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Electronic Communication between Immobilized Ferrocenyl-Terminated Dendrimers

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Metallocenyl dendrimers are a promising source of nanoscopic materials for applications in molecular electronics, catalysis, and chemical/biological sensing because their topology and the possibility of introducing special redox-active metal centers associated with functional groups allow the design of new properties that do not exist in the isolated redox moieties.[1−6] Moreover, efficient and fast electrochemical communication between the redox centers immobilized on the dendrimer outside edge has been observed.[4,5] Because many applications require the immobilization of the dendrimer on a substrate,[1−3] besides the necessity of strong grafting, the communication between the individual dendrimers is a point to address here. In this regard, fast charge transport was observed inside a redox monolayer composed of grafted ferrocenyl units on a Si-modified surface.[7]

Previous studies have shown that redox-active dendrimers adsorb onto electrode surfaces in solvents such as CH_2Cl_2.[1−3] We found that adsorption of ferrocenyl-terminated dendrimers occurs on an insulating material [glass, or even better, mica; see section 6 in the Supporting Information (SI)]. These modified interfaces, when investigated by scanning electrochemical microscopy (SECM),[8] displayed properties similar to those of the modified interfaces described below but were too unstable for practical applications in steady-state SECM. To improve this stability, it was reported that the presence of negative charges on the surface strongly enhances the immobilization of systems containing metallocenyl moieties.[9] On the basis of this idea, a negatively charged interface was prepared by electrochemical reduction of an aryl carboxylic diazonium salt.[10] This produced the corresponding reactive aryl radical, which was covalently attached to a carbon surface, leading to an arylcarboxylic multilayer (see Scheme S2 in the SI). Soaking the modified electrode in a KOH solution then yielded an arylcarboxylate multilayer. This robust caboxylated surface behaves as an almost blocking insulating interface. Immobilizations of dendrimers of different generations [noted as G0, G1, and G2, with 9, 27, and 81 ferrocene (Fc) sites per molecule, respectively] were realized by simply soaking the modified surface in a solution containing the dendrimer. The final interface was found to be very robust in various solvents (CH_2Cl_2, water, ethanol, etc.), and reproducible stable responses were obtained after immersion for at least several hours.

Voltammetric analyses of the dendrimer-modified electrodes (see Figure 1) showed symmetric, well-defined reversible waves at potentials close to that of the ferrocene/ferrocenium couple. The anodic-to-cathodic peak current ratio was close to unity, and a linear relationship between the scan rate and the current intensity was found, as expected for a surface-confined redox species.[11] Under similar preparation conditions, when the dendrimer generation was increased, the density of Fc sites (Γ_{Fc}) and the peak-to-peak differences (ΔE_p) increased, but the $E°$ values did not change, indicating a decrease in the global oxidation rate of the dendrimer layer under "direct" electrochemical conditions (see Table 1, Figure 1, and Figure S2 in the SI).

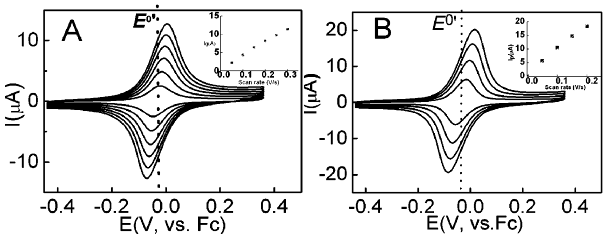

Figure 1. Cyclic voltammograms at various scan rates for (A) G0-adsorbed and (B) G1-adsorbed electrodes in 0.1 M $TBAPF_6/CH_2Cl_2$ solution.

Table 1. Electrochemical Parameters of the Dendrimers[a]

	G0	G1	G2
ΔE_p (V)	0.036	0.07	0.17
$E°$ (V vs Fc)	−0.03	−0.03	−0.03
Γ_{Fc} (mol cm^{-2})	6.4×10^{-10}	1.5×10^{-9}	2.7×10^{-9}
$\Gamma_{dendrimer}$ (mol cm^{-2})	7.1×10^{-11}	3.4×10^{-11}	3.4×10^{-11}

[a] Measured at 0.1 V s^{-1} in 0.1 M $TBAPF_6/CH_2Cl_2$ solution.

Electron transfers at the modified surfaces were probed by SECM using four mediators displaying increasing values of the redox potential ($E°_{med}$). In contrast to cyclic voltammetry, SECM probes the surface locally from the solution side with the dissolved redox mediator, providing a different view of the electron-transfer properties as lateral diffusion.[12] Three of the mediators [tris(*p*-tolyl)amine, ethynylferrocene (ethynyl-Fc), and Fc] have $E°_{med}$ more positive than that of the immobilized dendrimers (they could be used to oxidize the dendrimers), and one [decamethylferrocene (decamethyl-Fc)] has a less positive one (and could not oxidize the dendrimers). In this last case, for all of the dendrimers, the normalized current (I_t) at a gold ultramicroelectrode tip (UME) approaching the modified surface rapidly diminishes as the distance d between the UME and the substrate decreases (see Figure 2; a is the UME radius). The curves display good agreement with the theoretical variation expected for an insulating substrate. This reflects the absence of regeneration of the mediator at the interface (negative feedback). It demonstrates that the oxidized mediator produced at the UME cannot reach the carbon surface because of the strong blocking properties of the layer when the dendrimers are not oxidized. The approach curves recorded for the other three mediators show different situations. They transit from negative to positive feedback (I_t increases as d decreases) as $E°_{med}$ becomes more and more positive. Moreover, among the modified surfaces and for

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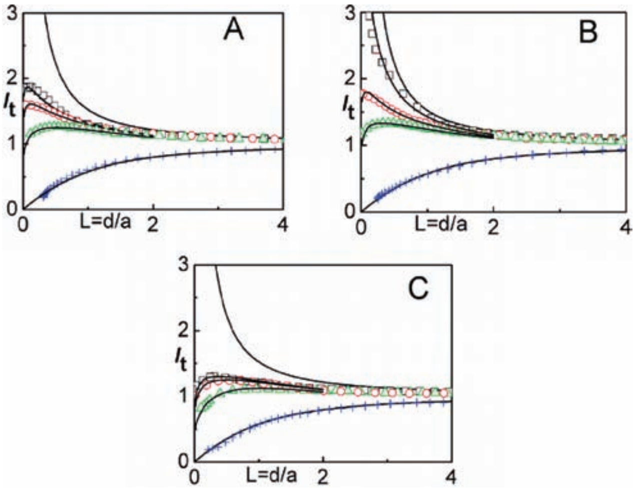


Figure 2. SECM approach curves (Au UME, radius $a = 4.5$ μm; d is the UME−substrate distance) on surfaces modified by dendrimers (A) G0, (B) G1, and (C) G2 in 0.1 M $TBAPF_6/CH_2Cl_2$ solution with the following mediators (10^{-3} M): (□) tris(*p*-tolyl)amine, (○) ethynyl-Fc, (△) Fc, (+) decamethyl-Fc. Solid lines are theoretical curves for transiting from conducting to insulating substrate behavior (from top to bottom).

Table 2. Apparent Electron-Transfer Rate Constants k_{el} for the Adsorbed Dendrimers G0, G1, and G2 with the Four Mediators

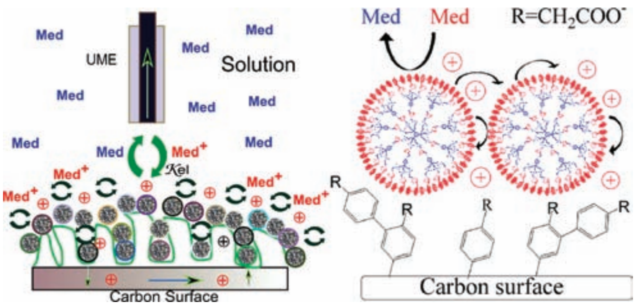
		k_{el} (10^{-2} cm s^{-1})		
mediator	E°_{med}[a]	G0	G1	G2
tris(*p*-tolyl)amine	0.35	5.5 ± 0.2	>16 ± 2	2.7 ± 0.1
ethynyl-Fc	0.18	4.2 ± 0.1	7.5 ± 0.2	3.2 ± 0.2
Fc	0.00	5.0 ± 0.2	5.1 ± 0.2	2.3 ± 0.1
decamethyl-Fc	−0.45	insulating	insulating	insulating

[a] Redox potential of the mediator (V vs Fc).

a given mediator, the effect is more pronounced for dendrimer G1 than for G0 or G2. These variations are quantified through the evolutions of k_{el}, the rate constant for electron transfer between the oxidized form of the mediator and the interface, which could easily be determined using the Bard−Mirkin formalism.[8] As seen in Table 2, k_{el} increases with E°_{med}, and the maximum variation occurs for G1. Since no regeneration of the mediator occurs on interfaces without dendrimers or when the dendrimers are not oxidized, we could exclude the occurrence of direct electron transfer between the oxidized mediator and the carbon substrate by tunneling or by permeation of the mediator through pinholes as an explanation of these variations.

Under our steady-state conditions and because the substrate is not electrically connected, large values of k_{el} imply the occurrence of the following steps (see Scheme 1): (i) fast oxidation of the dendrimers in contact with the solution by the oxidized mediator Med^+; (ii) fast transport of the injected positive charges inside the layer (or the carbon substrate); and (iii) ejection of the charges to balance the injection of positive charges that occurs on large areas outside the diffusion cone of the UME. Thus, the variations of k_{el} reflect both the oxidation rate of an individual dendrimer and the kinetics of electron transfer between adjacent dendrimers. In regard to the variation with the mediator, a more positive E°_{med} increases the driving force for the first direct electron transfer and thus explains the increase of k_{el} with E°_{med}. In regard to changes in k_{el} upon passing from G0 to G2, previous electrochemical studies in solution indicate that the intrinsic electron-transfer rate does not change considerably with the generation.[1] Thus, these k_{el} differences reveal the variations in the communication between dendrimers. The Fc surface density Γ_{Fc} is higher with G2, which should favor better conductivity inside the layer. However, the G1-adsorbed surface displays the largest k_{el} for a given mediator and is the most sensitive to E°_{med}. This maximum suggests that charge transfer inside or between two G2 dendrimers is less efficient. At this point, it is difficult to draw a clear-cut answer, as the structural organization of the dendrimers inside the layer could also interfere with the charge transfer with the intrinsic properties of a redox dendrimer.

Scheme 1. SECM Experiments on Dendrimer-Adsorbed Surfaces: Local Reduction and Charge Transport



Both this simple procedure for preparing robust dendrimer interfaces and probing of their transport properties in a collective manner by the determination of apparent electron-transfer rates could be easily extended to situations where the redox dendrimer is sensitive to the medium. This could be promising for the design of novel electrochemical sensors or electronic devices.

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Supporting Information Available: Structures of dendrimers and experimental details concerning the preparation and electrochemical and AFM image characterization of the surfaces. This material is available free of charge via the Internet at http://pubs.acs.org.

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