

# The electrochemically tuneable hydrogen bonding interactions between a phenanthrenequinone-functionalized self-assembled monolayer and a phenyl-urea terminated dendrimer

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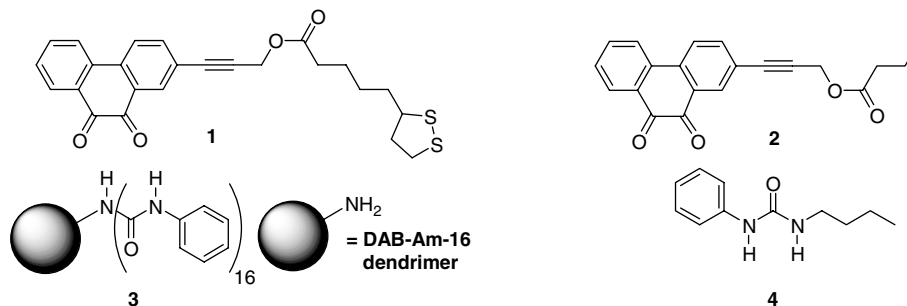
**Abstract**—We report the application of electrochemistry to detect and modulate hydrogen bonding interactions between a phenanthrenequinone-functionalized self-assembled monolayer and a phenyl-urea terminated dendrimer.

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The construction of hyperbranched macromolecular architectures utilizing engineered non-covalent interactions is a rapidly developing area within contemporary dendrimer chemistry.<sup>1</sup> Recently, electrochemistry has emerged as an important tool for modulating and detecting dendrimer-based supramolecules in solution.<sup>2</sup> However, in order for pragmatic molecular electronics and nanotechnological components to be fabricated from these systems, the supramolecules must be transferred from the solution to the solid-state.<sup>3</sup> In particular, the immobilization of the components of these systems onto a conducting support will promote their near-seamless interfacing to contemporary silicon-based I/O

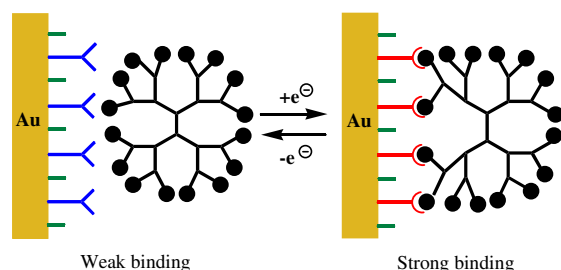
systems (via a potentiostat), and as a result, afford a convenient means to modulate<sup>4</sup> and interrogate these systems at the solid/liquid interface. Here, we describe our first steps towards this goal by demonstrating the electrochemically tuneable hydrogen bonding interactions between a phenanthrenequinone (PQ)-functionalized self-assembled monolayer (SAM) and a phenyl-urea terminated dendrimer (Fig. 1).<sup>5</sup>

Compounds **1** and **2** were synthesized as detailed in the [Supplementary data](#). Compounds **3** and **4** were prepared using the previously reported methodologies.<sup>2b</sup> <sup>1</sup>H NMR spectroscopy was used to confirm the formation



**Keywords:** Supramolecular chemistry; Surface chemistry; Electrochemistry.

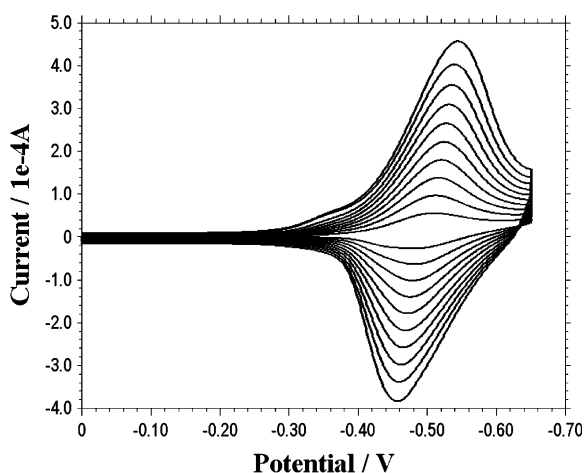
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**Figure 1.** Schematic representation of the electrochemically tuneable hydrogen bonding interactions between a PQ-functionalized monolayer and a phenyl-urea terminated dendrimer.

of weak hydrogen bonds between electro-active model compound **2** and hosts **3** and **4**.<sup>6</sup> The addition of aliquots of **2** to a solution of **3** or **4** in DMF-*d*<sub>7</sub> led to the broadening and small downfield shifts ( $\sim 0.1$  ppm) of the resonances for both urea protons, thereby indicating the formation of low-affinity hydrogen bonded complexes ( $K_a$  was estimated to be  $\sim 1 \text{ M}^{-1}$  for **2,4**).<sup>2h</sup>

SAM-modified electrodes from **1** were fabricated by immersing a coiled gold wire (99.999%, length 80 mm, diameter 0.5 mm) into a solution of disulfide **1** ( $10^{-3} \text{ M}$ ) in  $\text{CH}_2\text{Cl}_2$  for 12 h. After washing the electrodes with acetone and  $\text{CH}_2\text{Cl}_2$  and allowing them to dry in air, the SAM-modified electrodes were placed into a solution ( $0.1 \text{ M Bu}_4\text{NPF}_6$  in DMF) and their CV data were recorded.<sup>7</sup> The redox waves of the PQ moieties of the SAMs displayed a linear increase in current with scan rate, which is indicative of a surface-confined behaviour (Fig. 2). The CV data also allowed the surface coverage ( $\Gamma$ ) to be estimated to be  $7 \times 10^{-10} \text{ mol cm}^{-2}$ . The peak half-width value ( $\Delta E_{\text{fwhm}}$ ) was found to be 150 mV, which deviates significantly from the ideal 90 mV, thereby indicating that the PQ moieties exist in a number of microenvironments within the SAM. Interestingly, the redox wave for the PQ/PQ<sub>rad</sub><sup>-</sup> couple of the immobilized electro-active unit of the SAM-modified electrodes appeared to be resilient to dissolved oxygen.



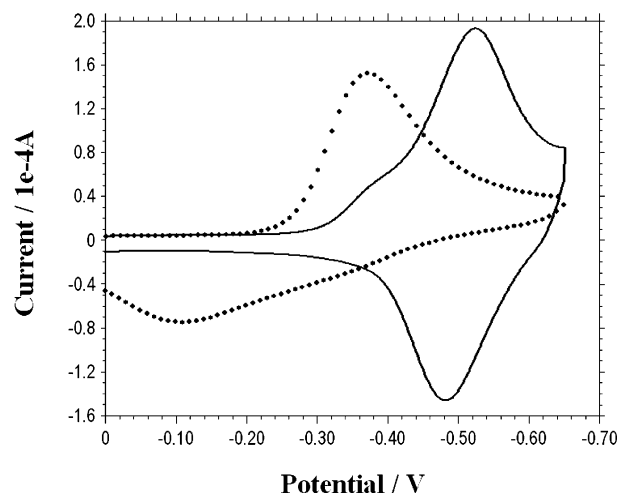
**Figure 2.** CV studies of SAMs of **1** at different scan rates: 0.1 (smallest current), 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9,  $1.0 \text{ V s}^{-1}$  (largest current).

Indeed, in most instances it was not necessary to purge the electrolyte solution prior to recording the CVs.

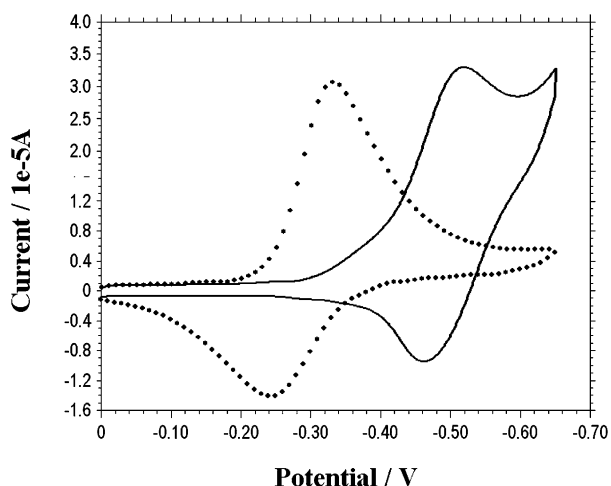
Mixed monolayers were fabricated by immersing a gold wire electrode into an equimolar ( $\sim 10^{-3} \text{ M}$  in  $\text{CH}_2\text{Cl}_2$ ) mixture of disulfide **1** and butyl disulfide. The latter was selected in order to help isolate the PQ units of the SAM, thereby preventing intermolecular electron transfer reactions from taking place. Furthermore, the butyl spacer group should allow the PQ recognition element to protrude from the surface of the monolayer, allowing effective recognition to take place between the quinone moieties of the immobilized PQ derivatives and the urea units of **3** or **4**.

We then explored the addition of an excess of dendrimer **3** to the electrolyte solution containing the mixed-monolayer-functionalized electrode. The addition of the dendrimer resulted in a significant positive shift in the position of the redox wave of the PQ moiety. Interestingly, the reversibility of the resulting redox waves was shown to be dependent upon scan rate. At fast scan rates the redox wave was irreversible (Fig. 3), however, as the scan rate was decreased, the CVs became significantly more reversible (Fig. 4). At this slower scan rate, the maximum observed shift in the half-wave potential for the PQ<sub>rad</sub><sup>-</sup> state was  $+200 (\pm 20) \text{ mV}$ . This corresponds to a substantial  $19.3 \text{ kcal mol}^{-1}$  stabilization of the PQ<sub>rad</sub><sup>-</sup> state, resulting in over a 2000-fold increase in the binding strength between the immobilized PQ and the urea units of the dendrimer ( $1_{\text{rad}} \cdot \mathbf{3}$ ,  $K_a = 2411 (\pm 200) \text{ M}^{-1}$ ).<sup>2h</sup> When the experiments were repeated with the parent amino-terminated dendrimer (DAB-AM-16), significantly different CV data were obtained, with only a small negative shift in the PQ/PQ<sub>rad</sub><sup>-</sup> couple observed (see Supplementary data).

When the CV experiments of the PQ-functionalized electrodes were recorded in the presence of **4**, a significantly smaller shift of  $+60$  to  $+90 \text{ mV}$  in the half-wave potential for the PQ/PQ<sub>rad</sub><sup>-</sup> couple was observed (see Supple-



**Figure 3.** CV data for mixed SAMs of **1** recorded in the absence (—) and in the presence (···) of an excess ( $2 \times 10^{-3} \text{ M}$ ) of urea dendrimer **3** (scan rate =  $0.5 \text{ V s}^{-1}$ ).



**Figure 4.** CV data for mixed SAMs of **1** recorded in the absence (—) of and in the presence (···) of an excess ( $2 \times 10^{-3}$  M) of urea dendrimer **3** (scan rate =  $0.05 \text{ V s}^{-1}$ ).

mentary data).<sup>8</sup> The larger shift upon the addition of the dendrimer is most likely a consequence of the multiple binding sites of dendrimer **3**. This so-called ‘dendrimer effect’ has previously been observed in the solution electrochemistry of ferrocene-based dendrimers, upon the addition of a complementary guest.<sup>2c,f</sup> Furthermore, the resulting voltammograms for the surface confined PQ derivative, recorded in the presence of **4**, did not show the same scan rate dependency as the previous experiments with **3**, as all CVs recorded between 1 and  $0.025 \text{ V s}^{-1}$  displayed near-reversible redox waves. It is noteworthy that the CV measurements performed on a solution of freely diffusing derivative **2**, recorded before and after the addition of **3**, displayed smaller shifts in half-wave potential (typically less than 100 mV) than those observed when the PQ moiety was immobilized onto an electrode surface (see Supplementary data).

A possible explanation of the differing electrochemical reversibility between the voltammograms of **2** and the PQ-functionalized monolayer (when recorded in the presence of **3** at different scan rates), relates the diffusion efficiency of electrolyte counterions to the working electrode, following the redox modulated interactions between monolayers of **1** and dendrimer **3**. Upon reduction of the PQ moiety of the SAM, the PQ recognition sites are ‘sealed’ by the urea groups of the dendrimer. Oxidation of the  $\text{PQ}_{\text{rad}^-}$  back to neutral species requires counterion migration, which will be hindered by the presence of the bulky dendrimer on the surface. Furthermore, the large size of the dendrimer may decrease its dissociation rate from the PQ binding sites. These factors will tend to slow down the electrochemical oxidation of the  $\text{PQ}_{\text{rad}^-}$  to PQ, and as a result, at fast scan rates the voltammogram is irreversible; whereas, reversibility is approached as the scan rate is lowered.

In summary, we have shown that electrochemistry can be utilized to detect and modulate hydrogen bonding interactions between an appropriately functionalized SAM and a dendrimer. In particular, by performing

variable scan rate CV measurements, we were able to successfully probe dendrimer/monolayer recognition processes. Indeed, at slow scan rates, the resulting near-reversibility of the waveform allows a 2000-fold increase in binding efficiency between the PQ moieties of the SAM and the dendrimer to be estimated. Further work is underway in our laboratory to exploit the application of electrochemistry to probe dendrimer/monolayer interactions. In particular, we aim to investigate the effect different dendrimer generations have on perturbations of the half-wave potential of the immobilized PQ derivative, and to develop new systems with molecular electronics and advanced materials applications. The results from these investigations will be reported in due course.

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### Supplementary data

Details of the synthesis and characterization of **1–4**. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.03.117.

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8. In order to maintain the compatibility between electrochemical measurements (i.e., maintaining the same total concentration of urea recognition units), 16 M equiv (compared to dendrimer) of model compound **4** was used in the CV experiments.