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The electrochemically tuneable recognition properties of an electropolymerised flavin derivative†

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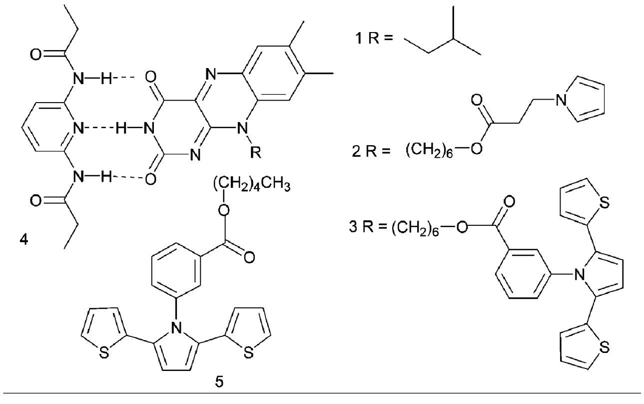
Received (in Cambridge, UK) 23rd July 2004, Accepted 3rd September 2004
First published as an Advance Article on the web 6th October 2004

The electrochemically tuneable recognition properties between an electropolymerised flavin derivative and 2,6-diethylamidopyridine are reported.

The development of surface immobilised conducting polymers bearing functionalities capable of recognising and detecting complementary species is a burgeoning field.[1] In particular, the electropolymerisation of appropriately functionalised monomers, is arguably the most convenient and rapid way of fabricating modified electrodes with voltammetric sensing applications.[1b,2] In endeavours to create new biosensor and bioelectronics components, biologically significant redox-active molecules have been incorporated into the polymer films.[3] For example, novel sensors and enzyme probes have been successfully fabricated by electropolymerising flavin-based units onto electrode surfaces.[4]

It has previously been shown that intermolecular hydrogen bonding efficiency between isobutylflavin **1** and complementary 2,6-diethylamidopyridine **4** in CH_2Cl_2, can be significantly improved (500-fold) by electrochemically generating the radical anion state of **1**.[5] Therefore, the immobilisation of flavin units as an electropolymerised thin film may afford a novel means to use electrochemically controllable host–guest complexation to tailor the structure and properties of an electrode surface. The electropolymerisation process will allow us to take the important step in transferring these systems from the solution to the solid-state, thereby affording well-defined architectures which can operate in unison. Furthermore, by prudent choice of the electropolymerisable moiety, it should be possible to modulate the electronic properties of the conducting polymer backbone, thereby further promoting their future exploitation as components for pragmatic molecular electronics devices. Here, we report our preliminary investigations focusing upon the electropolymerisation of flavin derivatives **2** or **3** as films onto an electrode surface, and the subsequent electrochemically controlled binding of the latter to **4**.



Compounds **2** and **3** were synthesised from *N*-(10)-hydroxyhexyl flavin[6] and 3-(pyrrol-1-yl)propionic acid[7] or 2,5-dithienyl-1-(3-carboxyphenyl)pyrrole, respectively, using EDCI/DMAP catalysed esterification procedures (see ESI†). Flavin-functionalised electrodes were formed by the dynamic electropolymerisation of **2** or **3** onto a platinum disc electrode (see ESI†). For the electropolymerisation of **2** (from CH_3CN), repeated cycling of the potential between −0.5 and +2.0 V, resulted in the appearance of a new redox wave centred around +0.12 V, corresponding to the electrochemical oxidation of the polymer film. Likewise the electropolymerisation of **3** from a solution in CH_3CN/toluene (1 : 1), resulted in the appearance of a new redox wave centred around +0.15 V (Fig. 1). In accordance with previously reported data for the electropolymerisation of 2,5-dithienylpyrroles, polymer growth appeared to stop after a few redox cycles.[8]

After washing the flavin-functionalised working electrodes with copious amounts of acetone, and allowing the polymer films to dry in air, the electrodes were placed into a 0.1 M solution of Bu_4NPF_6 in CH_2Cl_2 and their CVs were recorded between 0 and -1.1 V (see ESI†). The polymerisation process gave rise to a single redox wave, presumably due to the formation of the flavin radical anion species ($\mathbf{2_{rad}}$- or $\mathbf{3_{rad}}$-, respectively), which compare favourably with the redox processes of the flavin unit of flavoenzymes, and thus affords a more attractive biomimetic system than previously reported solution-based models.[9] In particular, the immobilisation of the flavin unit in this fashion apparently reduces the possibility of inter-flavin proton transfer between a neutral flavin and its corresponding radical anion state.[10]

The CVs of electropolymerised thin films of **2** or **3** recorded at different scan rates displayed a linear increase in current with scan rate for the flavin reduction process, which is indicative of

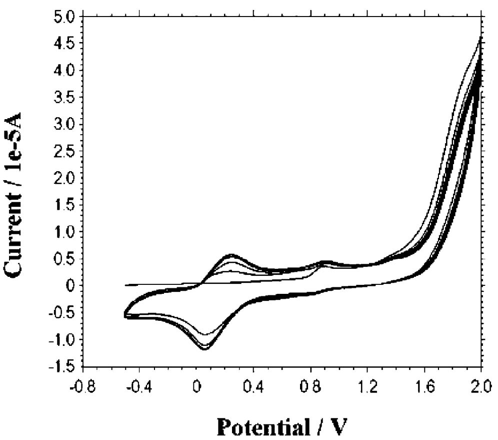


Fig. 1 CV showing the electrochemical polymerisation of a ~2 × 10^{-4} M solution of **3** in toluene/acetonitrile (1 : 1). The CV shows 8 cycles between −0.5 and +2.0 V.

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† Electronic supplementary information (ESI) available: synthesis and electrochemical measurements. See http://www.rsc.org/suppdata/cc/b4/b411297k/

DOI: 10.1039/b411297k

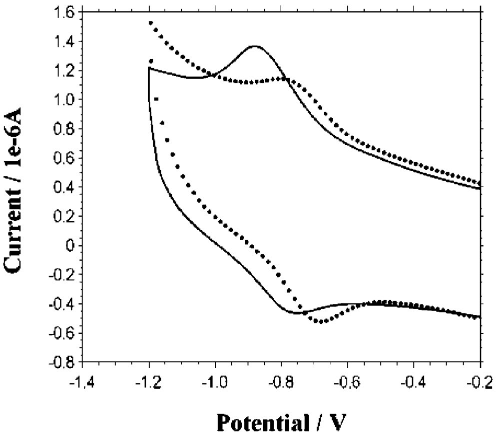

Fig. 2 CV studies showing the reduction of the electropolymerised films (fabricated by 8 cycles between −0.5 and +2 V) of **3** (in CH_2Cl_2) (—) and in the presence of a 3 × 10^{-2} M solution of **4** (……).

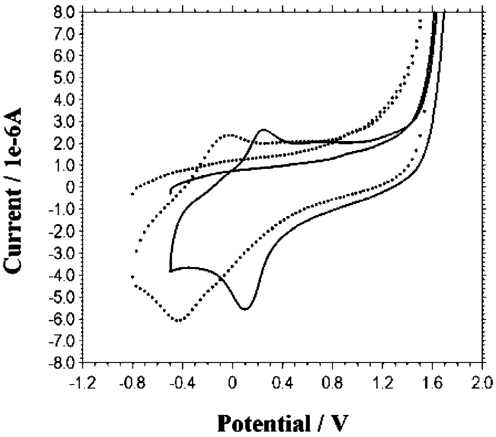

Fig. 3 CV studies showing the oxidation of the electropolymerised films of **3** in toluene/acetonitrile (1:1) (—) and in the presence of a 3 × 10^{-2} M solution of **4** (……).

surface-confined behaviour (see ESI†). The monolayers proved to be reasonably stable, displaying a similar current/voltage response for more than 10 scan cycles. The estimated surface coverage of the electropolymerised films of **2** ($\Gamma = 2 \times 10^{-12}$ mol cm^{-2}) or **3** ($\Gamma = 5 \times 10^{-13}$ mol cm^{-2}) (polymerised from a 10^{-4} M solution in CH_3CN), calculated from the average charge recorded under the reduction wave of the flavin, are consistent with the thiophene units of **3** creating a space between the flavin units within the polymer film. Thus, for the molecular recognition studies that were to follow, we opted to use polymer films fabricated from compound **3**, which should promote the effective recognition of **4**.

We then explored the role hydrogen bonding interactions between the flavin-functionalised electrodes and complementary guest **4** have on the redox properties of the flavin moiety of the polymer, by adding an excess of **4** to the electrolyte solution. A maximum observed shift in the half-wave potential for the **3**/$\mathbf{3}_{\mathbf{rad}}$**-** redox couple of +100 (±10) mV was observed (Fig. 2). This corresponds to a substantial stabilization of the flavin radical anion (9.6 kJ mol^{-1}), and is consistent with almost a 50-fold increase in the binding strength of the complex (**4.3**$_{\mathbf{rad}}$**-**, K_a = 26411 ± 200 M^{-1}).[11] When the experiments were repeated in CH_3CN/toluene (1 : 1), initially similar shifts in the half-wave potential of the flavin were observed, however, the redox waves became less reversible upon repeated electrochemical cycling (see ESI†).

As it has been previously reported that hydrogen bonding interactions can modulate the redox properties of appropriately functionalised electropolymerised films, we then investigated the effect the addition of excess **4** has on the redox properties of the polymer backbone of electropolymerised films of **3**.[12] In order to produce a well-defined redox wave for the resulting polymer, electropolymerisations were conducted in CH_3CN/toluene (1 : 1), using a voltage window between −0.5 to +1.5 V. The electrodes were washed and dried, and the CVs were recorded in CH_3CN/toluene (1 : 1) (Fig. 3). As for 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 V, which presumably causes the electrolyte to be expelled from the polymer, and results in the appearance of a redox wave centred around +0.17 V. Upon the addition of excess **4** to the electrolyte solution, the initial redox wave disappeared and a new wave appeared which was shifted by −0.4 V. In order to investigate whether specific recognition between the flavin moiety of electropolymerised **3** and the diaminopyridine moiety of **4** was responsible for this effect, we recorded the CVs of electropolymerised films of **5** before and after the addition of excess **4**. Very similar CV data were obtained for this study (see ESI†), indicating that specific recognition between the flavin and 2,6-diamidopyridine was not responsible for the perturbations in the polymer's electrochemical properties.

In conclusion, we have shown that the flavin functionalised electrodes can be readily fabricated by electropolymerising **2** or **3**, and that the architecture of the latter does not significantly impair the electrochemically tuneable hydrogen bonding interactions with **4**. Furthermore, we have shown that addition of **4** to the electrolyte solution has the propensity to significantly perturb the electronic properties of the polymer. Thus, these combined effects provide an encouraging precedent for the future development of the advanced materials and nanotechnological applications of systems of this type.

GC gratefully acknowledges the EPSRC for supporting this work. VMR acknowledges the NSF for grant CHE-0213354.

Notes and references

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