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ORIGINAL PAPER

# Electrochemical behavior of a new *s*-triazine-based dendrimer

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**Abstract** The electrochemical behavior of a new G-2-*s*-triazine-based dendrimer, 2,4,6-tris-{4-{4,6-bis-{4-{4,6-bis-[(1*S*,2*S*)-1,3-dihydroxy-1-(4-nitrophenyl)-prop-2-ylamino]-*s*-triazin-2-yl}-piperazin-1-yl}-*s*-triazin-2-yl}-piperazin-1-yl}-*s*-triazine, (**I**), was studied in dimethylsulfoxide solution by cyclic voltammetry, on platinum and graphite electrodes. The electrochemical properties of **I** were compared with that of one of its precursor, *N*-{4,6-bis{4-{4,6-bis[(1*S*,2*S*)-1,3-dihydroxy-1-(4-nitrophenyl)-prop-2-ylamino]-*s*-triazin-2-yl}-piper azin-1-yl}-triazin-2-yl}-piperazine), (**II**), together with that of the starting material, (1*S*,2*S*)-2-amino-1-(4-nitrophenyl)-propane-1,3-diol ("*p*-nitrophenylserinol"), (**III**).

**Keywords** Electrochemical behavior · *s*-triazine-based dendrimer

## 1 Introduction

Dendrimers are branched compounds with a fractal structure that exhibit a high degree of constitutional order, with the possibility of containing selected chemical units at predetermined sites of their molecules [1]. They are constructed from $(AB)_n$ monomers ($n$ usually 2 or 3) in an iterative fashion, using convergent or divergent strategies. In the divergent strategy, dendrimers are built from a central core out to the periphery, while in the convergent approach, dendrimers are built from the periphery to the central core [2].

The synthetic availability of dendrimers in a wide range of sizes, combined with their unique structure, makes them versatile building blocks for a wide range of applications including molecular/ionic recognition [3, 4], self assembly processes [5–9], molecular batteries, sensors and catalysts [4, 10]. Their resemblance to biocomponents such as viruses, enzymes and proteins makes them interesting for theoretical studies and biomedical applications [11]. Dendrimer-modified surfaces can potentially be applied to chromatographic separations, as catalysts and as multiple redox reaction centers [12–15].

Dendrimers containing redox active groups are especially important because of their interesting electron-transfer properties [16, 17]. The peripheral redox active units undergo multiple electron transfer and the redox properties can be modulated by the size and nature of the dendritic branches [18, 19].

Recently, the electrochemical behavior of redox dendrimers has attracted the attention of many researchers. Compounds such as unsymmetric viologen dendrimers [20], iron–sulfur cluster core dendrimers [21], dendrimers containing *meta*-terphenyl peripheral groups and a 4,4′-bipyridinium core [22], ferrocene-cored dendrimers [3, 23, 24], ferrocene-containing carbohydrate dendrimer [25], arylalkyl ether dendrimers based on $AB_2$ and $AB_4$ monomer [26], viologen-based dendrimers [27], phenylazomethine dendrimers [28], 4,4′-bipyridinium core of first, second and third generation dendrimers [1], dinuclear and hexanuclear dendritic ruthenium(II) bipyridine complexes with

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2,3-bis(2-pyridyl)pyrazine (2,3-dpp) [29] have been synthesized and characterized.

Among the redox active dendrimers, those containing *s*-triazine units are of interest especially for their electroluminescent [28, 30] and electrochemical properties (e.g. [31]). The *s*-triazine unit can play two important roles: (i) it can act as the branch point of a dendrimer and (ii) it has good electron affinity, hence may act as an electron transport component [30].

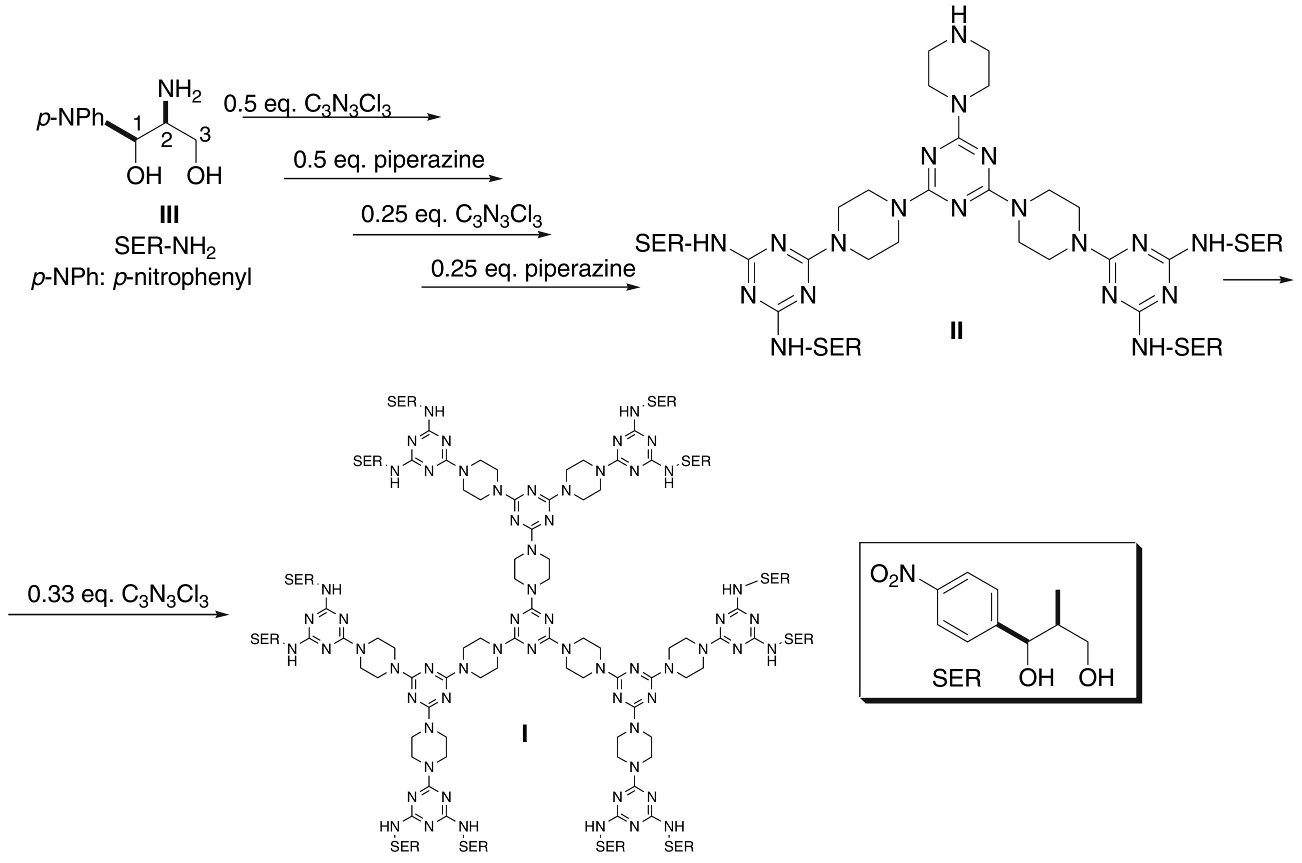
In this context, the aim of this work is the study of the electrochemical properties of the first G-2-*s*-triazine-based dendrimer, 2,4,6-tris-{4-{4,6-bis-{4-{4,6-bis-[(1*S*,2*S*)-1,3-dihydroxy-1-(4-nitrophenyl)-prop-2-ylamino]-*s*-triazin-2-yl}-piperazin-1-yl}-*s*-triazin-2-yl}-piperazin-1-yl}-*s*-triazine (**I**), having the commercially available (1*S*,2*S*)-2-amino-1-(4-nitrophenyl)-propane-1,3-diol (“*p-nitrophenylserinol*”) as peripheral units, the *s*-triazine as core and branch points and piperazine as linker (Scheme 1).

Cyclic voltammetry measurements (CV) were used to investigate the electrochemical behavior of **I** under various experimental conditions as different electrode materials, pH and potential scan rate. Its behavior was compared with that of two of its precursors, the *N*-substituted piperazine dendron **II** and the free peripheral group, the *p*-nitrophenylserinol itself, **III**.

## 2 Experimental

### 2.1 Reagents

The synthesis of **I** occurred in five linear steps, following a convergent and non-protective strategy, in 27% overall yield. It started from **III** by selective nucleophilic replacement of chlorine in cyanuryl chloride and continued, in the same way, by iterative and alternative connection of the *s*-trazine or piperazine units in very mild conditions as reported previously [32–34]. Current NMR spectra were recorded on a Brucker® AM300 (300 MHz $^1$H, 75 MHz $^{13}$C) instrument. The $^1$H DNMR analysis of the compounds **I** and **II** was also carried out on a Brucker® AM400 (400 MHz $^1$H, 100 MHz $^{13}$C) instrument since, at room temperature, they revealed restricted rotation around the >N$^{sp^3}$(piperazine, *p*-nitrophenylserinol)-C$^{sp^2}$(triazine) bonds.



**Scheme 1**

The supporting electrolyte for voltammetric measurements was a dimethylsulfoxide (DMSO, Merck, Darmstadt, Germany) solution containing KCl. All other reagents were of analytical grade and used as received.

### 2.2 Electrode preparation

A spectrographic graphite rod (Ringsdorff-Werke, GmbH, Bonn-Bad Godesberg, Germany), of ~3 mm diameter, was wet polished on fine (grit 400 and 600) emery paper (Buehler, Lake Bluff, IL, USA). Then, graphite rod of suitable length was carefully washed with deionized water, dried, and finally press-fitted into a PTFE holder in order to obtain an electrode having, in contact with the solution, a flat circular surface of ~0.071 cm$^2$. The platinum electrode was a typical BAS electrode.

### 2.3 Electrochemical measurements

Electrochemical experiments were carried out using a typical three-electrode cell. The platinum or graphite electrode was used as working electrode, a platinum ring as counter electrode and an Ag|AgCl/KCl$_{sat}$ as reference.

Cyclic voltammetry was performed on a PC-controlled electrochemical analyzer (Autolab-PGSTAT 10, EcoChemie, Utrecht, The Netherlands).

The electrolyte solution was deoxygenated by bubbling argon for 15 min before measurements. The experimental results are the average of at least three identically studied electrodes, if not otherwise mentioned.

## 3 Results and discussion

The electrochemical behavior of compound **I** was investigated by CV in solution of DMSO, in different experimental conditions (electrode material, scan rate and potential cycling), and was compared with that of the starting **III** and dendron **II**.

Figures 1 and 2 present the cyclic voltammograms obtained for compounds **I–III** in DMSO solution, on platinum and on graphite electrodes. In all cases the cyclic voltammograms present a well-defined peak pair, with a formal standard potential *vs.* Ag|AgCl/KCl$_{sat}$ in the negative domain (Table 1).

This peak pair may be attributed to a reversible monoelectronic exchange leading to the formation of a nitro radical anion R-NO$_2^{-\cdot}$ generated by the peripheral *p*-nitrophenyl groups (Eq. 1) [35]:

$$R{-}NO_2 + 1e^- \rightleftarrows R{-}NO_2^{-\cdot} \qquad (1)$$

where R is $C_6H_4$–CH(OH)–CH(NH$_2$)–CH$_2$OH.

On platinum, compounds **I** and **II** revealed a second peak pair at positive potentials around 0.130 V *vs.* SCE. This was assigned to a monoelectronic exchange reaction, involving the G-2 *s*-triazine rings (Scheme 2).

We note that, since compounds **I** and **II** are, in fact, *N*-substituted-2,4,6-triamino1,3,5-triazines (*melamines*, Scheme 1), they exhibited, at room temperature ($^1$H NMR), the already well documented restricted rotation around the >N$^{sp^3}$(exocyclic)-C$^{sp^2}$(*s*-triazine) bonds [36–38]. This was created by the oriented electronic delocalization required by the high $\pi$-deficiency of *s*-triazine, to induce the partial double bond character of these connections, e.g. the peripheral HN$^{sp^3}$-C$^{sp^2}$ (G-2 *s*-triazine) and N$^{sp^3}$(piperazine)-C$^{sp^2}$(G-2 *s*-triazine) (Scheme 2). Actually, following the extended conjugation creating rotamerism in **I** and **II**, the increase in the G-2 *s*-triazine HOMO energetic level is expected, the oxidations (**I**, **II** → **Ia**, **IIa**) being facilitated (Scheme 2). Indeed, in DMSO, melamines **I** and **II** were non-statistic mixtures of blocked rotamers, as fully confirmed by $^1$H DNMR spectra on a 400 MHz time scale (see Experimental). Thus, the hypothesis that **I** and **II** could generate, in voltammetric conditions, the imminium radical cations of type **Ia**, **IIa**, as blocked rotamers either, should be not ruled out.

An anodic peak recorded on the voltammogram of the starting compound **III** was attributed to the irreversible formation, after a bielectronic exchange, of an unstable nitrenium cation, most likely trapped in situ by the rest of the electron donors, present in the system (Eq. 2):

$$SER{-}NH_2 \rightarrow SER{-}NH^+ + 2e^- + H^+ \qquad (2)$$

On graphite, besides the previously mentioned peaks, a supplementary peak pair appears for compounds **I** and **II** around –500 mV *vs.* Ag|AgCl/KCl$_{sat}$ (Fig. 2). This may be attributed to another monoelectronic exchange reaction also producing stabilized radical cations of type imminium **Ib**, **IIb** (Scheme 3).

The radical cations **Ib**, **IIb** also originated from an electronic delocalization, this time produced by three stronger and identical electron donors, the piperazine amino groups, against the same strong electron acceptors, the G-1 and core *s*-triazine $\pi$-deficient systems. Besides rotamerism, revealed by $^1$H DNMR, the delocalization much increased the HOMO energetic level of the *s*-triazine and the oxidation reaction to

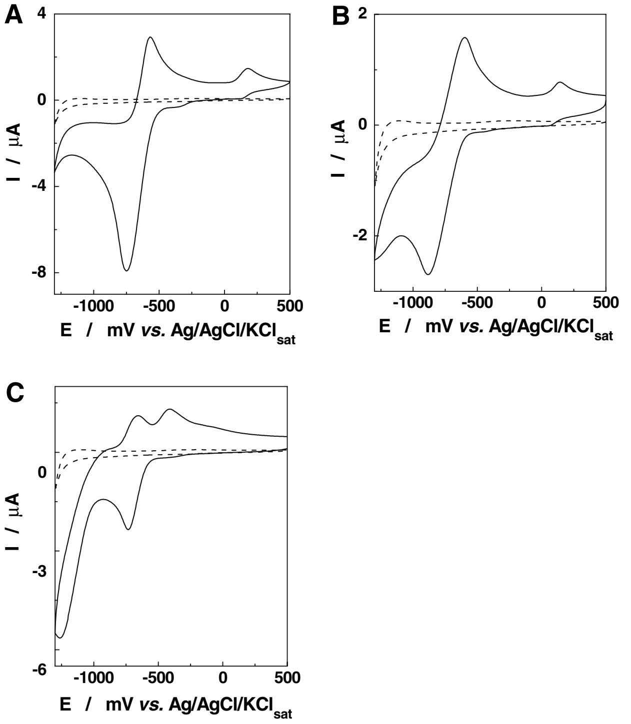


**Fig. 1** Cyclic voltammograms for solutions with compounds **I** (**A**), **II** (**B**) and **III** (**C**) (—) and for supporting electrolyte (- - -), on platinum electrode. Experimental conditions: concentration of solutions, 1 mM; starting potential, –1300 mV *vs.* Ag|AgCl/KCl$_{sat}$; scan rate, 50 mV s$^{-1}$; supporting electrolyte, dimethylsulfoxide + 10$^{-1}$ M KCl

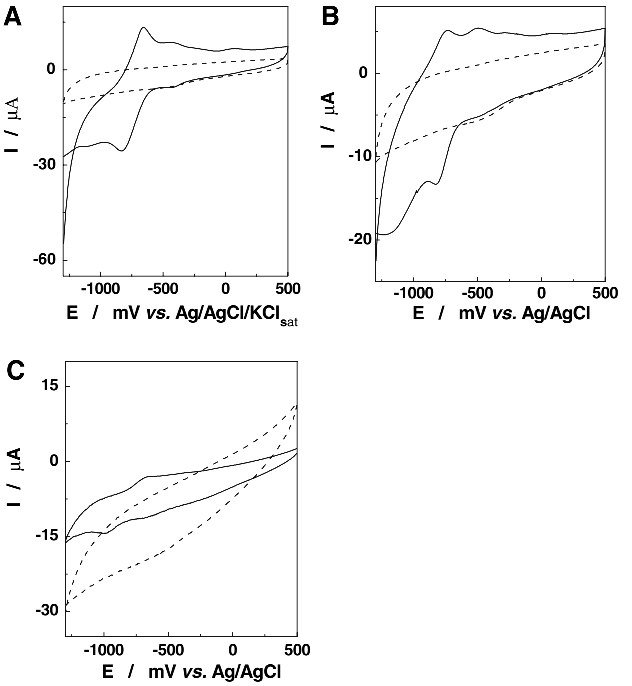


**Fig. 2** Cyclic voltammograms for solutions with compounds **I** (**A**), **II** (**B**) and **III** (**C**) (—) and for supporting electrolyte (- - -), on graphite electrode. Experimental conditions: scan rate, 10 mV s$^{-1}$; the other conditions, as in Fig. 1

**Table 1** Electrochemical parameters of the voltammetric response to compounds **I–III** in solution, on platinum electrode

| Electrode material | Compound | $E_{pa}$/mV* | $E_{pc}$/mV* | $\Delta E_p$/mV | $E^{0'}$/mV |
|---|---|---|---|---|---|
| Platinum | **I** | –571 | –744 | 173 | –658 |
| | **II** | –604 | –864 | 260 | –734 |
| | **III** | –678 | –728 | 50 | –703 |
| Graphite | **I** | –666 | –806 | 140 | –736 |
| | **II** | –756 | –802 | 46 | –779 |
| | **III** | –678 | –975 | 297 | –827 |

Experimental conditions as in Fig. 1

* mV *vs.* Ag|AgCl/KCl$_{sat}$

produce **Ib** and **IIb** should occur more readily than that depicted in Scheme 2.

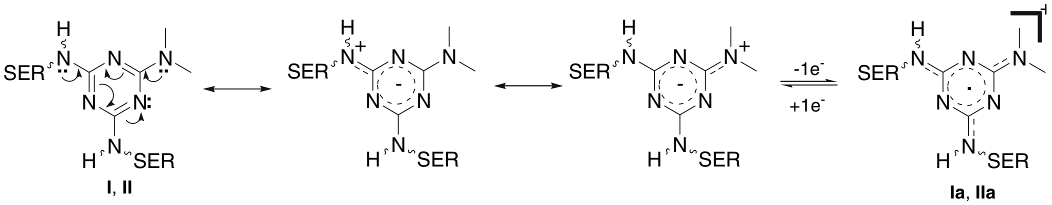
Further, our attention focused only on the first peak pair, corresponding to the formation of nitro radical anion R-NO$_2^{\cdot-}$. The electrochemical parameters corresponding to this peak pair from the voltammetric response for compounds **I–III** are presented in Table 1.

The values of $\Delta E_{peak}$ showed that compound **III** presents reversible electrochemical behavior ($\Delta E_p$ = 50 mV) on platinum and compound **II** presents a reversible electrochemical behavior on graphite. This may be due to the steric and conformational compatibility between these compounds and the electrode material. However, on platinum, the degree of reversibility is better for compound **I** (smaller $\Delta E_p$ value) in comparison with its precursor, (compound **II**) reflecting a faster electron transfer in the first case. In the case of compound **I**, the microenvironment around the triazine core is richer in *p*-nitrophenyl groups; hence it can be reduced more easily.

The different behavior of the compounds on the two electrode materials may be attributed to the different adsorptive and electrocatalytic properties of graphite and platinum toward reduction/oxidation of the investigated compounds.

A positive shift of the $E^{0'}$ values for compound **I** was observed on both electrode materials (see Table 1) as compared with the $E^{0'}$ values for compound **II** suggesting that compound **I** is more difficult to oxidize than compound **II**. This behavior can be explained by the bigger size of compound **I** and its different steric orientation towards the electrode surface and reflects the increased stability of the dendrimer. A similar positive shift with increasing dendrimer generation was observed for half-wave potentials obtained for dendrimers containing *meta*-terphenyl peripheral groups

**Scheme 2**



**Scheme 3**

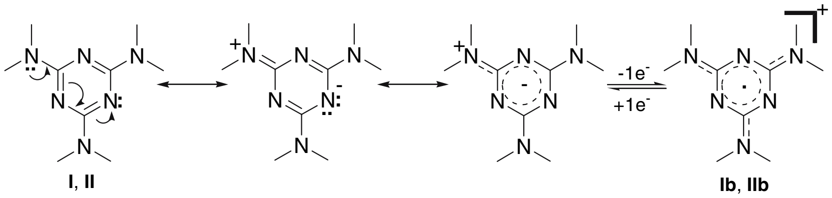


**Table 2** Log–log linear regression parameters for the dependence of the peak current on the potential scan rate (0.08–0.64 V s$^{-1}$ on platinum electrode and 0.01–0.08 V s$^{-1}$ on graphite electrode) observed for compound **I**

| Electrode material | Slope | | R/no. of exp. points | |
|---|---|---|---|---|
| | Oxidation | Reduction | Oxidation | Reduction |
| Platinum | 0.60 ± 0.06 | 0.44 ± 0.03 | 0.9755/7 | 0.9895/7 |
| Graphite | 0.71 ± 0.08 | 0.44 ± 0.03 | 0.9711/6 | 0.9883/6 |

Experimental conditions as in Fig. 1

and a 4,4′-bipyridinium core, in $CH_3CN$ [22] and unsymmetric viologen dendrimers, in DMSO [20]. In this case this trend can be explained through the increasing hydrophobic character of the dendrimer backbone, influencing the solvation of the two positive charges of the pyridinium core, which becomes dominant over its electron-rich character in determining redox potentials with increasing dendrimer generation [22].

In order to investigate the scan rate influence on the electrochemical behavior of compound **I**, cyclic voltammetric measurements were performed over a wide range of potential scan rates (0.08–0.64 V s$^{-1}$ for platinum and 0.01–0.08 V s$^{-1}$ for graphite), in DMSO solutions. The slopes of the log $I_p$ *vs.* log $v$ plots for the dendrimer were close to the theoretical value (0.5), on both electrode materials, indicating diffusion control (Table 2). The higher value (0.71 ± 0.08) observed in the case of graphite may be explained by partial adsorption of compound **I** on this material, due to a better compatibility between the dendrimer molecules and the graphite.

The influence of potential cycling on the electrochemical response of compounds **I–III** was investigated under potentiodynamic conditions by continuous cycling of the electrode potential, (25 cycles) in the potential range—1300÷600 mV *vs.* Ag|AgCl/KCl$_{sat}$ in DMSO solution on platinum. A progressive decrease of the peak current was observed (Table 3) suggesting blocking of the platinum electrode surface by the reaction products. In the case of compound **I**, the slope of the $I_p$ *vs.* $t$ dependence is greater than in the case of compounds **II** and **III**, indicating a more rapid fouling of the platinum electrode surface, in accordance with the molecular size of the investigated compounds. This conclusion was confirmed by the voltammograms recording during an experiment consisting in cycling (six cycles) platinum in DMSO containing compound **I** solution, followed by electrode cleaning and re-recording its voltammetric response. The same voltammograms were observed for the first cycle and for the electrode after cleaning, whereas during cycling the response was altered, denoting electrode surface fouling (results not shown).

**Table 3** Linear regression parameters for the dependence of peak current on cycling time, corresponding to compounds **I–III** in solution, on platinum electrode

| Compound | $I_{t=0}/10^6$ A | | Slope/$10^8$ A s$^{-1}$ | | R/no. of exp. points | |
|---|---|---|---|---|---|---|
| | Oxidation | Reduction | Oxidation | Reduction | Oxidation | Reduction |
| **I** | 4.7 ± 0.7 | 7.8 ± 0.5 | 1.1 | 1.5 | 0.9451/5 | 0.9846/5 |
| **II** | 1.8 ± 0.04 | 1.6 ± 0.02 | 0.09 | 0.07 | 0.9747/5 | 0.9785/5 |
| **III** | 0.6 ± 0.08 | 1.6 ± 0.05 | 0.01 | 0.07 | 0.9366/5 | 0.8855/5 |

Experimental conditions: scan rate, 50 mV s$^{-1}$; for the other conditions, see Fig. 1

## 4 Conclusions

A comparison of the electrochemical behavior of the first G-2-*s*-triazine-based dendrimer, 2,4,6-tris{4,6-bis {4,6-bis[(1*S*,2*S*)-1,3-dihydroxy-1-(4-nitrophenyl)-propyl-2-amino]-triazin-2-yl}-piperazin-1-yl}-triazin-2-yl}piperazin-1-yl}-triazine, **I**, in DMSO with that of its precursor, *N*-{4,6-bis{4-{4,6-bis[(1*S*,2*S*)-1,3-dihydroxy-1-(4-nitrophenyl)-propyl-2-amino]-triazin-2-yl}-piperazin-1-yl}-triazin-2-yl}-piperazine, **II,** revealed that compound **I** is more difficult to oxidize in solution than compound **II**, on platinum as well as on graphite electrodes, reflecting an increased stability of the dendrimer. The different behavior of the compounds on the two electrode materials may be attributed to the different adsorptive and electrocatalytic properties of graphite and platinum toward the reduction/oxidation of the investigated compounds. A progressive decrease in the peak current on platinum during potential cycling was observed, suggesting blocking of the electrode surface by the reaction products.

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