

Experimental Section

Representative procedure: NO₂ was used as a liquid at 0 °C. To a pear-shaped flask (100 mL) were added NHPI (98 mg, 0.6 mmol) and cyclohexane (5 mL). The flask was closed with a glass stopper and weighed. Then NO₂ (0.75 mL) was quickly added using a Hamilton gas-tight syringe, and the flask was resealed with the glass stopper. The flask was weighed again in order to measure the NO₂ added (115 mg, 2.5 mmol). The flask was cooled in an ice bath and then quickly attached to a condenser, and the mixture was stirred at 70 °C for 14 h. After the reaction, GC and GC-MS analyses were performed. The yields of the products were estimated from the peak areas based on the internal standard technique using GC. The products were isolated by column chromatography on silica gel with hexane/ethyl acetate (10/1–3/1, v/v), and were identified by comparison of their analytical data with those of authentic samples.

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Immobilization of Redox-Active Ligands on an Electrode: The Dendrimer Route**

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Macrocyclic systems that respond electrochemically when interacting with a guest ion have been extensively studied,^[1] notably in connection with their potential applications as chemosensors. In such host molecules, the complexing ability of the ligand can be tuned by the electrochemical potential applied. Most of these compounds are built by covalent grafting of a receptor subunit onto a redox-active component. Thus, in the case of metal-cation recognition, various ligating fragments, for example, crown ethers, have been attached to an electroactive moiety such as a metallocene or a quinone derivative.^[1] Alternatively, the ability of the tetrathiafulvalene (TTF) core to act as the redox-active subunit is now well established.^[2] Indeed, TTF derivatives are able to exist in three different stable redox stages (neutral, radical cation, and dication) and therefore allow the electrochemical release of metallic cations to be controlled.

A further exciting challenge, less explored, lies in the preparation of sensing devices that can transfer the above-mentioned recognition properties, observed in solution, at the interface of a solid electrode and a liquid.^[3] Results in this direction have been obtained thanks to a) electropolymerization of suitably substituted redox-responsive ligands (e.g., a pyrrole- or a thiophene-based monomer),^[3, 4] and b) preparation of self-assembled monolayers.^[5] Modified electrodes were also recently obtained by Casado et al. by electrodeposition of organometallic-containing silicon dendrimers.^[6] On the other hand, TTF dendrimers, possessing 21 TTF moieties in the highest generation, were described by Bryce et al.,^[7] but no mention was made of their immobilization on an electrode surface.

We describe here the synthesis of a series of dendrimers with up to 96 redox-active TTF moieties on the periphery, which allow the generation of polycationic species bearing up to 192 positive charges on the surface. Modified electrodes incorporating these electroactive TTF dendrimers were

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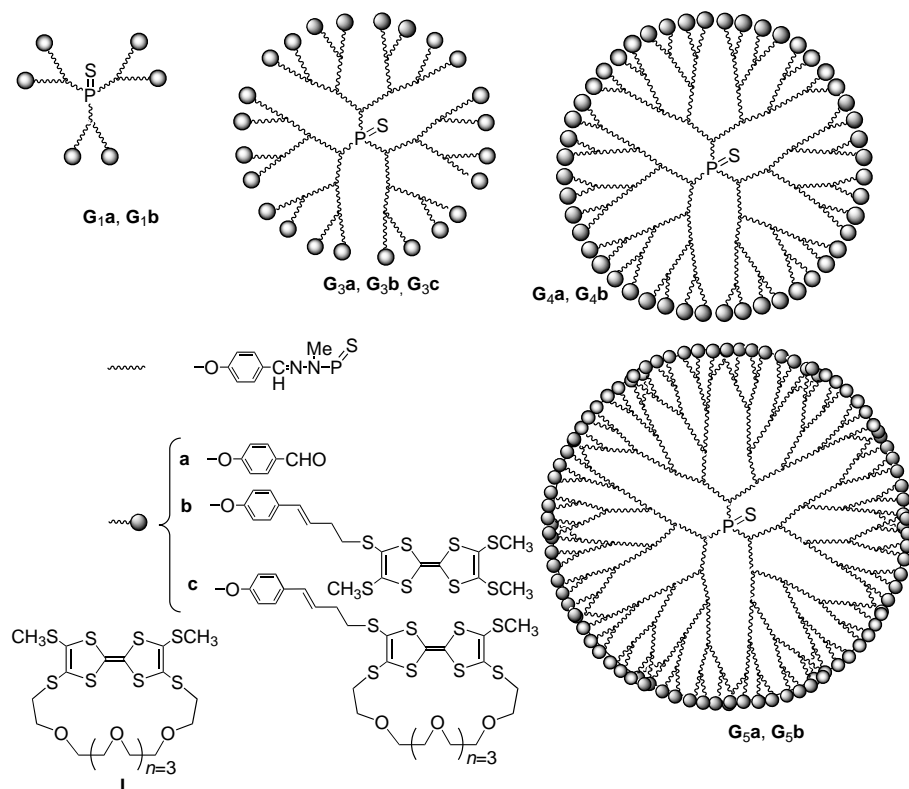
[**] We thank the Ministère de l'Enseignement Supérieur et de la Recherche and the CNRS for financial support. MESR and Fundacion Ramon Areces (Spain) are also gratefully acknowledged for funding grants (to G.T. and R.M.S. respectively). We are grateful to Dr. R. Filmon for SEM experiments.



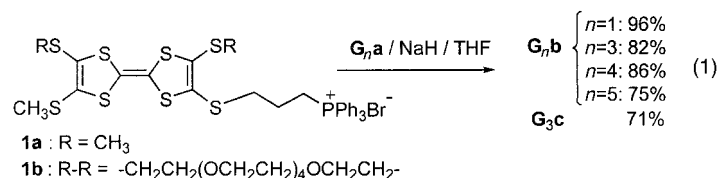
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obtained by electrodeposition. Applicability of these systems was illustrated by the preparation of the first dendrimer-modified electrode able to reproduce the electrochemical sensing of a metal cation (i.e., Ba^{2+}) thanks to the grafting of crown ether/TTF units on the periphery of the dendrimer.

Dendrimers **G₁b**, **G₃b**, **G₄b**, and **G₅b** (generations 1, 3, 4, and 5), bearing respectively 6, 24, 48, and 96 TTF moieties on their periphery, were obtained in good yields (76–96 % after



workup) by a poly-Wittig olefination between the corresponding polyformyl dendrimers (**G₁a** to **G₅a**)^[8] and the phosphonium salt **1a** [Eq. (1)], which was synthesized by a classical three-step sequence from the corresponding cyanoethylsulfanyl precursor.^[9] Analogously, the crown ether/TTF-substituted dendrimer **G₃c** was prepared from **1b** and **G₃a** in a 71 % yield.



The solution electrochemistry of **G_nb** ($n = 1, 3, 4$, and 5) was first studied [Pt working electrode (diameter = 1 mm) in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (9/1) (Bu_4NPF_6 , 0.1 M)]. All **G_nb** exhibit the classical well-defined two-step reversible oxidation encountered in parent TTF systems. From the cyclic voltammograms (CVs) we observed a clear tendency of the dendrimers to deposit onto the electrode surface, as shown by the narrow shape of the redox waves.^[10]

To obtain insight into the nature of the interactions between the π -donating TTF moieties, electrooxidation of **G_nb** was analyzed by time-resolved and near-IR spectroelectrochemistry under thin-layer conditions (Figure 1 shows the result for **G₃b**). No significant difference was observed between the four generations of dendrimers. Electrochemical oxidation of **G_nb** in the first redox process leads to the development of three absorption bands with maxima at 500 (narrow), 800 (very broad and intense) and 2200 nm (weak). These values, by comparison with those of the parent tetramethylthiotetrathiafulvalene (TMT-TTF) studied under similar conditions,^[11] are respectively assigned to the radical cation $\text{D}^{+\cdot}$ (where D denotes the tetrathio-TTF fragment), to the π dimer $\text{D}_2^{2+\cdot}$, and to the mixed-valence dimer $\text{D}_2^{+\cdot}$. In this potential range, the broadness of the absorption band corresponding to the π dimer compared to the other bands suggests that the cation radical species are, as expected, in strong interaction.^[7a] Interestingly, when a potential of 1.0 V is reached, a single absorption band is observed (700 nm), which is unequivocally assigned to D_2^{2+} .^[11] Such behavior differs from observations made with other TTF dendrimer derivatives, for which interacting TTF cation radicals are still observed at this potential.^[7a] Therefore, spectroelectrochemical data give indirect evidence for oxidation of each TTF moiety to TTF^{2+} .

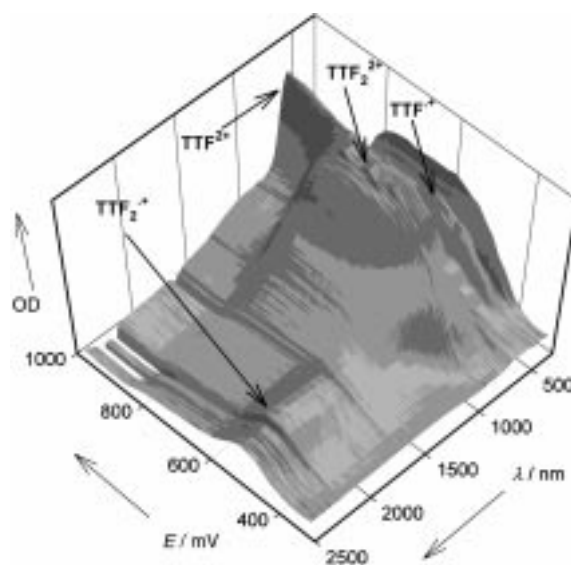


Figure 1. Spectroelectrochemistry under thin-layer ($d \approx 50 \mu\text{m}$) conditions (Pt electrode, $\varnothing = 2 \text{ mm}$) for **G₃b**; $c_{\text{dend}} = 1/24 \text{ mM}$ in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (9/1), Bu_4NPF_6 (0.2 M), scan rate 0.001 V s^{-1} ; reference electrode Ag/AgCl . OD = optical density.

To favor immobilization of **G_nb** on the electrode surface, we changed the solvent to THF (0.1M Bu₄NPF₆), which allowed a more efficient film growth as the dendrimers were oxidized. Electrodeposition was performed under potentiostatic conditions ($E_p = 0.60$ V) or by recurrent potential scans (0.2–1.0 V). In the latter case, film growth was manifested by a regular increase in both current peaks upon subsequent repeated cycling^[12] (Figure 2). Noticeably, electrodeposition appeared more pronounced for the higher homologues **G₃b**, **G₄b**, and **G₅b**, and was not dependent on the nature of the electrode, since similar results were also obtained with gold or glassy-carbon electrodes.

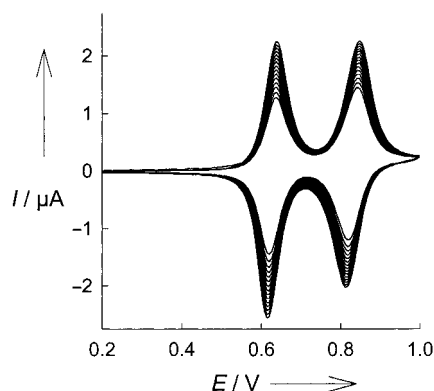


Figure 2. Electrodeposition of **G₃b**; $c_{\text{dend}} = 0.5/24$ mM in THF; Bu₄NPF₆ (0.1M), Pt electrode ($\varnothing = 1$ mm); scan rate 0.1 V s⁻¹; reference electrode Ag/AgCl.

The electrochemical response of the films was studied by cyclic voltammetry in fresh dichloromethane, acetonitrile, or a mixture thereof containing Bu₄NPF₆ (Figure 3). Two well-defined reversible oxidation peaks were observed, which are

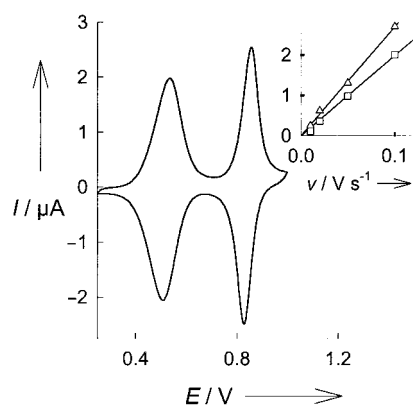


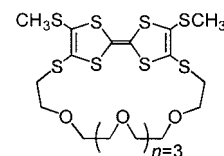
Figure 3. Cyclic voltammogram of a Pt electrode ($\varnothing = 1$ mm) modified with **G₃b** ($\Gamma_{\text{TTF}} = 1.2 \times 10^{-8}$ mol cm⁻²), measured in CH₂Cl₂/CH₃CN (9/1), Bu₄NPF₆ (0.1M). Inset: plot of I_{pa1} (\square) and I_{pa2} (\triangle) versus scan rate (ν); reference electrode Ag/AgCl.

characteristic of surface-confined redox couples, with the expected linear relationship of both peak currents (I_{pa1} and I_{pa2}) with the potential sweep rate ν (Figure 3, inset). In accordance with the above-mentioned spectroelectrochemical study and as a consequence of the strong interactions

occurring between TTF units in these multi-TTF species, the first redox wave is much broader than the second one.^[13] The surface coverage Γ of electroactive TTF moieties in the film was determined by integration of redox waves in the cyclic voltammogram ($\Gamma_{\text{TTF}} = 1.2 \times 10^{-8}$ mol cm⁻² for the film of Figure 3). It is noteworthy that no change in the electrochemical responses was observed upon repeated potential cycling, even after the sample standing in air for days, and this confirms the high stability of the modified electrodes.

These deposition properties were exploited for the immobilization of dendrimer **G₃c** on a platinum electrode. This sterically hindered dendrimer bearing 24 TTF/crown ether assemblies on its periphery was efficiently transferred onto the surface electrode under potentiostatic (0.6 V) or repeated cycling conditions in THF (Bu₄NPF₆). Electrochemical and spectroelectrochemical properties of the films obtained were essentially the same as for the corresponding nonligating **G₃b**, with two well-resolved redox waves and a linear relationship of the current to the scan rate. Scanning electron micrographs show that deposition of dendrimer **G₃c** on a Pt electrode gives rise to homogeneous coverage over the whole surface.^[14]

The most remarkable feature of these dendrimer films incorporating redox-responsive units is their unique capability to replicate the complexation/expulsion properties detected in homogeneous solution.^[6e,15] Indeed, we previously demonstrated the efficiency and the selectivity of the parent crown ether/TTF ligand **I** in controlling the reversible complexation/expulsion sequence of Ba²⁺.^[2b,e] This property of ligand **I** was illustrated by cyclic voltammetry experiments, in which the progressive addition of Ba²⁺ led to a positive shift of the first oxidation potential (Ba²⁺ complexation).



We observed that a **G₃c**-modified electrode behaves similarly. When exposed to a solution containing increasing concentrations of Ba²⁺ cations, the electrochemical response shows two distinctive regions (Figure 4): a progressive positive shift of E_{pa1} is observed for $[\text{Ba}^{2+}] = 1 \times 10^{-4}$ to 8×10^{-4} M, and then a constant E_{pa1} value at higher concentrations.^[16] This behavior is very similar to that observed in homogeneous solutions for Ba²⁺ titration by **I**, with a first area corresponding to the progressive coordination of Ba²⁺ by the peripheral crown ether/TTF ligands of **G₃c**, and then a plateau indicative of the saturation point. Though lower than in homogeneous solution with compound **I**, for which $\Delta(E_{\text{pa1}}) = 100$ mV,^[2b,e] the shift of E_{pa1} on immobilized **G₃c** reaches a value of $\Delta(E_{\text{pa1}}) = 85$ mV, without affecting the reversibility of the redox system. Contrary to observations made with **I** in solution, for which E_{pa2} remains unchanged upon addition of Ba²⁺, a slight positive shift is observed for E_{pa2} in the film ($\Delta(E_{\text{pa2}}) = 30$ mV for $[\text{Ba}^{2+}] = 0$ to 8×10^{-4} M). Similar observations were made recently by Echegoyen et al. for self-assembled monolayers of ligating TTFs, and were attributed to cooperativity effects between neighboring crown rings.^[5a]

We have prepared modified electrodes by electrodeposition of dendrimer structures incorporating up to 96 TTF moieties. The applicability of this strategy is exemplified by the immobilization of an electroactive receptor on an electrode

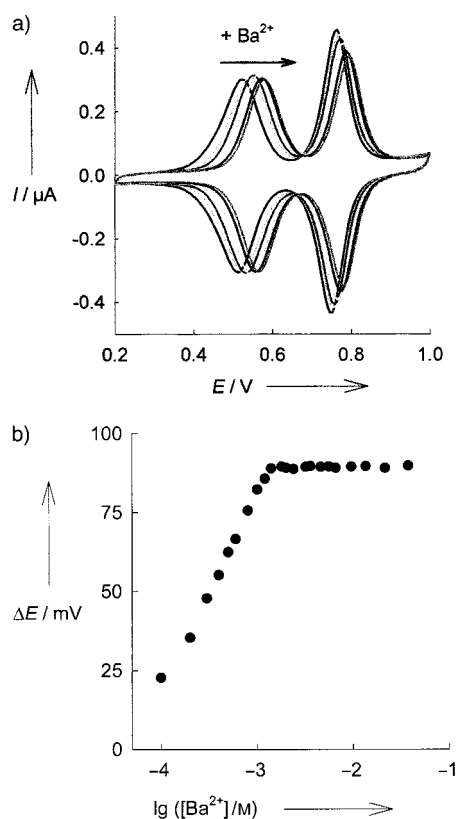


Figure 4. Electrochemical studies with a Pt electrode ($\varnothing = 1$ mm) modified with **G₃c** ($\Gamma_{\text{TTF}} = 5.3 \times 10^{-10}$ mol cm $^{-2}$, CH $_2$ Cl $_2$ /CH $_3$ CN (1/1), Bu $_4$ NPF $_6$ (0.1 M), scan rate 0.1 V s $^{-1}$). a) Electrochemical response in the presence of increasing concentrations of Ba(ClO $_4$) $_2$ ([Ba $^{2+}$] = 0, 1×10^{-4} , 2×10^{-4} , 4×10^{-4} , 6×10^{-4} , 8×10^{-4} M; reference electrode Ag/AgCl), b) plot of $\Delta E (= E_{\text{pa}}([\text{Ba}^{2+}] = 0) - E_{\text{pa}}([\text{Ba}^{2+}] \neq 0))$ versus $\lg([\text{Ba}^{2+}])$.

surface to give a modified electrode that responds to the presence of barium cations.

Experimental Section

Experimental procedure for the synthesis of dendrimers **G_nb** ($n = 1, 3, 4, 5$) and **G₃c**:^[14] To a suspension of NaH ($3 \times 2^\circ$ equiv + 5 %) in THF (5 mL) were added **G_na** (1 equiv) and the phosphonium salt **1a** or **1b** ($3 \times 2^\circ$ equiv + 5 %). The resulting mixture was stirred at room temperature for 14 h (**1a**), or at 40 °C overnight (**1b**), then water was added (1 mL). The solution was evaporated to dryness, the residue was extracted with CH $_2$ Cl $_2$ /H $_2$ O (1/1) saturated with NaCl, and the organic phase was recovered. The aqueous phase was washed twice more with CH $_2$ Cl $_2$. All the organic phases were combined, dried with anhydrous Na $_2$ SO $_4$, and evaporated to dryness to afford an orange oil. This oil was washed three times with CH $_2$ Cl $_2$ /pentane (1/10) to give an orange solid.

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- [16] We initially noted an unexpected negative shift of E_{pa} for high barium perchlorate concentrations ($> 10^{-3}$ M). This anomaly could be suppressed by using a reference electrode equipped with a double junction (recommendation of Prof. L. Echegoyen, who previously observed similar behavior with other electroactive species). A joint project is in progress on this aspect.