling between groups attached onto the 3 and 8 positions of the phen nucleus (*meta* to the N atoms) and the metal binding site.

In conclusion, it has been shown that subtle substituent effects allow control of the electronic and complexation/decomplexation behaviour of conjugated polyrotaxanes. *In situ* conductivity measurements and ESR spectroelectrochemistry are underway to evaluate the electronic properties of these conjugated structures.

## Experimental

### Synthesis

Oxygen or water-sensitive reactions were conducted under a positive pressure of argon in oven-dried glassware, using Schlenk techniques. Common reagents and materials were purchased from commercial sources. The following materials were prepared according to literature procedures: 3,8-dibromo-1,10-phenanthroline,[9] 5-trimethylstannyl-2,2′-bithiophene,[10] **3**,[12] $Cu(CH_3CN)_4BF_4$.[16] Column chromatography was carried out on silica gel 60 (E. Merck, 70–230 mesh). $^1$H NMR spectra were obtained on either Bruker WP 200 SY (200 MHz) or AM 400 (400 MHz) spectrometers. Fast atom bombardment mass spectrometry (FAB MS) data were recorded in the positive ion mode with a xenon primary atom beam in conjunction with a 3-nitrobenzyl alcohol matrix and a ZAB-HF mass spectrometer. A VG BIOQ triple quadrupole spectrometer was used for the electrospray mass spectrometry measurements (ES-MS) also in the positive ion mode.

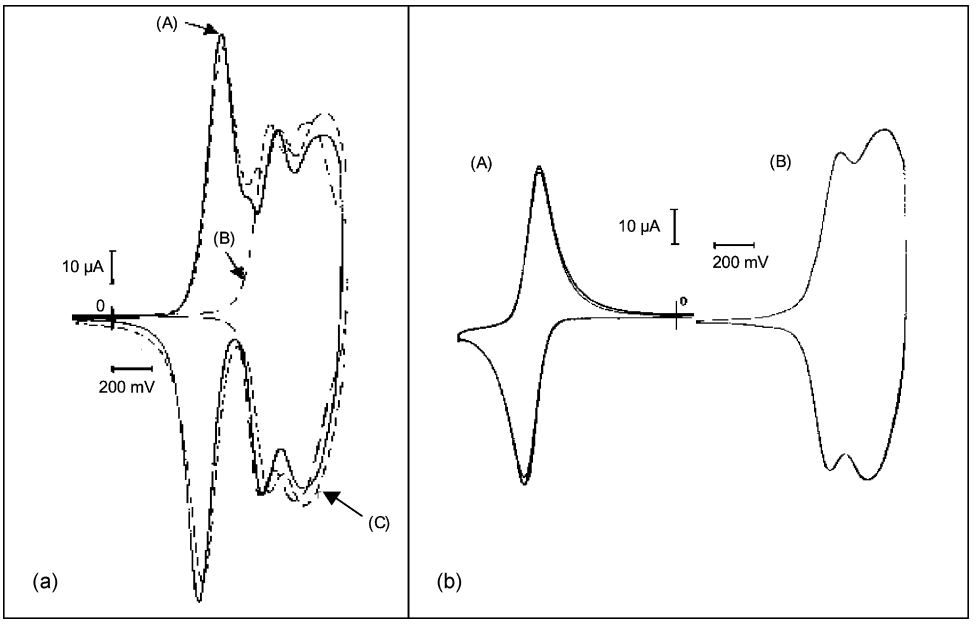



**Fig. 2** Cyclic voltammetry (100 mV $s^{-1}$) in $CH_2Cl_2$–$Bu_4NPF_6$ (0.3 mol $L^{-1}$), Pt electrode, $Ag^+/Ag$ reference of: (a) (A) a freshly prepared poly-(**2**,**3**,Cu)$^+$ film (solid line), (B) after dipping for 20 min in $CH_3CN$ [$Bu_4NCN + LiClO_4$] (0.1 mol $L^{-1}$) (dashed line) and (C) after dipping for one hour in $CH_3CN$ [$Cu(CH_3CN)_4BF_4$] (0.1 mol $L^{-1}$) (dot and dashed line); (b) a poly-(**2**,**3**,Cu)$^+$ film after dipping for 20 min in $CH_3CN$ [$Bu_4NCN + LiClO_4$] (0.1 mol $L^{-1}$) followed by dipping for one hour in $CH_3CN$ $Co(ClO_4)_2(H_2O)_6$ (0.1 mol $L^{-1}$): (A) three successive cathodic scans, (B) second anodic scan.

**3,8-Bis(2,2′-bithien-5-yl)-1,10-phenanthroline 1.** A solution of Pd(II)$(Ph_3)_2Cl_2$ (76 mg, 0.11 mmol) in THF (2 mL) is cooled in a dry ice/acetone bath, and n-butyllithium is added (110 μL of a 2 mol $L^{-1}$ solution in cyclohexane, 0.22 mmol). The colour turns rapidly from yellow to blue-black. After 15 min stirring, the cooling bath is removed. By using the cannula transfer technique, this solution is added to a solution of 3,8-dibromo-1,10-phenanthroline (390 mg, 1,15 mmol) and 5-trimethylstannyl-2,2′-bithiophene (920 mg, 2,70 mmol) in 50 mL DMF. The reaction mixture is heated for 15 h at 120 °C. The DMF is then evaporated and the crude residue, without further treatment, is deposited onto a silica gel column. Elution with $CH_2Cl_2$–MeOH (0 to 5% v/v) allows the isolation of 430 mg of **1** (74% yield). $^1$H NMR (400 MHz, $CD_2Cl_2$) $\delta$ 9.38 (d, 2H), 8.36 (d, 2H), 7.84 (s, 2H), 7.54 (d, 2H), 7.34–7.28 (m, 4H), 7.26 (d, 2H), 7.08 (dd, 2H). ESMS $m/z$ 509.4 [$MH^+$]. UV-vis ($CH_2Cl_2$) $\lambda_{max}$/nm (log$\varepsilon$) 312 (4.36), 404 (4.80), 425(sh) (4.72).

**Synthesis of 2,9-dimethyl-3,8-bis(2,2′-bithienyl-5-yl)-1,10-phenanthroline 2.** 120 mg (236 μmol) of **1** are suspended in 10 mL THF. Methyllithium (930 μL of a 1.4 mol $L^{-1}$ solution in ether) is added at room temperature. The colour turns immediately to black. After 65 h stirring at room temperature, 10 mL of a saturated solution of $NH_4Cl$ in water are added, and the solvents evaporated. The remaining aqueous slurry is extracted with $CH_2Cl_2$. The combined organic fractions are then treated with $MnO_2$ (750 mg, added over 1 h). After drying over $MgSO_4$, filtration over celite, evaporation of the solvent and chromatography over silica gel ($CH_2Cl_2$–MeOH, 0 to 5% v/v), 69 mg of pure 2,9-dimethyl-3,8-bis(2,2′-bithienyl-5-yl)-1,10-phenanthroline are recovered as an orange solid (54% yield). $^1$H NMR (400 MHz, $CD_2Cl_2$) $\delta$ 8.22 (s, 2H), 7.73 (s, 2H), 7.30–7.16 (m, 8H), 7.02 (dd, 2H), 3.01 (s, 6H). ESMS $m/z$ 537.3 [$MH^+$]. HRMS calcd. for $C_{30}H_{20}N_2S_4$ 537.0587, found 537.0601. UV-vis ($CH_2Cl_2$) $\lambda_{max}$/nm (log$\varepsilon$) 315 (4.76), 375 (4.89).

**Preparation of threaded complex (1, 2, Cu)·$BF_4$.** By the cannula transfer technique, $Cu(CH_3CN)_4BF_4$ (13 mg, 40 μmol) in degassed acetonitrile (5 mL) was added under argon and at room temperature to a stirred degassed pale yellow solution of **3** (23 mg, 40 μmol) in $CH_2Cl_2$ (5 mL). A deep orange coloration appeared immediately. After 15 min at room temperature, a solution of thread **1** (18.8 mg, 37 μmol) in $CH_2Cl_2$ (5 mL) was added to the solution which immediately turned dark red. After the solution was stirred for 30 min under argon at room temperature, the solvents were removed under vacuum and the product redissolved in $CH_2Cl_2$, then washed with $H_2O$ containing a small amounts of ascorbic acid. Filtration (silica gel, 5% MeOH/$CH_2Cl_2$) gave the desired product (45 mg, 95%) as a dark red powder. $^1$H NMR (400 MHz, $CD_2Cl_2$) $\delta$ 8.71 (s, 2H), 8.68 (d, 2H), 8.43 (s, 2H), 8.21 (s, 2H), 8.16 (s, 2H), 8.14 (d, 2H), 7.47–7.44 (m, 6H), 7.32 (d, 2H), 7.29–7.26 (m, 4H), 7.07 (dd, 2H), 5.93 (d, 4H), 3.90–3.40 (m, 20H). ESMS $m/z$ 1137.1 $[M - BF_4]^+$, 629.4 $(M - \mathbf{1} - BF_4]^+$. HRMS calcd. for $C_{62}H_{50}N_4O_6S_4Cu$ 1137.1909, found 1137.1885. UV-vis ($CH_2Cl_2$) $\lambda_{max}$/nm (log$\varepsilon$) 285(4.76), 330 (4.71), 422(4.76) 550 (sh)(3.30).

**(1, 3, Cu)·$BF_4$.** Using the same procedure, (**2**, **3**, Cu)·$BF_4$ was prepared in 85% yield. $^1$H NMR (400 MHz, $CD_2Cl_2$) $\delta$ 8.69 (d, 2H), 8.56 (s, 2H), 8.19 (s, 2H), 8.15 (s, 2H), 8.14 (d, 2H), 7.47 (d, 4H), 7.35–7.25 (m, 6H), 7.17 (d, 2H), 7.09 (dd, 2H), 5.98 (d, 4H), 3.90–3.20 (m, 20H), 2.35 (s, 6H). ESMS $m/z$ 1165.4 $[M - BF_4]^+$, 629.3 $(M - \mathbf{2} - BF_4]^+$. HRMS calcd. for $C_{64}H_{54}N_4O_6S_4Cu$ 1165.2222, found 1165.2201. UV-vis ($CH_2Cl_2$) $\lambda_{max}$/nm (log$\varepsilon$) 290 (4.79), 305 (4.77), 330 (4.80), 375 (sh)(4.64), 400 (sh)(4.57), 550 (sh)(3.30).

## Electrochemistry

Electrochemical syntheses and studies were performed in a dry-box under an argon atmosphere using a PAR 273 A from EG&G Princeton Applied Research and with a typical three-electrode cell. All the electrochemical experiments were carried out in a 3-electrode cell with a $Ag^+/Ag$ reference electrode (silver wire dipped in a $10^{-2}$ mol $L^{-1}$silver nitrate solution with 0.1 M $Bu_4NPF_6$ in $CH_3CN$). Potentials were relative to this 0.01 mol $L^{-1}$ $Ag^+/Ag$ reference electrode ($E_{1/2}$(ferrocene) = 0.18 V and $E_{1/2}$(Cu(dap)$_2$$BF_4$) = 0.48 V *vs* this reference for $10^{-3}$ mol $L^{-1}$ solutions in the same supporting

electrolyte). The electrolyte solutions used were all 0.3 mol $L^{-1}$ n-$Bu_4NPF_6$ in $CH_2Cl_2$. A 0.07 $cm^2$ platinum electrode was used as working electrode. Electrosyntheses of the polyrotaxane films were performed from $2 \times 10^{-3}$ mol $L^{-1}$ monomer solutions by continuous cycling between $-0.1$ V or $-0.2$ V and 1.05 or 1.20 V for (**1**, **3**, Cu)$^+$ or (**2**, **3**, Cu)$^+$ respectively, at $v = 50$ mV $s^{-1}$. The films obtained were then copiously washed with fresh $CH_2Cl_2$ before cycling. For demetallation experiments, cyanide solutions were made from n-$Bu_4NCN$ dissolved in $CH_3CN$ and lithium/cyanide solution from stoichiometric amounts of n-$Bu_4NCN$ and $LiClO_4$ dissolved in $CH_3CN$. The films were dipped for 20 min in one of these solutions and washed with $CH_3CN$, then with $CH_2Cl_2$ before cycling. Remetallation with copper was performed by dipping the films for one hour in a copper(I) solution made from $Cu(CH_3CN)_4BF_4$ dissolved in $CH_3CN$, followed by copious rinsing with fresh $CH_3CN$ and, subsequently, by $CH_2Cl_2$. The metallation with cobalt was done in a similar manner by dipping films for one hour in a $10^{-1}$ mol $L^{-1}$ $Co(BF_4)_2$ acetonitrile solution.

## Acknowledgements

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