



# Tuning properties of carbon surfaces functionalized with amino-ended dendron layers by exploring their supramolecular interactions



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## ABSTRACT

An effective tailoring of carbon surfaces functionalized with a first-generation amino-ended dendrons was achieved by a simple self-assembly strategy. The morphology, as well as the viscoelastic and electrical properties of the modified surfaces were characterized at a micro-nanoscale level, by Cyclic Voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS), Atomic Force Microscopy (AFM) and Kelvin Probe Force Microscopy (KPFM). Thermodynamic parameters of the adsorption were investigated by EIS, studying the blocking properties of the modified surfaces towards the redox conversion of  $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ . AFM images were used to characterize the topography of the modified surfaces and also their viscoelastic properties by the acquisition of phase images.  $\pi$ - $\pi$  stacking interactions between dendrons and the carbon surface control the aggregation at low coverages, while forces of intermolecular Hydrogen-bond among dendrons appear at high coverages leading to more compact regions. The implications of the amino-ended dendron layer on the electrical properties of the modified surface have been analyzed through KPFM in comparison with nitro-ended dendron films, showing a decrease of the local contact potential difference after the incorporation of molecules having electron-donor ( $-\text{NH}_2$ ) functional groups, in contrast with the increase showed for molecules with electron-acceptor ( $-\text{NO}_2$ ) ones.

## 1. Introduction

Self-assembly of molecules by physisorption is a particularly easy way of producing a film onto an electrode with the aim of manipulating the surface properties or reactivity. Mainly, relatively weak Van der Waal's interaction forces play a crucial role in the electrode modification as a result of a physical attraction between the surface and adsorbates. Thus, self-assembly usually causes slight or non-conformational changes of the adsorbates, and can be both, easy and cost-effective [1]. In addition, surface modification using dendritic molecules is a simple method that offers important advantages over other polymers to tailor the surface. These molecules bearing multi-functionality, multi-valency and defined internal cavities; provide materials with the ability to interact synergically with the environment and structures incorporated therein [2]. The resulting product usually exhibits new properties compared to the original material, for example, control over the functional periphery groups may confer hydrophobicity or hydrophilicity characteristics to the surface, more biocompatibility, etc. [3]

The multi-functionality and versatility afforded by dendritic

molecules is an extremely useful feature. For example, a large number of chemical groups are exposed over the surface, being capable of undergoing chemical reactions generating useful reactive sites on the tailored layer. Moreover, the nature of the peripheral groups alters the interfacial behaviour of the film depending on the interactions that take place: hydrogen-bond, hydrophobic interactions,  $\pi$ - $\pi$  stacking, etc. As a consequence, differences in properties such as hardness or viscosity and surface nanostructuring could be found. Tsukruk et al. studied the effect on surface structure and morphology of Langmuir-Blodgett monolayers formed by hyperbranched polymers, and reported morphological differences due to a balance between the nature of the peripheral groups and the type of acting interactions [4]. Furthermore, organic molecules used as building blocks in surface functionalization provide numerous prospects for the immobilization of other striking structures, such as enzymes for example, generating interesting nanoscale architectures [5]. Mansur et al. covalently immobilized enzymes on amine-modified surfaces by glutaraldehyde as a bi-functional linker [6]

This investigation examines the spontaneous adsorption of G1-NH<sub>2</sub> onto carbon electrodes in order to explore the effect of Hydrogen-bond

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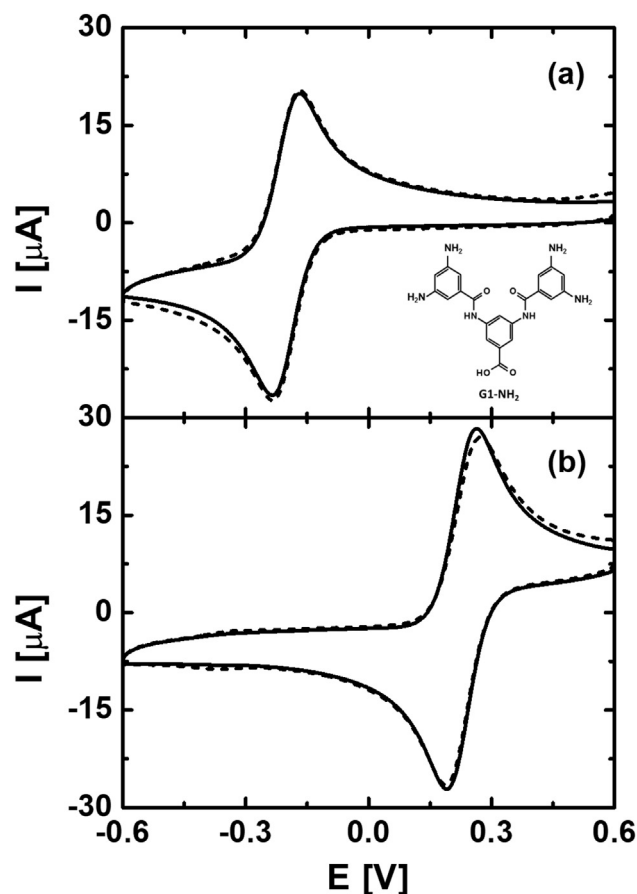


Fig. 1. Cyclic voltammograms for a GCE (solid line) and G1-NH<sub>2</sub>/GCE (dashed line) in 0.1 M PBS (pH 7) containing (a) 2 mM Ru(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub> or (b) 2 mM K<sub>3</sub>Fe(CN)<sub>6</sub> at 0.1 Vs<sup>-1</sup>. Incubation conditions: 180 min in 50.0 mM of G1-NH<sub>2</sub> in DMSO solutions. Inset: scheme of the first-generation of amino-aryl ended dendrons.

interactions in the dendronization process. The dendron immobilization was monitored by Cyclic Voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS), Atomic Force Microscopy (AFM) and Kelvin Probe Force Microscopy (KPFM). The electrochemical results supported by those of the microscopies and electrochemistry techniques allow us to claim that dendronized carbon surfaces with amino-ended groups are promising electron transfer mediators in electrochemical sensors

## 2. Experimental section

### 2.1. Materials

G1-NH<sub>2</sub> dendrons (see inset in Fig. 1(a)) were synthesized following the Kakimoto's procedure [7,8]. The rest of commercially available chemicals were reagent grade and used without further purification. All solutions were prepared immediately prior to their use. Phosphate buffer solutions (PBS) contain 0.1 M Na<sub>2</sub>HPO<sub>4</sub>/NaH<sub>2</sub>PO<sub>4</sub>. Water was purified with a Millipore Milli-Q system.

### 2.2. Glassy carbon electrodes preparation

The 3.0 mm diameter glassy carbon electrodes (GCE) (CH Instruments, Inc. Austin, TX) were polished using 1, 0.3 and 0.05 μm alumina (Buehler), and then rinsed with water and ethanol before its modification. Then, the electrodes were sonicated for 1 min in distilled water, dried in a N<sub>2</sub> flux and incubated along different times in a Dimethylsulfoxide (DMSO) solution containing G1-NH<sub>2</sub>. After

incubation, the functionalized surface was subsequently rinsed with abundant volumes of ethanol and water, and directly employed in an electrochemical cell.

### 2.3. Electrochemical measurements

All electrochemical measurements were performed at room temperature with a CH Instruments multipurpose electrochemical analyzer. A conventional three-electrode system consisting of a glassy carbon working electrode, a Ag/AgCl 3.0 M NaCl electrode (from BAS) as the reference electrode and a platinum foil counter electrode was employed. All potentials were reported versus the Ag/AgCl reference electrode at room temperature. Nitrogen gas was employed to deaerate aqueous solutions previous to their use. If not otherwise mentioned, scans were started at the positive end of the potential range in cyclic voltammetry (CV). The impedance data were evaluated by non-linear least square fits using the Zview software [9]. An amplitude perturbation of 10 mV was employed for EIS at frequencies ranging from 100 kHz to 0.01 Hz.

### 2.4. Atomic and kelvin probe force microscopies (AFM-KPFM)

A commercial Nanotec Electronic SPM System with a PLL/dynamic measurement board operating in tapping mode was employed to collect AFM and KPFM images at room temperature, and atmosphere conditions (Kelvin setup: Vac voltage of 500 mV applied to the tip, at an electrical modulation frequency of 4/7 kHz). The WS × M free software was used to perform acquisition and image processing [10]. V-shaped Olympus RC800PSA cantilevers (Olympus Corporation, Tokyo, Japan) made of silicon-nitride coated with Au/Cr (resonant frequency in the range of 70–90 kHz, nominal spring constant in the range of 0.05–0.1 N/m and radius of curvature of 20 nm) were used for AFM images; BudgetSensors cantilevers (Innovative Solutions Bulgaria Ltd., Bulgaria) made of silicon with an electrically conducted coating of Cr/Pt (resonant frequency in the range of 60–90 kHz, nominal spring constant in the range of 1–7 N/m and radius of curvature of 20 nm) were used for KPFM images. Freshly cleaved highly oriented pyrolytic graphite (HOPG) surfaces were employed for AFM and KPFM measurements. These surfaces were prepared by immersion in a DMSO solution containing 1 mM of G1-NH<sub>2</sub> for different incubation times, subsequently rinsed with abundant volumes of ethanol and water, dried under nitrogen flux and directly analyzed

## 3. Results and discussion

The adsorption of the dendritic layer onto GCE was indirectly followed by CV and EIS through the blocking properties of the coated electrode using diffusion controlled redox couple as probes. Fig. 1(a) shows the cyclic voltammograms recorded from -0.6 to 0.6 V versus Ag/AgCl for GCE and G1-NH<sub>2</sub>/GCE in Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+/3+</sup> in PBS (pH 7) at 0.1 Vs<sup>-1</sup>. A similar voltamperometric behaviour of the Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+/3+</sup> couple is observed for both, indicating that surface modification of the electrode apparently does not block the electron transfer reaction of the positive redox probe at neutral pH. Fig. 1(b) shows the cyclic voltammograms recorded from -0.6 to 0.6 V versus Ag/AgCl for GCE and G1-NH<sub>2</sub>/GCE in a Fe(CN)<sub>6</sub><sup>3-/4-</sup> solution at 0.1 Vs<sup>-1</sup>. The bare GCE exhibits the electrochemical response for the negative redox couple associated to the reversible diffusion controlled electron transfer reactions. The voltammogram for G1-NH<sub>2</sub>/GCE shows a little decrease in the peak current indicating that electrode surface modification apparently produces only a small inhibition.

EIS is a helpful method for probing the electron transfer properties between the electrolyte and the electrode surface. In this study, EIS was employed to explore the charge transfer resistance (R<sub>ct</sub>) of dendronized

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