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Electrochemical Response of the Threading/de-threading Process of Calix[6]arene-based Pseudorotaxanes Anchored on Glassy Carbon Electrodes

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ABSTRACT

The development of functional materials and smart surfaces has received tremendous attention in recent years. The anchoring of molecular machines and the transfer of their properties on to solid substrates may facilitate the design of new smart devices. Herein, we report an approach to the covalent modification of glassy carbon electrodes with electrochemically responsive tris(*N*-phenylureido)calix[6]arene-based pseudorotaxanes. The main focus of this study has been the electrochemically driven threading/de-threading process of the redox active dialkylviologen axial component of the supramolecular assemble. After the creation of an amine monolayer on the electrode, pseudorotaxane systems were generated at the surface using different approaches. It was revealed, through electrochemical investigations, that the reversibility of the threading/de-threading process of the axle depended on the nature of the alkyl substituents on the axle.

1. Introduction

During the last decades, the tremendous advance in the comprehension of molecular recognition processes has allowed the transfer of the principles and methods of *Supramolecular Chemistry* [1,2] to the construction of new nanodevices and functional materials and in particular to supporting Host-Guest systems on solid surfaces [3–5]. Relatively less explored is how the functioning mode of a prototype of molecular machine [6,7] is affected by its anchoring on a solid support or by the nature of the solid support. This is particularly true in those cases where these systems should operate under the action of electrochemical stimuli and the nature of the interaction between the anchored active coating and the solid support could modify the response unpredictably. Cooke and co-workers [8] reported that the reversibility of electrochemically responsive pseudorotaxanes, obtained by anchoring tetrathiofulvalene derivatives on gold in a self-assembled monolayer (SAM), is significantly – and adversely – modified compared to the behaviour observed in solution. In contrast, Beer et al. reported that redox active bis-ferrocenyl rotaxanes, exploited in solution for chemical sensing, maintain their properties when organized in SAMs on gold electrodes [9]. In related work, the same authors reported that a [2]catenane, able to bind chloride ions in solution selectively, lost its binding properties when anchored to gold electrodes [10]. Some of us demonstrated that the ability of tris(*N*-phenylureido)calix[6]arene derivatives, such as **1** (Fig. 1), to act as three-dimensional heteroditopic receptors, able to form oriented pseudorotaxanes and rotaxanes with viologen salts [11–13], is substantially maintained when anchored on Si(100) [14] and polycrystalline Cu [15] surfaces, and that the electrochemically driven threading/de-threading was unaffected by the nature of the inorganic surface. The formation of these pseudorotaxane-based systems was later exploited for the assembly of gold nanoparticles on functionalized Si(100) surfaces [16].

Glassy carbon (GC) electrodes have been extensively studied as anchoring supports for monolayers aimed at analytical applications [17,18]. Yet, despite its high electrical conductivity, the stability in a wide potential window, the possibility to directly monitor the extent of the surfaces functionalization with redox active species and the electrochemical properties conferred by the monolayer, to the best of our knowledge, no studies have been so far reported on the role of GC as a supporting matrix for prototypes

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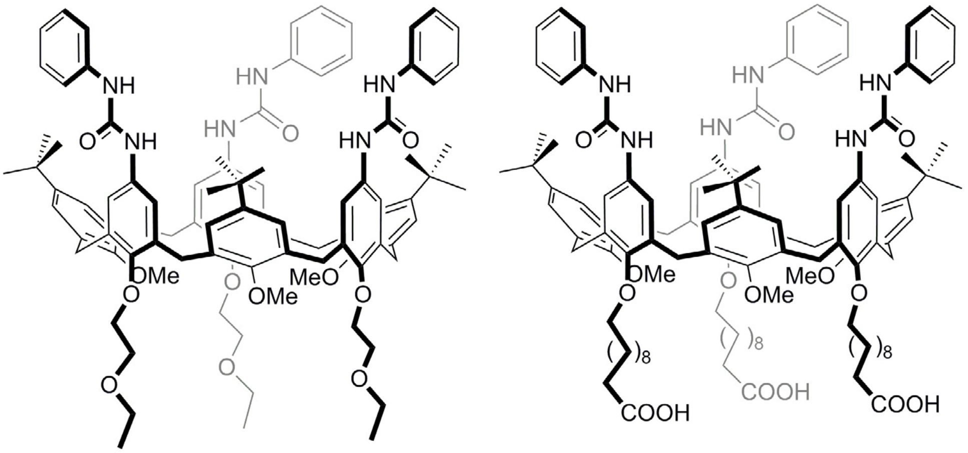


Fig. 1. Calix[6]arene derivatives focus of this study.

of molecular machines based on pseudorotaxanes and rotaxanes and their working mode. Herein, we present a study aimed at evaluating the electrochemical response of calix[6]arene-based pseudorotaxanes and rotaxanes supported on GC electrodes.

2. Experimental

2.1. Chemicals and Synthesis

All solvents were dried using standard procedures; all other reagents were of reagent grade quality obtained from commercial suppliers and were used without further purification. NMR spectra were recorded at 400 MHz for ^{1}H and 100 MHz for ^{13}C. Melting points are uncorrected. Chemical shifts are expressed in ppm (δ) using the residual solvent signal as internal reference (7.26 ppm for $CHCl_3$, 3.31 for CH_3OH and 2.50 for DMSO). Mass spectra were recorded in ESI mode. The synthesis of Calix[6]arenes **1** [19] and **4** [20], compound **8** [21] and 1-octadecyl tosylate **10** [14] has been reported in previous publications.

tert-butyl 11-bromoundecanoate(3). In a 250 mL round bottom flask, kept under nitrogen atmosphere and at 0° C through an external ice bath, to a solution of 11-bromoundecanoic acid (5 g, 19 mmol) in freshly distilled tetrahydrofuran (100 mL), trifluoroacetic anhydride (7.8 g, 38 mmol) was added dropwise. The reaction mixture was stirred for 2 hours at 0° C, then *tert*-butanol was added (7 g, 95 mmol). After stirring the resulting reaction mixture for 16 hours at room temperature, the solvent was removed under reduced pressure and the residue taken up with ethyl acetate (100 mL). The organic phase was washed with a 0.1 M solution of $NaHCO_3$ (100 mL) and twice with water (2×100 mL). The separated organic phase was dried over anhydrous Na_2SO_4, filtered to remove the drying agent and the solvent removed under reduced pressure to dryness to yield 5.2 g of **3** as a colorless oil (87%). ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 3.41$ (t, 2H, $J = 6.9$ Hz), 2.20 (t, 2H, $J = 7.5$ Hz), 1.85 (m, 2H, $J = 7.2$ Hz), 1.58 (m, 2H, $J = 7.2$ Hz), 1.45 (s, 9H), 1.29 (m, 14H); ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 173.3$, 79.9, 35.6, 34.0, 32.8, 29.3, 29.2, 29.0, 28.7, 28.1, 25.1; MS (ESI): m/z: 343.2 (100) $[M+Na]^+$, 344.2 (97) $[M+Na]^+$.

Calix[6]arene (5). In a 100 mL sealed glass autoclave, a heterogeneous mixture of calixarene **4** (1 g, 1.1 mmol), **3** (2 g, 6.2 mmol) and K_2CO_3 (0.7 g, 5.1 mmol) in CH_3CN (60 mL) was refluxed under vigorous stirring for 72 h. After cooling to room temperature, the solvent was evaporated to dryness under reduced pressure. The solid residue was taken up with ethyl acetate (80 mL) and the resulting organic phase washed with a 10% w/v solution of HCl (80 mL) and twice with water (2×80 mL). The separated organic phase was dried over anhydrous Na_2SO_4, filtered to remove the drying agent and the solvent evaporated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate 8:2) to yield 0.92 g of **5** as a pale yellow solid (54%). m.p. = 78–79 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 7.69$ (s, 6H), 7.23 (s, 6H), 4.4 (broad signal, 6H), 3.8 (m, 6H), 3.6 (broad signal, 6H), 2.88 (s, 9H), 2.21 (t, 6H, $J = 7.6$ Hz), 1.7-1.3 (multiple signals, 96H); ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 173.3$, 159.9, 154.3, 146.8, 143.6, 135.6, 132.2, 127.4, 123.1, 79.9, 74.0, 60.0, 35.6, 34.3, 31.5, 31.3, 30.9, 30.3, 29.5, 29.3, 29.1, 28.1 26.0, 25.1; MS (ESI): m/z: 1725.6 (86) $[M+Na]^+$, 1726.6 (100) $[M+Na]^+$, 1727.6 (64) $[M+Na]^+$

Calix[6]arene (6). In a 100 mL round bottom flask kept under nitrogen atmosphere, a tip of spatula of Pd/C catalyst was cautiously added to a suspension of compound **5** (0.52 g, 0.31 mmol) in methanol (50 mL), then hydrazine monohydrate (1.53 g, 30 mmol) was added dropwise. The resulting heterogeneous mixture was refluxed for 6 h, cooled to room temperature and then filtered, under nitrogen atmosphere, through a celite pad to remove the catalyst. The filtered solution was evaporated to dryness under reduced pressure to yield 0.48 g of **6** as a white solid (98%). Because of its instability to air, compound **6** was employed in the following synthetic step without any further purification.

Calix[6]arene (7). In a 50 mL round bottom flask kept under nitrogen atmosphere, to a solution of **6** (0.48 g, 0.3 mmol) in dichloromethane (20 mL), phenyl isocyanate (0.17 g, 1.44 mmol) was added dropwise. The reaction mixture was stirred for 2 hours at room temperature, then the solvent was evaporated to dryness under reduced pressure and the residue was purified by column chromatography on silica gel (hexane/ethyl acetate 7:3) to yield 0.42 g of **7** as a pale yellow solid (71%). m.p. = 111–112° C; ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 7.22$ (s, 6H), 7.12 (s, 6H), 6.94 (s, 6H), 6.31 (s, 6H), 4.42 (d, 6H, $J = 13.2$ Hz), 3.93 (broad signal, 6H), 3.58 (d, 6H, 14.4 Hz), 2.85 (s, 9H), 2.22 (broad signal, 6H), 1.91 (s, 6H), 1.59 (s, 12H), 1.47 (s, 54H), 1.32 (s, 36H); ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 173.4$, 155.0, 154.6, 152.3, 146.8, 138.3, 135.7, 133.1, 132.4, 128.9, 127.7, 123.4, 123.1, 120.5, 79.9, 73.1, 60.2, 35.6, 34.2, 31.5, 31.0, 30.6, 29.6, 29.5, 29.3, 29.1, 28.1, 26.3, 25.1; MS (ESI): m/z: 1971.0 (71) $[M+H]^+$, 1972.0 (100) $[M+Na]^+$, 1973.0 (71) $[M+Na]^+$.

Calix[6]arene (2). In a 10 mL round bottom flask kept under nitrogen atmosphere, to a solution of **7** (0.02 g, 0.01 mmol) in dichloromethane (2 mL), trifluoroacetic acid (0.3 g, 1 mmol) was added dropwise. The reaction mixture was stirred for 1 hour at room temperature, then the solvent was removed under reduced pressure to yield 0.015 g of **2** as a pale yellow solid (83%). ^{1}H NMR ($CDCl_3$, 400 Hz) δ = 7.22 (s, 6H), 7.12 (s, 6H), 7.11 (s,9H), 6.9 (s, 6H), 6.31 (s, 6H), 4.39 (d, 6H, *J* = 13.2 Hz), 3.93 (t, 6H, *J* = 6.4 Hz), 3.58 (d, 6H, 14.4 Hz), 2.89 (s, 9H), 2.36 (t, 6H, *J* = 7.2 Hz), 1.9- 1.8 (m, 12H), 1.64 (s, 12H), 1.47 (s, 36H), 1.32 (s, 54H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 179.1, 168.5, 155.0, 154.6, 152.3, 146.8, 138.3, 135.7, 133.8, 133.1, 132.2, 128.9, 127.7, 123.4, 123.1, 120.5, 73.0, 60.3, 34.2, 31.5, 31.0, 30.6, 29.6, 29.5, 29.3, 29.1, 28.1, 26.3, 25.1; MS (ESI): m/z: 1824.7 (80) [M+Na]$^+$, 1825.7 (100) [M+Na]$^+$, 1826.7 (70) [M+Na]$^+$.

Axle 9. In a sealed 100 mL glass autoclave, a solution of **8** (0.5 g, 0.8 mmol) and 11-bromoundecanoic acid (0.7 g, 2.6 mmol) in CH_3CN (40 mL) was refluxed for 4 days. Afterwards, the solution was evaporated to dryness under reduced pressure. The solid residue was triturated with CH_3CN to afford 0.4 g of **9** as a yellow solid (50%). m.p. = 240–243 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ = 12.0 (br.s, 1H) 9.5.9.4 (m, 4H), 8.83 (d, 4H, *J* = 6.8 Hz), 7.49 (d, 0.5H, *J* = 8.0 Hz), 7.3-7.1 (m, 10H), 7.11 (d, 0.5H, *J* = 8.0 Hz), 5.18 (s, 1H), 4.7–4.6 (m, 4H), 4.11 (t, 2H, *J* = 6.8 Hz), 2.20 (s, 1H), 2.18 (t, 2H, *J* = 7.6 Hz), 2.0–1.9 (m, 4H), 1.6-1.4 (m, 4H), 1.3–1.2 (m, 16H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ = 174.9, 172.4, 149.0, 146.2, 146.1, 139.5, 138.1, 129.0, 128.9, 128.5, 127.5, 127.1, 125.9, 64.9, 61.3, 61.2, 56.3, 34.1, 31.2, 31.0, 29.2, 29.1, 29.0, 28.8, 28.2, 25.9, 25.3, 25.0, 24.9, 21.2; MS (ES): m/z: 635.5 (100) [M−H]$^+$, 636.5 (86) [M−H]$^+$.

Salt 11. In a 100 mL round-bottomed flask, 1-octadecyl tosylate **10** (1 g, 2.4 mmol) and 4,4′-dipyridyl (1.1 g, 7.1 mmol) were dissolved in CH_3CN (50 mL) and the solution was refluxed for 24 h. Then the solvent was evaporated at reduced pressure and the oily residue obtained was triturated with EtOAc (3 × 20 mL) until of **11** precipitated as a white solid recovered by suction filtration (1 g, 64%). m.p. = 97–99 °C; ^{1}H NMR (CD_3OD, 400 MHz) δ = 9.12 (d, 2H, *J* = 6.0 Hz), 8.85 (d, 2H, *J* = 6.8 Hz), 8.52 (d, 2H, *J* = 5.6 Hz), 7.99 (d, 2H, *J* = 6.4 Hz), 7.72 (d, 2H, *J* = 7.6 Hz), 7.24 (d, 2H, *J* = 8.0 Hz), 4.68 (t, 2H, *J* = 7.6 Hz), 2.37 (s, 3H), 2.18 (t, 2H, *J* = 6.8 Hz), 1.4–1.3 (m, 30H), 0.92 (t, 3H, *J* = 6.0 Hz); ^{13}C NMR (CD_3OD, 100 MHz) δ = 153.9, 150.4, 142.3, 142.2, 140.2, 128.4, 125.7, 125.6, 122.1, 61.4, 31.7, 31.1, 29.4, 29.3, 29.2, 29.1, 28.7, 25.8, 22.3, 19.9, 13.0; MS (ESI): m/z: 409.3 (100) [M−TsO]$^+$, 410.3 (33) [M−TsO]$^+$.

Axle 12. In a sealed 100 mL glass autoclave, a solution of salt **11** (0.5 g, 0.9 mmol) and 11-bromoundecanoic acid (0.6 g, 2.7 mmol) in CH_3CN (40 mL) was refluxed for 4 days. Afterwards, the solution was evaporated to dryness under reduced pressure. The solid residue was triturated with CH_3CN to afford 0.6 g of **12** as a yellow solid (62%). m.p. = 250–253 °C; ^{1}H NMR (DMSO-*d6*, 400 MHz) δ = 12.0 (broad signal, 1H) 9.39 (d, 4H, *J* = 6.2 Hz), 8.79 (d, 4H, *J* = 6.2 Hz), 7.49 (d, 1H, *J* = 8.0 Hz), 7.12 (d, 1H, *J* = 8.0 Hz), 4.69 (t, 2H, *J* = 7.2 Hz), 2.38 (s, 2H), 2.18 (t, 2H, *J* = 7.6 Hz), 2.0 (br.s, 4H), 1.5 (br.s, 2H), 1.3–1.2 (m, 42H), 0.85 (t, 3 H, *J* = 6.0 Hz); ^{13}C NMR (DMSO-*d6*, 100 MHz) δ = 175.0, 149.1, 146.2, 146.0, 138.2, 128.5, 127.1, 125.9, 61.4, 40.5, 40.3, 40.1, 39.9, 39.7, 39.5, 39.3, 34.1, 31.7, 31.2, 29.5, 29.4, 29.1, 29.0, 28.8, 25.9, 24.9, 22.6, 21.2, 14.4; MS (ESI): m/z: 593.6 (100) [M−H]$^+$, 594.6 (81) [M−H]$^+$.

2.2. Modification of GC Electrodes with calix[6]arene 2

In a 10 mL flask, to a solution of calixarene **2** (0.09 g, 0.05 mmol) in DMF (5 mL), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) (0.027 g, 0.21 mmol) and *N*-hydroxysuccinimide (NHS) (0.024 g, 0.21 mmol) were added. The solution was stirred for 1 h and then the electrodes were dipped for at least 4 h. The electrodes were then rinsed with water (5 mL), acetonitrile (5 mL) and left to dry in air.

2.3. General Procedure for the Modification of GC Electrodes with Pseudorotaxanes $1\supset9$ and $1\supset12$

In a 10 mL flask, to a solution of calix[6]arene **1** (0.07 g, 0.05 mmol) in CH_2Cl_2 (5 mL) a molar excess of the appropriate axle (**9** and **12**, 0.07 mmol) was added. The solution was stirred at r.t. for 1 hour and then filtered to remove the excess of the salt; afterwards EDC (0.009 g, 0.07 mmol) and NHS (0.008 g, 0.07 mmol) were added to the solution, which was stirred for 1 h and then the electrodes were dipped in the solution. After 4 h, the electrodes were rinsed with water (5 ml), acetonitrile (5 ml) and left to dry in air for five minutes.

2.4. Electrochemical Experiments

Electrochemical experiments were performed in a conventional three electrode cell using an Autolab PGSTAT30 Potentiostat/Galvanostat and data were analysed with Origin 7.0 software. A Ag/Ag$^+$ electrode was used as the reference electrode, and a 1 cm^2 platinum gauze as the counter electrode. Ferrocene was used as internal standard. The working electrode was a 3 mm diameter (0.071 cm^2) glassy carbon disc (HTW, Hochtemperatur-Werkstoffe GmbH, Germany) sealed in glass tube and wired up with copper wire by using melted indium (Aldrich). Prior to modification, the GC working electrodes were dry polished with silicon carbide polishing paper (grade 1200) and rinsed with deionized water followed by sonication for 5 min in acetonitrile. Electrochemical Impedance Spectroscopy (EIS) response was analysed by means of a classic Randles equivalent circuit and fitted using the Autolab FRA software. The modification of glassy carbon surfaces with amine monolayers was performed as previously reported [18].

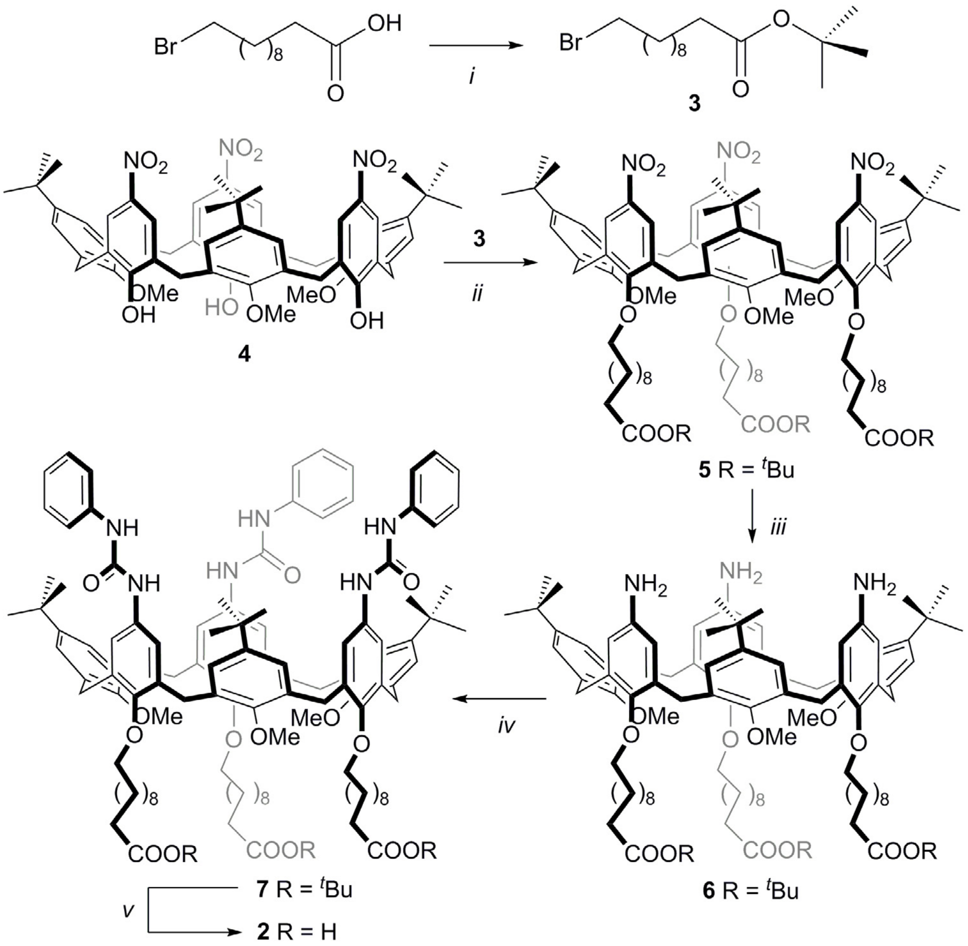
3. Results and discussion

3.1. Design and synthesis of calix[6]arene derivatives suitable for GC electrodes modification

Since in calix[6]arene derivatives such as **1** (Fig. 1) the two domains able to bind viologen salts are at the upper rim, namely the three phenylureas and the electron-rich aromatic cavity, the potential grafting points for the functionalisation of GC electrodes were placed at the lower rim, in the form of three ω-undecanoic chains (*vide infra*). Such an approach to the anchoring of the macrocycle on the electrode allows its recognition sites to be exposed toward the solution, favouring the threading of a viologen-based “axle” into the calix[6]arene “wheel” in low polarity solvents, as previously shown in solution [13,22]. Furthermore, long undecyl alkyl chains were chosen as spacers between the electron-rich cavity and the electrode in order to minimise any possible effect of the GC surface on the formation/decomplexation processes of the pseudorotaxanes.

The novel calix[6]arene-based wheel **2** was obtained as illustrated in Scheme 1. Trinitro calix[6]arene (**5**) was synthesised in 54% yield by reacting, in refluxing acetonitrile using K_2CO_3 as base, the known calix[6]arene precursor **4** with an excess of ester **3**. The nitro groups of **5** were converted in high yields to amines with hydrazine monohydrate using Pd/C as catalyst. Reaction of the resulting triamino **6** with phenylisocyanate in dry dichloromethane calix[6]arene **7** in 71% yield. Finally, **2** was obtained, in 27% overall yield, by removal of the *tert*-butyl protecting groups of **7** with trifluoroacetic acid (TFA) in dichloromethane.

The structure of wheel **2** was confirmed through MS and NMR analysis. As expected, the latter measurements, run in $CDCl_3$, showed that the calix[6]arene macrocycle adopts, on the NMR time-scale, a pseudo-*cone* conformation in which the three alternate *N*-phenylureido aromatic rings define a trigonal prism,

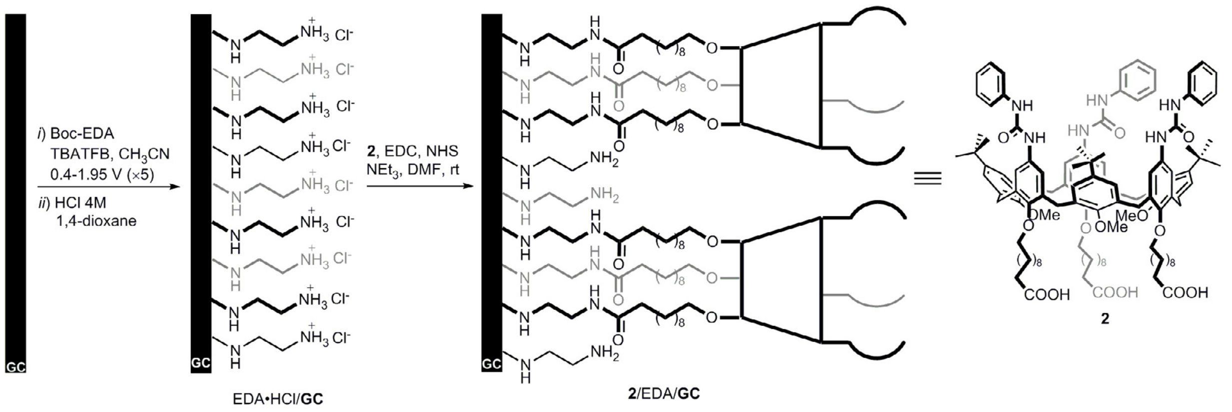


Scheme 1. Reagents and Conditions: *i*) TFAA, *t*-butanol, THF, 0 °C to r.t., 16 h, 87%; *ii*) K_2CO_3, CH_3CN, reflux, 72 h, 54%; *iii*) $NH_2NH_2{\bullet}H_2O$, Pd/C, MeOH, reflux, 6 h, 98%; *iv*) C_6H_5NCO, CH_2Cl_2, r.t., 2 h, 71%; *v*) TFA, CH_2Cl_2, r.t., 1 h, 83%.

while the remaining phenolic units are tilted, orienting their relative methoxy groups inside the electron-rich cavity of the macrocycle [11,22]. For this reason, in the ^{1}H-NMR spectrum of **2**, the signal associated to the methoxy protons is characterised by significant broadness and is up-field shifted ($\delta = 2.9$ ppm) compared to the expected chemical shift (*ca.* 3.8 ppm). Further diagnostic signals are the two doublets at $\delta = 4.4$ and 3.6 ppm ($J = 14.4$ Hz) assigned to the bridging methylene units of the aromatic rings.

3.2. Modification of the GC electrodes

Within the techniques available for the grafting of organic monolayers at GC surfaces, the oxidation of primary amines at carbon electrodes represents one of the most efficient and versatile approaches, as it allows functionalising the carbon surface with stable and uniform layers. It must be noted that, although the electrochemical methodologies for creating such monolayers have reached quite advanced control over the modification process, imperfections and formation of multilayers are still possible. Nonetheless, the generated monolayers allow further modification by introducing suitable linking groups through solid phase synthesis techniques (SPPS) [23,24]. Thus GC electrodes were modified with a uniform monolayer of *N-tert*-butyloxycarbonyl ethylenediamine (Boc-EDA) by sweeping the potential of the electrode in the 0.4–1.95 V range (vs. Ag/AgCl), for 5 times, in a 20 mM solution of Boc-EDA in acetonitrile with tetrabutylammonium tetrafluoroborate (TBATFB) 0.1 M as supporting electrolyte, using the meniscus setup described previously (See SI) [25]. After the removal of the Boc group in acidic conditions (HCl 4 M), the electrode was available for further covalent functionalization using the diamine linker as anchoring point. Among the possible covalent bonds that an amine function could form, the amide bond is very stable, and can be readily obtained by reacting the mono-grafted EDA linker with a molecule characterised by a ω-carboxylic acid alkyl chain. The covalent attachment of the tricarboxy-modified calix[6]arene **2** onto GC electrodes was therefore achieved by dipping a series of the previously described amino-coated electrodes in a solution of **2** in DMF with ethyl (dimethylaminopropyl) carbodiimide (EDC) and *N*-hydroxysuccinimide (NHS) (coupling agents frequently used for solid-phase synthesis) (Scheme 2). Since **2** is a non-redox active compound, the characterisation and quantification of the species at the surface by direct cyclic voltammetry was not possible. As a consequence, we recorded a cyclic voltammogram (CV) in a 0.1 M KCl solution containing 5 mM $K_3[Fe(CN)_6]$ after each synthetic step to monitor the interfacial changes occurring at the GC surface. All the CVs recorded are presented in Fig. 2. The intensity of the redox peaks at $E_{mp} = 0.2$ V *vs.* Ag/Ag$^+$, associated with the Fe^{2+}/Fe^{3+} pair, is highly affected by the changes in thickness of the organic layer covering the electrode surface. The decrease of intensity of this peak in the CV corresponding to the electrode modified with **2** (dot-dashed line in Fig. 2), confirmed that the coupling reaction had occurred and a monolayer of calix[6]arenes was formed at the electrode. A further verification of the successful electrode modification was obtained by EIS measurements [26]. Modifying the nature of the



Scheme 2. Schematic representation of GC surface functionalization with EDA-Boc, followed by Boc deprotection and coupling with calix[6]arene **2**.

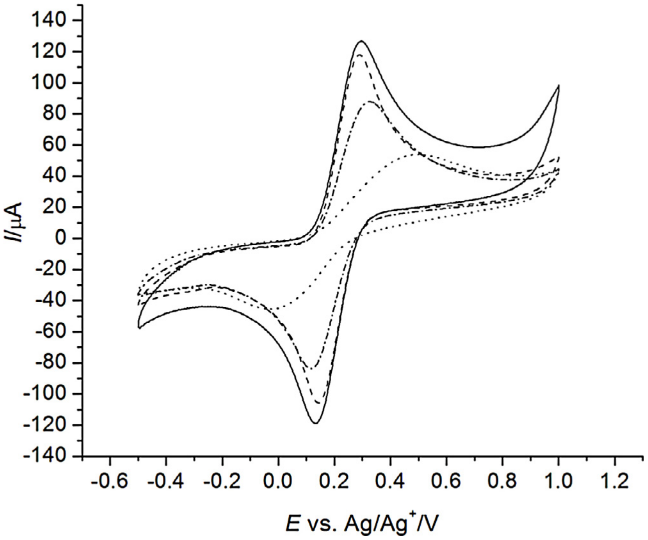


Fig. 2. Cyclic voltammograms recorded at a scan rate of 100 mV s^{-1} in 0.1 M KCl solution containing 5 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (1:1) before (solid) and after electrochemical modification with EDA-Boc (dotted), deprotection with HCl 4 M in dioxane (dashed) and grafting of calixarene **2** (dot-dashed).

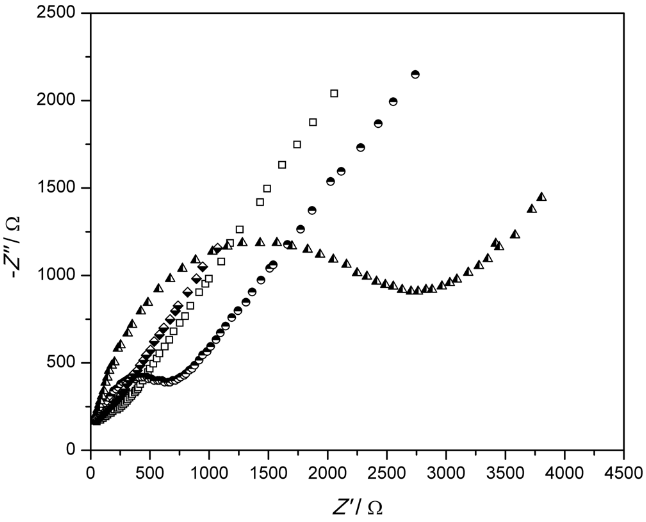


Fig. 3. Nyquist plots of electrochemical impedance spectra obtained at glassy carbon electrode in presence of 1 mM $K_3Fe(CN)_6$ electrochemical probe + 0.1 M KCl aqueous solution for: bare (diamonds), EDA-Boc functionalized (triangles), $-NH_2$ modified (squares) and calixarene **2** modified (dots) electrode. Fixed potential of 220 mV ± 10 mV within the frequency range of 0.1 to 106 Hz.

coating layer, a substantial alteration of the resistance inferred to the electrode was observed (Fig. 3). Starting with a resistance value of 258 Ω for a bare GC electrode, after the complete functionalization of the surface, we measured an increased resistance value of 339 Ω for the modified electrode. The small variation of the resistance value recorded upon derivatization of the CG electrode with **2** is probably due to the bulkiness of this compound that prohibits the constitution of a dense organic monolayer on the electrode.

3.3. Pseudorotaxane Formation at Chemically Modified GC Electrodes

Before studying the formation of possible pseudorotaxane complexes at the liquid-solid interphase between the calix[6]arene-modified GC electrodes (**2**/EDA/GC) and the *N,N*-dioctyl viologen ditosylate (**DOV**×2TsO), taken as a typical prototype of a *N,N*-dialkylviologen-based axle, we initially evaluated the electrochemical behaviour of the free salt and of its pseudorotaxane complex with calix[6]arene **1** (**1**⊃**DOV**×2TsO) in low polarity solvents. The CVs, recorded at a scan rate of 100 mV s^{-1} in a solution of 0.1 M $TBAPF_6$ in DCM, are reported in Fig. 4 as dashed line. The formal standard potential ($E^{\circ\prime}$), associated with the redox process, were calculated as the average of anodic potential (E_a) and cathodic potential (E_c) using Eq. (1):

$$E^{\circ\prime} = (E_a + E_c)/2 \quad (1)$$

Consistent with our previous results, obtained with similar calix[6]arene derivatives [13], axle **DOV**×2TsO, when threaded in the cavity of **1** (**1**⊃**DOV**×2TsO) shows a shift of the $E^{\circ\prime}_1$ of its first redox peak of *ca.* 160 mV to lower potentials (dashed line, Fig. 4) compared to the free axle (dotted line, Fig. 4). This shift has been explained as being due to the stabilization induced by the electron-rich cavity of the macrocycle on the viologen core of **DOV**. The peak associated to the second redox process presents the same $E^{\circ\prime}_2$ for both the free and the complexed axle, suggesting that after the first reduction step the radical cation specie formed (**DOV**$^{\bullet}$×TsO) dethreads from the cavity of **1**. The results obtained for the GC electrodes modified with **2** were comparable with what had been seen for **1**⊃**DOV**×2TsO in solution. The $E^{\circ\prime}_1$ measured was shifted to lower potentials compared to the free **DOV**×2TsO (solid line, Fig. 4), although to a lesser extent (*ca.* 100 mV). More importantly, after the first reduction step, the reduced viologen cation generated apparently dethreads from the cavity, since its $E^{\circ\prime}_2$ value is comparable to the one obtained performing the

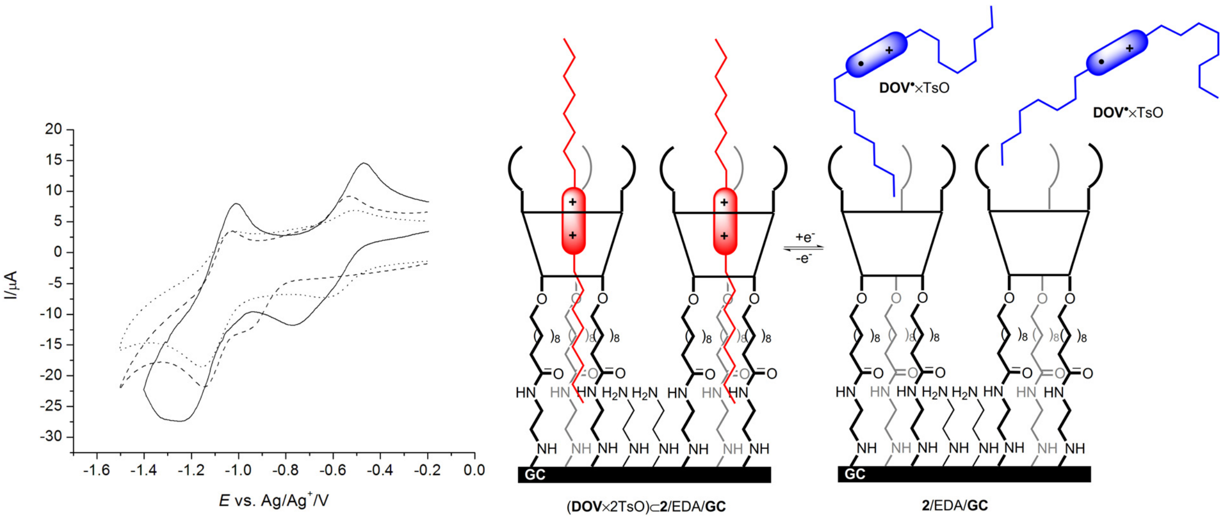


Fig. 4. (left) CVs recorded at a scan rate of 100 mV s^{-1} in a 0.1 M TBAPF$_6$ solution in DCM of a 5 mM solution of **DOV** × 2TsO with (dotted line) or without (dashed line) wheel **1** and of **DOV** × 2TsO in presence of the calix[6]arene-modified GC electrodes **2**/EDA/**GC** (solid line); (right) schematic representation of the corresponding complexation processes in solution and at the solid/liquid interphase of the electrode.

measurement on the free **DOV**×2TsO (dotted line, Fig. 4). These results suggested that *N*,*N*-dialkylviologen-based axles like **DOV**×2TsO can easily have access to the aromatic cavity of tris (*N*-phenylureido)calix[6]arene derivatives even when the latter are covalently attached on the glassy carbon surface.

The threading/de-threading process of the pseudorotaxane is only partially reversible, as suggested by the clear changes in the redox peaks, which occurred by increasing the scans number (Fig. 5). After four scans, the dissociation of the complex on the surface is complete, as demonstrated by the disappearance of its relative reduction peak in the CV, while the only reduction peaks present are relative to the free **DOV**×2TsO in solution. Such non-reversibility of the pseudorotaxane formation could be explained by considering the diffusion processes occurring: the guest, after reduction and the consequent de-threading, is dispersed in the bulk solution and, once oxidised, the re-complexation process is not favoured. Calculating the current associated with the redox processes of the pseudorotaxane covalently bound to the GC surface, (**DOV**×2TsO)⊂**2**/EDA/**GC**, it was possible to determine the surface coverage (Γ) of the electrode using Faraday's law described in Eq. (2):

$$\Gamma = Q/nFA\rho \tag{2}$$

where Q is the charge, obtained from integration of the baseline-corrected area under the oxidation/reduction peaks, F the Faraday constant, A the geometric area of the electrode (0.071 cm^2), $n = 2$ the number of electrons transferred, and ρ is the roughness factor of the surface. According to literature [27], ρ values could vary between 4 and 8 for the polishing technique adopted and 4 was used in these calculations. The calculated surface coverage, $\Gamma = 139$ pmol cm^{-2}, is about one order of magnitude smaller compared to previous results reported in literature for thick EDA-Boc monolayer electrografted to GC electrodes [18].

Several explanations may justify the lower amount of molecules attached to the surface: *a*) ideally, each molecule of **2** covalently binds three amine moieties on the surface, reducing considerably the theoretical number of possible pseudorotaxanes on the surface; *b*) the three carboxylic groups of the calixarene may

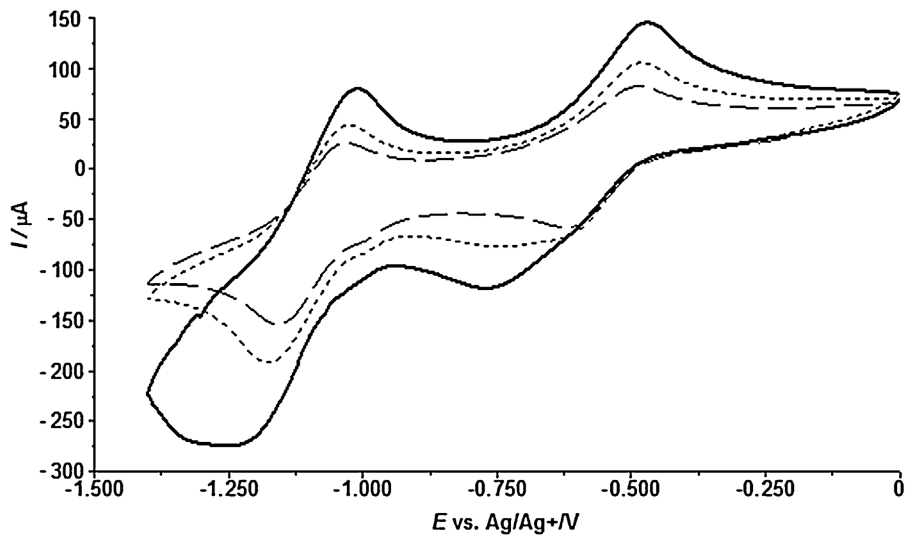
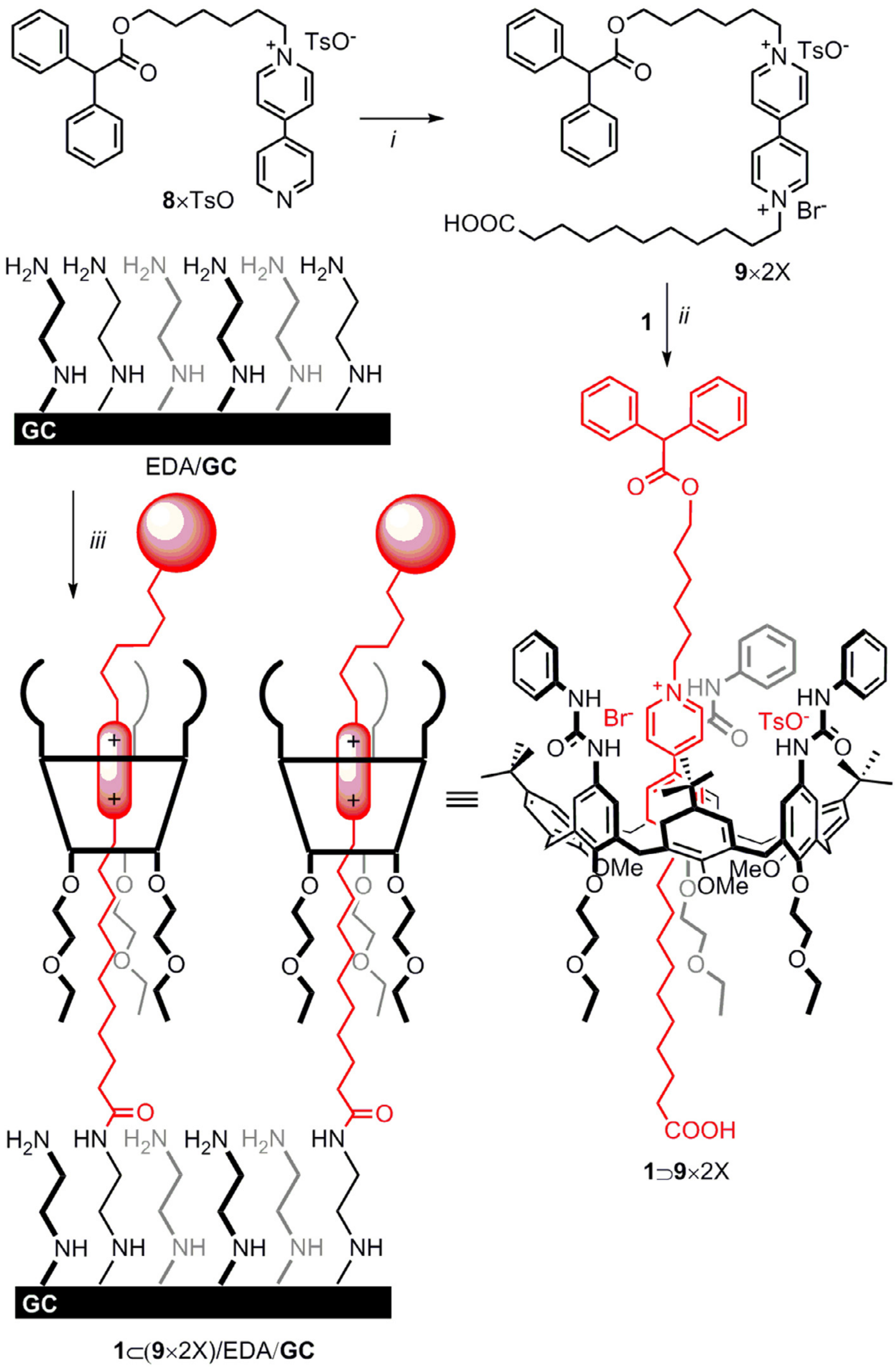


Fig. 5. Cyclic voltammograms recorded at a scan rate of 100 mV s^{-1} in 0.1 M TBAPF$_6$ solution in dichloromethane GC electrodes modified by calixarene derivative **2**⊃**DOV**×2TsO. Second (solid), third (dotted) and fourth (dashed) scan are represented.

bind three not closely located amine functions, reducing with the steric hindrance of its cavity the effective number of available sites on the electrode surface; *c*) the redox active centre, represented by the viologen-based guest, is not covalently attached to the electrode: it is plausible that certain host molecules appended to the electrode refuse to form pseudorotaxanes due to their wrong orientation toward the solution; *d*) since the calculations were performed on the second scan of the CV measurement, they do not consider the amount of pseudorotaxane irreversibly dissociated during the first scan.

3.4. Creation of a Rotaxane-like System at the GC Electrode

The good results obtained for the formation of calix[6]arene-based pseudorotaxanes at the GC surface prompted us to investigate the possibility to build-up [2]rotaxane systems using a similar strategy. Compared to pseudorotaxanes, [2]rotaxanes are in fact two-component interlocked systems in which the axial (or threaded) component is confined inside the circular one (wheel) because of the bulkiness of two stoppers placed at its termini which prevent the wheel from slipping off the axle. In this context, we thought the carbon surface of the GC electrode could serve both



Scheme 3. Reagents and conditions: *i*) 11-bromoundecanoic acid, CH_3CN, reflux, 4 days, 50%; *ii*) CH_2Cl_2, r.t., 1 h; *iii*) EDC, NHS, DCM, 5 h, r.t.

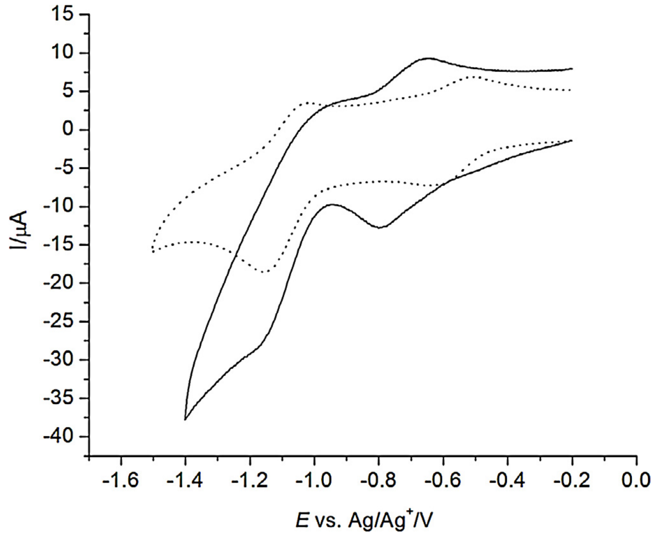


Fig. 6. CVs recorded at a scan rate of 100 mV s^{-1} in a 0.1 M TBAPF$_6$ solution in DCM of (solid) a 5 mM solution of DOV × 2TsO and (dotted) modified GC electrodes **1**⊂(**9**×2X)/EDA/**GC.**

as a supporting material and as a stopper for the [2]rotaxane axial component as depicted in Scheme 3. To this end, we designed the asymmetric viologen axle **9**×2X, where X can be either tosylate or bromide, bearing a diphenylacetyl group (the stopper) on a C6 alkyl chain and a ω-carboxylic function on C11 alkyl chain on the opposite side, suitable for the coupling to an amine monolayer. This axle provides all the necessary features to: *a*) perform unidirectional threading into wheel **1** only from the macrocyle upper rim; *b*) its carboxy terminal group may react with the deprotected EDA-Boc functions grafted on the GC surface.

Axle **9**×2X was synthesised by refluxing the known mono-alkylated bispyridinium salt **8**×TsO with excess of 11-bromoundecanoic acid in acetonitrile. The axle was mixed with wheel **2** to form the pseudorotaxane **1**⊃**9**×2X before its attachment to the GC electrode surface. The preparation was carried out using a convergent approach by simply mixing in dichloromethane equimolar amounts of wheel **1** and axle **9**×2X (Scheme 3).[1] The modification of the electrode was achieved with a solid-phase synthesis approach similar to the that previously discussed (Scheme 3). In particular, a slight excess of axle **9**×2X was added to a solution of wheel **1** in dichloromethane. After stirring for one hour, the solution went from colourless to deep red indicating the complete formation of the pseudorotaxane **1**⊃**9**×2X. The red solution was filtered off to remove the uncomplexed and not soluble viologen axle **9** and the combination of coupling agents were then added to the filtered solution. Following the formation of the activated ester, an EDA modified GC electrode (EDA/GC) was dipped into the above solution for four hours under magnetic stirring. As usual, the modified electrodes **1**⊃(**9**×2X)/EDA/**GC** were characterised by cyclic voltammetry in a 0.1 M solution of TBAPF$_6$ in DCM. The CV (Fig. 6) confirmed the successful anchoring of the pseudorotaxane systems **1**⊃**9**×2X on the GC electrode. As previously discussed, the surface of the electrode hinders the slipping of the wheel from the axle, and thus the supramolecular complexes grafted on the surface through the axle can be now considered as real rotaxane systems in which the calix[6]arene wheel cannot escape from the surface in the solution. Proof of the stability of the **1**⊃(**9**×2X)/EDA/**GC** electrode was provided by the intensity of the redox peaks relative to **9** which remained unchanged even after 30 scans of the potential. The potential values of the reduction and oxidation peaks confirm the inclusion of the viologen unit of **9** inside the wheel **1**, showing a shift of the $E^{\prime\circ\prime}$ by *ca.* 200 mV to lower potentials compared to **DOV**×2TsO in the same solvent. Although the resulting peak was slightly shifted, the correct determination of the shift of the second redox peak ($E^{\circ\prime}{}_2$) was impossible, given the interference of molecular oxygen, whose reduction occurred in the same potential window. Nonetheless, as expected, the results make clear that the diphenylacetyl stopper present in axle **9** prevented its slipping from **1** and confined the redox-active viologen unit in the macrocycle cavity even in its reduced form.

Calculating the charge obtained from integration of the baseline-corrected area under the oxidation or reduction peak, we were able to estimate the amount of rotaxane units linked to the electrode. Using Eq. (2): a value of $\Gamma = 79\,\mathrm{pmol\,cm^{-2}}$ was obtained. This value is about half the value of $139\,\mathrm{pmol\,cm^{-2}}$ calculated in the previous experiment, where calix[6]arene **2** was directly covalently anchored to the electrode surface. The lower amount of redox active units on the surface is probably due to the presence of the complex in solution, being the process governed by an equilibrium, the yield of the reaction was noticeably reduced.

With the objective of comparing the electrochemical behaviour of a dialkylviologen salt covalently linked to the surface without the presence of wheel **1** to the experimental results obtained with the anchoring of **1**⊃**9**×2X, axle **9**×2X was coupled to a free amine monolayer using DMF as solvent [25]. However the attempted formation of the activated ester with EDC was unsuccessful: after the addition of EDC, the colour of the solution immediately changed from yellow to blue, suggesting the formation of a reduced form of the viologen core of the axle. We speculate that, EDC reacts more readily with the viologen core instead of forming the activated ester needed for the coupling with the modified electrode [28]. Such behaviour was not detected upon activation of the carboxylic acid group after the pseudorotaxane was formed: we supposed that the electron-rich cavity of the macrocyclic wheel shields the viologen unit from reaction with the coupling agent.

3.5. Modification of GC electrode with a pseudorotaxane assembly

Having optimised the conditions for the modification of GC electrodes with our calix[6]arene-based pseudorotaxanes and rotaxanes, we decided to study the effect that a long alkyl chain on the viologen unit could have on the threading/de-threading process under electrochemical stimuli. As demonstrated in our previous solution studies, [28] a long C18 alkyl chain acts as a very effective kinetic stopper in solution so we wanted to determine if it could similarly prevent the de-threading of the wheel once the pseudorotaxane was anchored at the surface. Indeed, it could be supposed that, due to its length, the loss of conformational freedom needed for the C18 alkyl chain to allow the slipping of the calix[6]arene macrocycle through its annulus, would be a very slow and disfavoured process even after the reduction of the viologen unit. It is reasonable to assume that the monitoring of this process by cyclic voltammetry will be strongly dependent on the scan rate employed. To this end, we designed a pseudorotaxane comprising wheel **1** threaded by axle **12**×2X, where X can be either bromide or tosylate. Such an axle required, as substituents on the bispyridinium redox active core, a *ω*-carboxy C11 alkyl chain, whose terminal carboxylic group would be used for the anchoring of the axle on the EDA/**GC** surface, and on the other side a C18 alkyl chain

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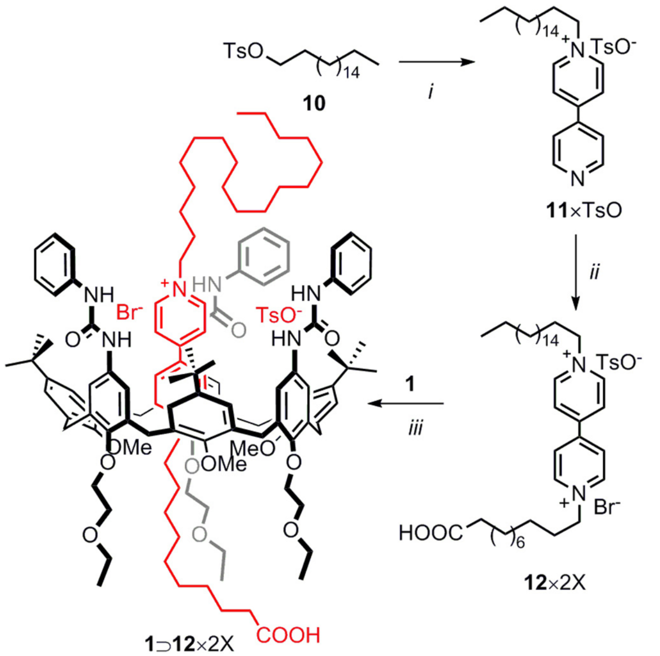
[1] Differently from dichloromethane, axle **9**×2X experiences good solubility in DMF. In the latter, very polar, solvent the formation of pseudorotaxane species between calix[6]arenes and viologen-based is greatly reduced. Most important, the directionality of the threading process, that in low polar solvent such as DCM would occur with the unstoppered (*ω*-carboxy) alkyl chain of **9** preferentially, if not exclusively, from the upper rim of **1**, in DMF would occur from both rims of the macrocycle yielding a mixture of two orientational pseudorotaxane isomers[21].



Scheme 4. Reagents and Conditions: *i*) 4,4′-bipyridyl, CH_3CN, reflux, 24 h, 64%; *ii*) 11-bromoundecanoic acid, CH_3CN, reflux, 4 days, 62%.

substituent. This dialkylviologen salt was synthesized following the synthetic route depicted in Scheme 4: the known 1-octadecyl tosylate **10** was refluxed in acetonitrile with excess of 4,4′-bipyridyl to obtain the monolakylated bispyridine derivative **11**$\times$TsO, which, in turn, was refluxed in acetonitrile with 11-bromoundecanoic acid to yield the target dicationic salt **12**$\times$2X as a yellow powder in 40% of overall yield. The **1**$\supset$**12**$\times$2X pseudorotaxane formation, its immobilisation on the EDA/**GC** electrodes and final characterisation of the modified surfaces **1**$\supset$(**12**$\times$2X)/EDA/**GC** was accomplished with the procedures previously described for pseudorotaxanes **1**$\supset$**9**$\times$2X (Scheme 3). The CVs recorded at 100 mV s^{-1} showed the typical pattern of signals relative to a rotaxane system, [13,29] in which both the reduction potential peaks are shifted to lower potential compared to a free viologen derivative in solution (Fig. 7). The decreasing intensity of the current associated with the redox peaks of the specie at the surface by scanning the potential window several times, indicates that, despite the C18 chain presence, the wheel partially de-threads form the axle. Lowering the experiments scan rate to 50 mV s^{-1}, the de-complexation process was complete after six scans. The result suggests that, upon reduction of the guest, the wheel slips from the axle and within the time interval needed to re-oxidise the viologen unit, the calix[6]arene host diffuses away from the electrode surface, thus rendering the regeneration of the pseudorotaxane impossible. Nonetheless, at a scan rate of 100 mV s^{-1}, the threading/de-threading process resulted reversible. We speculated that, the fast reduction/reoxidation process of the viologen, together with the steric effect of the octadecyl alkyl chain, avoided the complete decomplexation of the calix[6]arene wheel, favouring the re-inclusion of the viologen unit in the calixarene cavity once re-oxidised over diffusion processes (Fig. 7a).

4. Conclusions

We presented here a new approach to the covalent modification of GC electrodes with calix[6]arene and dialkylviologen based pseudorotaxanes and rotaxanes using solid-phase synthesis techniques. Initially, the surfaces were modified with a tris(*N*-phenylureido)calix[6]arene derivative: such functionalization conferred to the electrode the ability to take up *N*,*N*-dialkylviologen salts in low polarity media such as DCM

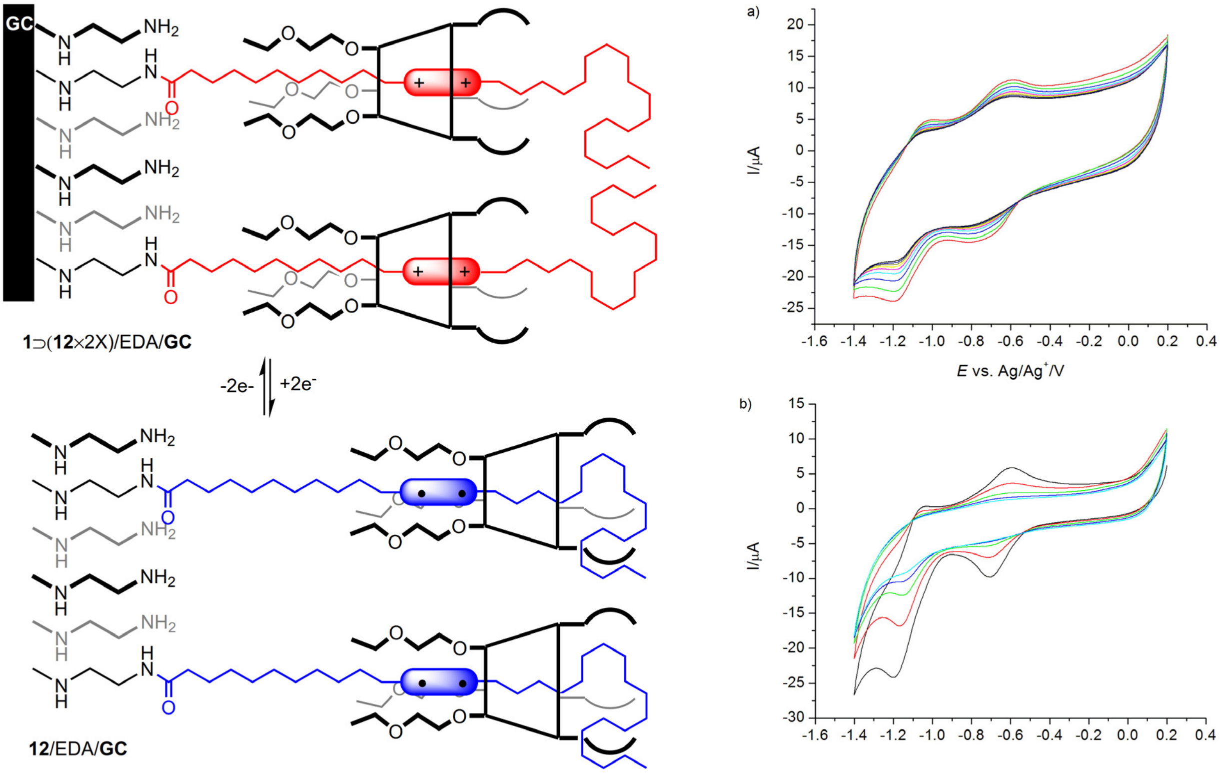


Fig. 7. (left) pseudorotaxane **1**$\supset$**12**$\times$2X immobilised on the EDA/**GC** surface and its electrochemical switch; (right) cyclic voltammograms (10 scans) recorded in a 0.1 M $TBAPF_6$ solution in ACN of the modified **1**$\supset$(**12**$\times$2X)/EDA/GC electrodes at a scan rate of: a) 100 mV s^{-1}; b) 50 mV s^{-1}.

and to assemble pseudorotaxane systems. In these conditions, the threading/de-threading processes of the viologen-based axle into the calix[6]arene-based wheel could be controlled by electrochemical stimuli generated by the same electrode to which the pseudorotaxane was anchored. Next, we designed two solution generated pseudorotaxane-like structures which could be anchored at the surface through the axle, showing different behaviour under electrochemical stimuli. In the first example, a bulky group present at one extremity of the axle inhibited its de-threading from the wheel after the reduction of the viologen unit, generating a rotaxane, while in the second, the axle was characterised by a long C18 alkyl chain whose ability to act as a kinetic stopper was strongly dependant on the scan rate of the electrochemical experiment. These studies gave further insight on the behaviour and stability of calix[6]arenes based pseudorotaxanes and rotaxanes covalently bound to electrode surfaces. Our results represent a step further toward the creation of electrochemically controlled molecular machines confined on GC surfaces for the development of smarter devices. Future studies could involve the insertion of a secondary recognition site on the axle, able to stabilise the mono-reduced form of the viologen axle: using this work as inspiration it should be possible to design molecular elevators, shuttles or other switchable Host-Guest systems.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.electacta.2016.12.169.

References

[1] P.A. Gale, J.W. Steed (Eds.), Supramolecular Chemistry, John Wiley & Sons, Ltd, Chichester, UK, UK, 2012.

[2] J.-M. Lehn, Supramo lecular Chemistry – Scope and Perspectives Molecules, Supermolecules, and Molecular Devices, Angew. Chem. Int. Ed. 27 (1988) 89–112, doi:http://dx.doi.org/10.1002/anie.198800891.

[3] V. Balzani, A. Credi, M. Venturi, Molecular machines working on surfaces and at interfaces, ChemPhysChem 9 (2008) 202–220, doi:http://dx.doi.org/10.1002/cphc.200700528.

[4] Y.-W. Yang, Y.-L. Sun, N. Song, Switchable host-guest systems on surfaces, Acc. Chem. Res. 47 (2014) 1950–1960, doi:http://dx.doi.org/10.1021/ar500022f.

[5] N. Katsonis, M. Lubomska, M. Pollard, B. Feringa, P. Rudolf, Synthetic light-activated molecular switches and motors on surfaces, Progr. Surf. Sci. 82 (2007) 407–434, doi:http://dx.doi.org/10.1016/j.progsurf.2007.03.011.

[6] V. Balzani, A. Credi, M. Venturi, Molecular Devices and Machines – A Journey into the Nano World, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, FRG, 2003.

[7] A. Credi, S. Silvi, M. Venturi, Molecular Machines and Motors: Recent Advances and Perspectives, Springer, 2014.

[8] M.R. Bryce, G. Cooke, F.M.A. Duclairoir, P. John, D.F. Perepichka, N. Polwart, V.M. Rotello, J. Fraser Stoddart, H.-R. Tseng, Surface confined pseudorotaxanes with electrochemically controllable complexation properties, J. Mat. Chem. 13 (2003) 2111–2117, doi:http://dx.doi.org/10.1039/B306274K.

[9] S.R. Bayly, T.M. Gray, M.J. Chmielewski, J.J. Davis, P.D. Beer, Anion templated surface assembly of a redox-active sensory rotaxane, Chem. Comm. 2 (2007) 2234–2236, doi:http://dx.doi.org/10.1039/B701796K.

[10] N.H. Evans, H. Rahman, A.V. Leontiev, N.D. Greenham, G.A. Orlowski, Q. Zeng, R.M.J. Jacobs, C.J. Serpell, N.L. Kilah, J.J. Davis, et al., Solution and surface-confined chloride anion templated redox-active ferrocene catenanes, Chem. Sci. 3 (2012) 1080–1089, doi:http://dx.doi.org/10.1039/C2SC00909A.

[11] A. Arduini, R. Ferdani, A. Pochini, A. Secchi, F. Ugozzoli, Calix[6] arene as a Wheel for Rotaxane Synthesis, Angew. Chem. Int. Ed. 39 (2000) 3453–3456, doi:http://dx.doi.org/10.1002/1521-3773(20001002)39:19<3453:AID-.

[12] F. Ugozzoli, C. Massera, A. Arduini, A. Pochini, A. Secchi, Calix[6] arene-based pseudorotaxanes: a solid state structural investigation, CrystEngComm 6 (2004) 227–232, doi:http://dx.doi.org/10.1039/B406591C.

[13] A. Credi, S. Dumas, S. Silvi, M. Venturi, A. Arduini, A. Pochini, A. Secchi, Viologen-calix[6] arene pseudorotaxanes. Ion-pair recognition and threading/dethreading molecular motions, J. Org. Chem. 69 (2004) 5881–5887, doi: http://dx.doi.org/10.1021/jo0494127.

[14] A. Boccia, V. Lanzilotto, R. Zanoni, L. Pescatori, A. Arduini, A. Secchi, Surface grafting and reactivity of calixarene-based receptors and pseudorotaxanes on Si(100), Phys. Chem. Chem. Phys. 13 (2011) 4444–4451, doi:http://dx.doi.org/10.1039/C0CP01916J.

[15] A. Boccia, V. Lanzilotto, V. Di Castro, R. Zanoni, L. Pescatori, A. Arduini, A. Secchi, Preparation, reactivity and controlled release of SAMs of calix[4, 6]arenes and calix[6] arene-based rotaxanes and pseudorotaxanes formed on polycrystalline Cu, Phys. Chem. Chem. Phys. 13 (2011) 4452–4462, doi:http://dx.doi.org/10.1039/C0CP01921F.

[16] A. Boccia, F. D'Orazi, E. Carabelli, R. Bussolati, A. Arduini, A. Secchi, A.G. Marrani, R. Zanoni, Assembly of gold nanoparticles on functionalized Si(100) surfaces through pseudorotaxane formation, Chem. Eur. J. 19 (2013) 7999–8006, doi:http://dx.doi.org/10.1002/chem.201204318.

[17] Y. Li, X. Lin, Simultaneous electroanalysis of dopamine, ascorbic acid and uric acid by poly (vinyl alcohol) covalently modified glassy carbon electrode, Sens. Actuators B 115 (2006) 134–139, doi:http://dx.doi.org/10.1016/j.snb.2005.08.022.

[18] M.A. Ghanem, J.-M. Chrétien, A. Pinczewska, J.D. Kilburn, P.N. Bartlett, Covalent modification of glassy carbon surface with organic redox probes through diamine linkers using electrochemical and solid-phase synthesis methodologies, J. Mat. Chem. 18 (2008) 4917–4927, doi:http://dx.doi.org/10.1039/B809040H.

[19] J.J. González, R. Ferdani, E. Albertini, J.M. Blasco, A. Arduini, A. Pochini, P. Prados, J. de Mendoza, Dimeric Capsules by the Self-Assembly of Triureidocalix[6] arenes through Hydrogen Bonds, Chem. Eur. J. 6 (2000) 73–80, doi:http://dx.doi.org/10.1002/(SICI)1521-3765(20000103)6:1<73:AID-CHEM73>3.0.CO;2-#.

[20] A. Casnati, L. Domiano, A. Pochini, R. Ungaro, M. Carramolino, J.O. Magrans, P.M. Nieto, J. Lopezprados, P. Prados, J. Demendoza, R.G. Janssen, W. Verboom, D.N. Reinhoudt, Synthesis of calix[6] arenes partially functionalized at the upper rim, Tetrahedron 51 (1995) 12699–12720, doi:http://dx.doi.org/10.1016/0040-4020(95)00826-t.

[21] A. Arduini, F. Ciesa, M. Fragassi, A. Pochini, A. Secchi, Selective Synthesis of Two Constitutionally Isomeric Oriented Calix[6] arene-Based Rotaxanes, Angew. Chem. Int. Ed. 44 (2005) 278–281, doi:http://dx.doi.org/10.1002/anie.200461336.

[22] A. Arduini, F. Calzavacca, A. Pochini, A. Secchi, Unidirectional threading of triphenylureidocalix[6] arene-based wheels: Oriented pseudorotaxane synthesis, Chem Eur. J. 9 (2003) 793–799, doi:http://dx.doi.org/10.1002/chem.200390089.

[23] J.-M. Chrétien, M.A. Ghanem, P.N. Bartlett, J.D. Kilburn, Covalent tethering of organic functionality to the surface of glassy carbon electrodes by using electrochemical and solid-phase synthesis methodologies, Chem. Eur. J. 14 (2008) 2548–2556, doi:http://dx.doi.org/10.1002/chem.200701559.

[24] M.A. Ghanem, J.-M. Chrétien, J.D. Kilburn, P.N. Bartlett, Electrochemical and solid-phase synthetic modification of glassy carbon electrodes with dihydroxybenzene compounds and the electrocatalytic oxidation of NADH, Bioelectrochemistry 76 (2009) 115–125, doi:http://dx.doi.org/10.1016/j.bioelechem.2009.02.008.

[25] J. Groppi, P.N. Bartlett, J.D. Kilburn, Toward the Control of the Creation of Mixed Monolayers on Glassy Carbon Surfaces by Amine Oxidation, Chem. Eur. J. 22 (2016) 1030–1036, doi:http://dx.doi.org/10.1002/chem.201503120.

[26] M.E. Orazem, B. Tribollet, Electrochemical Impedance Spectroscopy, John Wiley & Sons, Inc Hoboken, NJ, USA, NJ USA, 2008.

[27] S. Ranganathan, R.L. McCreery, Electroanalytical performance of carbon films with near-atomic flatness, Anal. Chem. 73 (2001) 893–900, doi:http://dx.doi.org/10.1021/ac0007534.

[28] C.L. Bird, A.T. Kuhn, Electrochemistry of the viologens, Chem. Soc. Rev. 10 (1981) 49–82, doi:http://dx.doi.org/10.1039/CS9811000049.

[29] A. Arduini, R. Bussolati, A. Credi, A. Secchi, S. Silvi, M. Semeraro, M. Venturi, Toward directionally controlled molecular motions and kinetic intra- and intermolecular self-sorting: threading processes of nonsymmetric wheel and axle components, J. Am. Chem. Soc. 135 (2013) 9924–9930, doi:http://dx.doi.org/10.1021/ja404270c.