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The electrochemical polymerisation of a [2]rotaxane

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Abstract—We report the synthesis of a dithienylpyrrole-stoppered rotaxane and its subsequent electrochemical polymerisation onto a platinum working electrode surface. We have shown that the tetracationic cyclophane moiety of the rotaxane does not impair electropolymerisation of this derivative. Indeed, functionalised films can be conveniently prepared by oxidative polymerisation of the dithienylpyrrole stopper units, to yield a network of rotaxane units interconnected by a conducting polymer backbone.

Interlocked structures fabricated from the electron deficient cyclophane cyclobis(paraquat-*p*-phenylene) ($CBPQT^{4+}$)[1] and a variety of electron rich guests have arguably become one of the most important building blocks for the synthesis of functional rotaxanes and catenanes.[2] In the recent years, there has been significant interest in transferring these systems from solution to the solid-state, where their ability to function coherently has allowed the fabrication of novel molecular machines and devices.[3] For the majority of these systems, this transferral has been achieved by the self-assembly of appropriately functionalised systems onto solid substrates. However, the self-assembly process usually provides only a method of surface attachment, and does not significantly augment the solution-state properties of these systems. Electropolymerisation of the components onto surfaces, on the other hand, not only provides a method for surface deposition, but also provides a conjugated backbone with interesting electrical and optical properties that could electronically link the components of the film.[4] Here, we report the synthesis of dithienylpyrrole-stoppered rotaxane **3** and its electrochemical polymerisation onto a platinum working electrode surface.

Rotaxane **3** was synthesised from axle derivative **2** using the clipping methodology shown in Scheme 1. ^1H NMR spectra of **3** performed in CD_3SOCD_3 were in accordance with data reported for related [2]rotaxanes.[5] For example, significant upfield shifts in the resonances of the 1,5-dialkyloxynaphthalene protons of **3** were observed (compared to the same protons of **2**), which are characteristic of shielding effects resulting from inclusion within the cavity of $CBPQT^{4+}$. UV–vis spectroscopy performed on purple rotaxane **3** revealed a broad absorption around 546 nm, which is in accordance with pseudorotaxane/rotaxane architectures of this type.[6] MALDI mass spectrometry gave rise to a molecular ion in accordance with the proposed structure of **3** (m/z 2103 $[M]^+$).

Cyclic (CV) and square wave voltammetry (SWV) experiments were performed on derivative **3** in DMSO and gave rise to two reduction waves corresponding to the sequential reduction of the tetracationic cyclophane moiety to its diradical dication state and then to its fully reduced state.[7] When the SWV data were compared to that of $CBPQT^{4+}$, the reduction wave for the first redox process of **3** was shifted by 124 mV to a more negative potential compared to this reduction wave for $CBPQT^{4+}$, whereas the second redox wave is largely unaffected (Fig. 1). Therefore, the data are consistent with a repositioning of the reduced cyclophane further along the axle following the electrochemical reduction of the cyclophane to its diradical dicationic state.

Keywords: Supramolecular chemistry; Rotaxane; Electropolymerisation; Electrochemistry.

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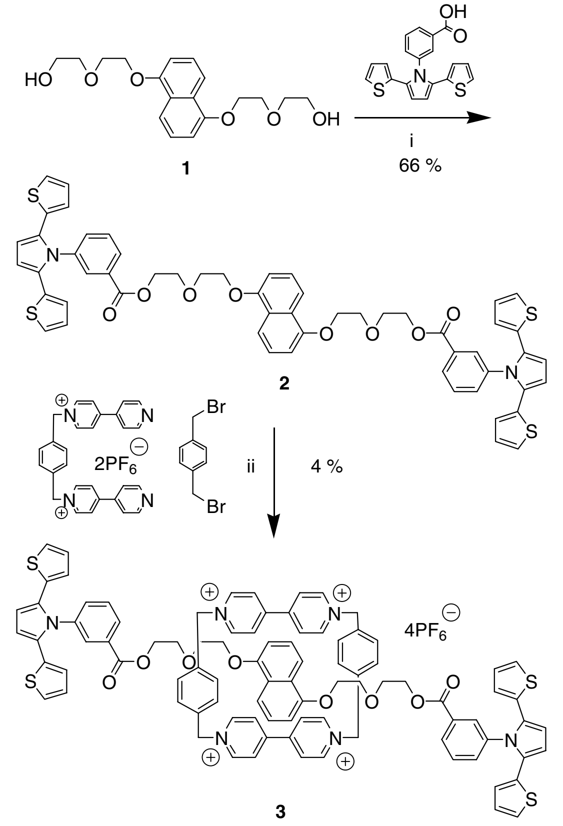

Scheme 1. Reagents and conditions: (i) EDCI, DMAP, DMF, 25 °C; (ii) (a) DMF, 25 °C, 2 weeks; (b) NH_4PF_6.

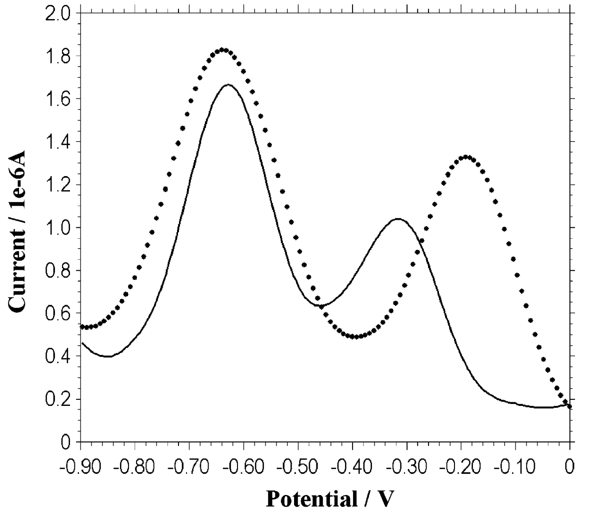

Figure 1. SWVs of rotaxane **3** (—) and $CBPQT^{4+}$ (•••) (6×10^{-5} M solution in DMSO).

With rotaxane formation confirmed for **3**, we turned our attention to whether this system could be electropolymerised onto an electrode surface. A major concern was that the positively charged cyclophane unit might hamper the electropolymerisation process by Coulombic repulsion between this unit and the growing polymer film. However, functionalised electrodes were readily formed by the oxidative electropolymerisation of **3** onto a platinum disc electrode (Fig. 2). It is noteworthy that solvent composition appeared to be a critical factor in determining whether polymerisation was observed. A 1:1 mixture of acetonitrile and toluene proved to be one of the best solvent combinations for readily detecting polymerisation onto the working electrode surface. Using this solvent combination, the electropolymerisation of **3** was readily observed by the formation of a new redox wave centred around +0.25 V due to the developing polymer film on the electrode surface. Similar electrochemical data were also obtained for axle **2**. Interestingly, the presence of the cyclophane appears to have negligible effect on the electropolymerisation process, as the position of the redox wave for the developing polymer films was virtually identical in both cases (Fig. 3).

After washing the functionalised working electrodes with copious amounts of acetone, and allowing the polymer films to dry in air, the electrodes were placed into a

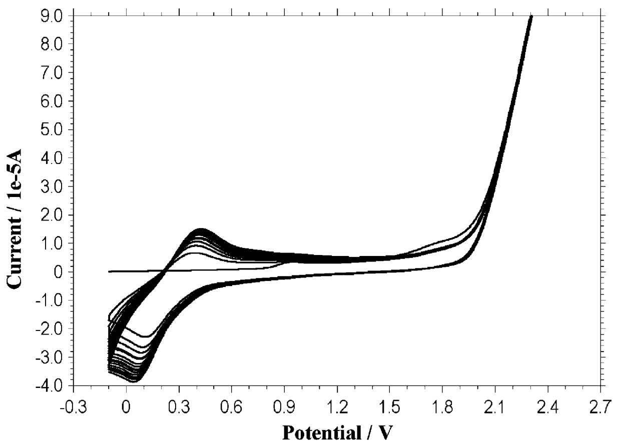

Figure 2. CV showing the electrochemical polymerisation of **3** from a 6×10^{-5} M solution in toluene/acetonitrile (1:1). The CV shows 16 cycles between −0.1 and +2.5 V. Scan rate = 0.5 V s^{-1}. $E_{1/2} =$ 0.25 V.

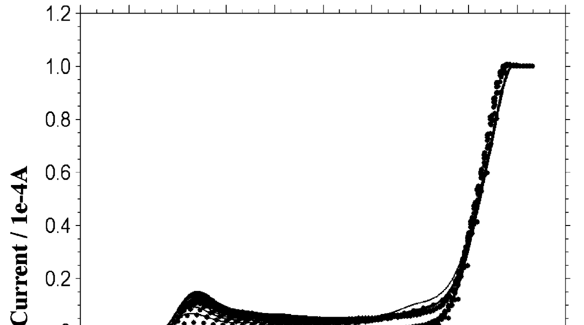

Figure 3. CVs showing the electrochemical polymerisation of **3** (—) and **2** (•••) from a 6×10^{-5} M solution in toluene/acetonitrile (1:1). Scan rate = 0.5 V s^{-1}.

0.1 M solution of Bu_4NPF_6 in acetonitrile/toluene (1:1) and the electrochemistry of the polymer backbone was investigated using CV. As for the earlier reported studies, the CVs showed that polymer films were deactivated by tetrabutylammonium ions being trapped within the polymer structure. Activation was achieved by scanning up to +2.5 V, which presumably causes the electrolyte to be expelled from the polymer, and results in the appearance of a redox wave centred around +0.2 V.[8] Interestingly, the cyclophane unit has a slight effect on the position of this redox wave when compared to the same redox processes for axle **2** (Fig. 4).

Using freshly prepared rotaxane-functionalised electrodes, we recorded the reductive scans between 0 and −1.0 V (Fig. 5). The polymerisation process gave rise to two redox waves, presumably due to the formation of the reduced states of the cyclophane moiety. A notable feature of these CVs was the relatively large peak current for the second reduction wave, which is presumably due to an overlapping redox wave for the polymeric backbone. To test this hypothesis, we recorded the reductive scans for electropolymerised films of **2**. The CVs indicated that an overlapping irreversible reduction wave does indeed occur in this region.

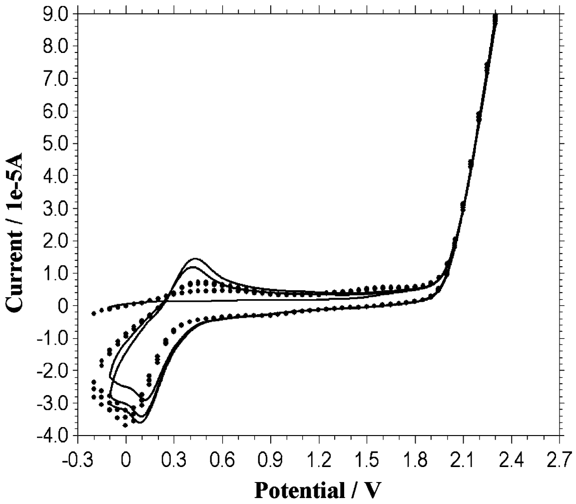

Figure 4. CV studies showing the oxidation of the electropolymerised films of **3** (—) and **2** (•••) in toluene/acetonitrile (1:1). Films were fabricated from a 6 × 10^{-5} M solution of **3** or **2** in acetonitrile/toluene. Scan rate = 0.5 V s^{-1}. $E_{1/2}$ of **3** = ~0.26 V and $E_{1/2}$ of **2** = ~0.22 V.

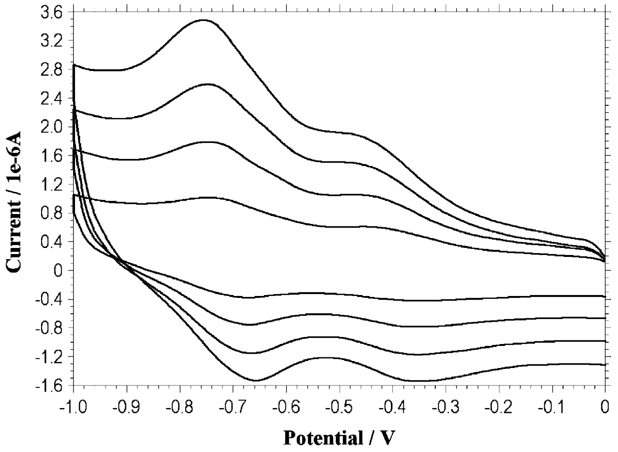

Figure 5. CV studies showing the reduction of the electropolymerised films of **3** in DMSO (1 V s^{-1} (largest peak current), 0.75, 0.5, 0.25 V s^{-1} (smallest peak current)). $E^1_{1/2} = -0.36$ V and $E^2_{1/2} = -0.68$ V. The films were fabricated by 16 cycles between −0.1 and +2.5 V in toluene/acetonitrile (1:1). Scan rate = 0.5 V s^{-1}.

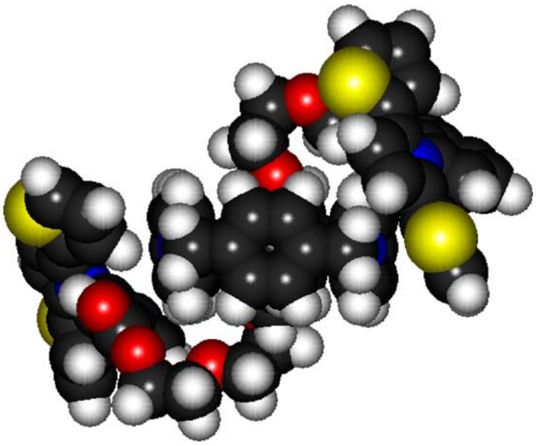

Figure 6. Energy minimised (MM+) structure of rotaxane **3**. Calculations performed using HyperChem Standard v. 5.1.

The reductive CVs of electropolymerised thin films of **3** recorded at different scan rates displayed a linear increase in current with scan rate for the cyclophane's reduction processes, which is indicative of surface-confined behaviour. The films proved to be reasonably stable, displaying a similar current/voltage response for more than 5 scan cycles. The estimated surface coverage Γ resulting from the electropolymerisation of **3** was 9 × 10^{-12} mol cm^{-2}.[9] This value is larger than the maximum coverage value of 1 × 10^{-12} mol cm^{-2}, estimated from the molecular mechanics-predicted molecular area of rotaxane **3** (169 Å^2, see Fig. 6). Therefore, the data are consistent with a multilayer film structure, presumably in the form of a three-dimensional cross-linked architecture.[10]

In conclusion, we have synthesised a new $CBPQT^{4+}$-based rotaxane that can be electropolymerised onto an electrode surface. We have shown that the tetracationic cyclophane moiety of **3** does not impair electropolymerisation of this derivative. Indeed, functionalised films can conveniently be prepared by oxidative polymerisation of the 2,5-dithienylpyrrole stopper units, to yield a network of rotaxane units interconnected by a conducting polymer backbone. Our investigations of the molecular electronics properties of this, and more elaborate electropolymerised rotaxane derivatives, will be reported in due course.

Acknowledgements

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Supplementary data

Details of the synthesis and characterisation of **2** and **3**. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2005.11.106.

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