Electrochemical Rectification Using Mixed Monolayers of Redox-Active Ferrocenyl Dendrimers and *n*-Alkanethiols

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A strategy for constructing a dendrimer-based electrochemical current rectifier that permits current flow in only one direction is described. This approach is based on the insulating properties of *n*-alkanethiol self-assembled monolayers and the ability of redox-active ferrocenyl dendrimers to mediate electron transfer. The dendrimer-based rectifying layer is prepared by direct adsorption of second-, third-, or fourth-generation ferrocene-functionalized poly(propylene imine) dendrimers onto Au surfaces, followed by adsorption of *n*-hexadecanethiol. Reflection infrared spectroscopy, ellipsometry, and electrochemical measurements are used to characterize the resulting two-component monolayers. The surface coverage of ferrocenyl dendrimers in the two-component monolayers is estimated to be about 50% of maximum coverage. Cyclic voltammetry in electrolyte solutions containing the redox-active probes $Fe(CN)_6^{4-}$, $Fe(bpy)_3^{2+}$, and $Co(bpy)_3^{2+}$ reveals that the ferrocenyl dendrimer/*n*-alkanethiol-modified electrodes exhibit excellent barrier properties that prevent direct oxidation/reduction of the solution-phase redox molecules. Electrochemical current rectification occurs via mediated electron transfer across the surface-confined ferrocenyl dendrimers.

Introduction

In this paper, we describe an electrochemical current rectifier that is based on electrode-confined, redox-active dendrimers. In particular, we show that a two-component monolayer consisting of ferrocene-functionalized poly-(propylene imine) (PPI) dendrimers and *n*-hexadecanethiol (C16SH) confined to a Au electrode serves as a blocking layer that prevents direct access of solution-phase redox molecules to the electrode surface. However, the ferrocenyl dendrimer fraction of the mixed monolayer is able to mediate electron transfer between the redox molecules in solution and the electrode surface. Depending on the relative potentials of the ferrocene functional groups and the bulk-phase redox probe, the composite monolayer results in unidirectional current flow.

At present, there is considerable interest in developing electronic and photonic device components that are based on chemical principles. The expectation is that these will be very small and have interesting new functions that complement those of solid-state electronics.[1−3] One simple function of such a molecular electronic device is current rectification. Using advanced molecular design and self-assembly techniques, many molecular-based rectifying devices have been reported.[4] For example, Langmuir−Blodgett films of quinolinium tricyanoquinodimethanide derivatives have been used to make unimolecular devices that exhibit rectifying behavior.[5,6] Murray and co-workers were the first to report an electrochemical approach to rectification. Their rectifying interface relied on an electrode modified with two different, spatially segregated ruthenium-containing polymers having different redox potentials.[7−12] They demonstrated that oxidation of redox moieties present in the outer polymer layer was constrained to occur via electron-transfer mediation through the inner layer. As a result of this electronic property, electron transfer through the bilayer polymer films was found to be unidirectional. Another example of polymer-based electrochemical rectification involved redox polymers containing quinone and viologen subunits and demonstrated the principle of pH-dependent rectification.[13−15]

The rectification performance of polymer-based rectifiers is limited by current leakage through imperfect polymer interfaces and through pinholes present within the polymers. Such problems are minimized with the use of thicker polymer layers, but this compromises the speed of such devices. This is because the speed is also related to the rate of electron hopping between redox moieties in the polymer layers.[16] Accordingly, thinner rectifying layers that have more efficient blocking properties and electron-

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transfer kinetics lead to more desirable performance characteristics. These principles have been demonstrated by using thin films composed of zirconium-phosphonate multilayers[17] and by using a thin layer of nickel clusters[18] in which penetration of solution-phase redox molecules was suppressed by electrostatic repulsion between the redox molecules and the films. Creager and co-workers[19] and Uosaki and co-workers[20] have demonstrated that an electrode modified with a monolayer of ω-ferrocenylalkanethiols can act as an electrochemical rectifier. This approach mainly relies on the excellent blocking properties of well-ordered *n*-alkanethiol monolayers.

The use of redox-active dendrimers for constructing efficient electrochemical rectifiers differs from previous approaches because of the unique structural and chemical properties of dendrimers. Specifically, dendrimers are more versatile than simple molecular monolayers because of their generation-dependent nanoscopic size ($\sim 1-10$ nm), the large number of functional groups on their surfaces, and the presence of void spaces within their interiors.[21-23] Using these properties, we have previously shown that dendrimers can be used as templates for preparing dendrimer-encapsulated nanoparticles,[24-27] catalysts,[28-33] chemical sensors,[34,35] and adhesion promoters.[36] It seems reasonable that one will eventually be able to combine some of these functions with the electrochemical properties described in this paper to yield "smart rectifiers" that respond in some way to their environment.

In this paper, we report that mixed monolayers containing dendrimers modified on their periphery with ferrocenyl groups[37-39] induce unidirectional current flow.

Specifically, two-component self-assembled monolayers of second-, third-, and fourth-generation ferrocene-functionalized PPI dendrimers and C16SH were prepared by sequential adsorption onto Au electrodes. The electrochemical rectifying behavior of these electrodes in contact with electrolyte solutions containing redox-active probes was evaluated using cyclic voltammetry. The excellent passivating properties of the dendrimers, coupled with the thinness of the monolayers and the high density of redox moieties affixed to the dendrimer peripheries, lead to excellent rectifying behavior.

Experimental Section

Materials. Second-, third-, and fourth-generation amine-terminated poly(propylene imine) dendrimers (PPI−$(NH_2)_X$) ($X = 8$, 16, and 32 for generations 2, 3, and 4, respectively) were used as received (DSM Fine Chemicals, The Netherlands). Ferrocenecarboxylic acid (97%), oxalyl chloride (2.0 M solution in dichloromethane), triethylamine (99.5%), and anhydrous dichloromethane (99.8%) were purchased from the Aldrich Chemical Co. (Milwaukee, WI) and used without further purification. Hexane (98.3%), diethyl ether (99%), and tetrahydrofuran (THF, 99.5%) were from EM Science. Hexadecanethiol (95%, Fluka Chemie AG) was purified by distillation before use.

The preparation of the ferrocene-functionalized dendrimers followed a literature procedure.[37,38] Briefly, coupling of ferrocenyl chloride with PPI−$(NH_2)_X$ ($X = 8$, 16, or 32) in dichloromethane containing triethylamine gave reaction mixtures of the corresponding ferrocenyl dendrimers (PPI−Fc_X, $X = 8$, 16, or 32), which were purified by repetitive reprecipitations from dichloromethane/hexane and dichloromethane/diethyl ether. Ferrocenyl chloride was prepared according to a previously reported procedure.[40]

$HClO_4$ (70%, Aldrich), $NaClO_4$ (99%, Aldrich), Na_2SO_4 (Mallinckrodt), $K_4Fe(CN)_6$ (99%, Aldrich), and 18 MΩ cm Milli-Q water were used to prepare aqueous electrolyte solutions. [Fe-$(bpy)_3](ClO_4)_2$ and $[Co(bpy)_3](ClO_4)_2$ (bpy = 2,2′-bipyridyl) were synthesized by previously reported procedures.[41,42]

Au-coated substrates were prepared by electron-beam evaporation of 10 nm of Ti followed by 200 nm of Au onto Si(100) wafers (Lance Goddard Associates, Foster City, CA). The wafers were subsequently diced into 2.6 cm × 1.3 cm pieces. Before each experiment, all wafers were cleaned in a low-energy ozone cleaner for 10 min (Boekel Industries, Inc., model 135500).

Surface Modification. The ferrocene-functionalized dendrimer monolayers were prepared by immersing an ozone-cleaned Au substrate in a THF solution of the dendrimer. The dendrimer concentrations of the solutions were 2, 4, and 8 μM for PPI−Fc_{32}, PPI−Fc_{16}, and PPI−Fc_8, respectively, which correspond to 64 μM ferrocene terminal groups for each generation. Immersion times varied from 1 h for PPI−Fc_{32} to 6 h for PPI−Fc_{16} and PPI−Fc_8. Dendrimer deposition was followed by careful rinsing with THF and water and then drying with N_2. For the preparation of mixed monolayers of PPI−Fc_X/C16SH, the dendrimer-modified Au substrate was subsequently soaked in a 1 mM ethanolic solution of C16SH for at least 24 h, followed by rinsing with ethanol and water and drying with N_2.

Characterization. Fourier transform infrared external reflection spectroscopy (FTIR-ERS) measurements were carried out using an FTS-6000 spectrometer (Bio-Rad, Cambridge, MA) equipped with a Harrick Scientific Seagull reflection accessory (Ossining, NY) and a liquid-N_2-cooled, narrow-band MCT detector. All spectra were obtained at 4 cm^{-1} resolution using *p*-polarized light at an 84° angle of incidence with respect to the Au substrate. Ellipsometric measurements were made in air with a Gaertner Scientific (Chicago, IL) model L2W26D ellipsometer using a 70.00 ± 0.02° angle of incidence with 632.8 nm laser light and assuming a film refractive index (n_f) of 1.46. The reported thickness is the average of 15 measurements made at five

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Scheme 1

Figure 1. FTIR-ERS spectra of ferrocenyl dendrimers adsorbed to Au substrates: (a) PPI—Fc_{32}-only monolayer; (b) mixed monolayer of PPI—Fc_{32} and C16SH; (c) PPI—Fc_{16}-only monolayer; (d) mixed monolayer of PPI—Fc_{16} and C16SH; (e) PPI—Fc_8-only monolayer; (f) mixed monolayer of PPI—Fc_8 and C16SH.
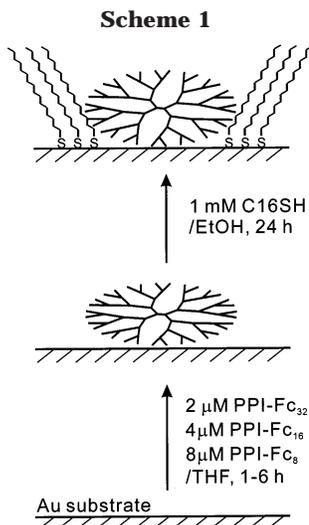
different locations on each of three independently prepared substrates. Electrochemical experiments were performed in a single-compartment, glass cell using a standard three-electrode configuration with a Pt-gauze counter electrode and a Ag/AgCl (3 M NaCl) reference electrode (Bioanalytical Systems, West Lafayette, IN). Cyclic voltammetry was performed using an EG&G PAR model 173 potentiostat with a PAR model 179 programmer and an $X-Y$ recorder. All electrolyte solutions were deaerated with N_2 for at least 10 min prior to electrochemical measurements. The PPI—Fc_X/C16SH-modified working electrode was contained within a Teflon O-ring holder that exposed an area of 0.10 ± 0.01 cm^2. The surface coverage of ferrocenyl dendrimers was determined by integrating voltammetric oxidation waves.[43] The surface coverage values were corrected for surface roughness, assuming a roughness factor of 1.2.[43,44]

Results and Discussion

Preparation and Characterization of Ferrocenyl Dendrimer/*n*-Alkanethiol Mixed Monolayers. There have been many reports of dendrimer immobilization on solid surfaces.[45] For example, we have shown that amine-terminated dendrimers can be covalently linked to Au surfaces via bifunctional coupling agents.[34,35] We have also shown that amine-terminated poly(amidoamine) (PAMAM) dendrimers form stable, densely packed monolayers via direct interaction of their primary and tertiary amine groups with Au surfaces.[46] In the present study, we relied on direct adsorption of the ferrocenylated dendrimers to the substrate, presumably via interior tertiary amines.

Mixed monolayers of PPI—Fc_X ($X = 8$, 16, and 32) and C16SH were prepared on evaporated Au surfaces and characterized using FTIR-ERS, ellipsometry, and cyclic voltammetry. The steps used to prepare the monolayers are shown in Scheme 1. A Au substrate was first exposed to a THF solution containing PPI—Fc_{32} (2 μM), PPI—Fc_{16} (4 μM), or PPI—Fc_8 (8 μM). The concentrations of the dendrimer solution and the solvent were optimized to yield a single, high-density dendrimer monolayer. The use of other solvents, such as CH_2Cl_2 or $CHCl_3$, or higher concentrations of dendrimer resulted in formation of more
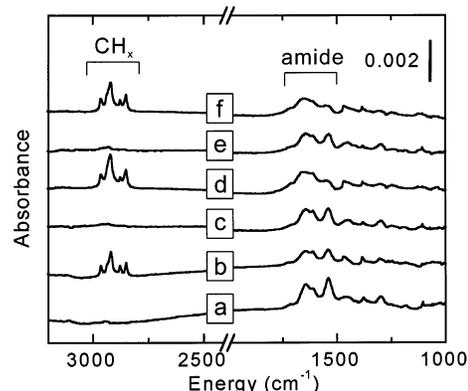
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than one dendrimer layer. Each of the dendrimer-modified surfaces was then exposed to a 1 mM ethanolic solution of C16SH, which resulted in formation of mixed monolayers of PPI—Fc_X/C16SH.

Figure 1 compares FTIR-ERS spectra of the PPI—Fc_X-only and PPI—Fc_X/C16SH mixed monolayers. The appearance of the amide I and II peaks at 1645 and 1540 cm^{-1}, which arises from the dendrimer/ferrocene linking chemistry, confirms the presence of the ferrocenyl dendrimer in all of the monolayers. The intensity of the peaks in the hydrocarbon stretching region (2800—3000 cm^{-1}) significantly increases upon adsorption of C16SH (Figure 1, spectra b, d, and f), indicating the presence of a high fractional surface coverage of C16SH. By comparing the relative intensities of the methyl bands (2965 and 2878 cm^{-1}) in a spectrum of a C16SH-only monolayer to those in the PPI—Fc_X/C16SH mixed monolayers, we estimate that about 50% (PPI—Fc_{32}/C16SH, 49%; PPI—Fc_{16}/C16SH, 44%; PPI—Fc_8/C16SH, 51%) of the Au surface is modified with C16SH in the mixed monolayers. The FTIR-ERS spectra of the mixed monolayers show a slight decrease in the amide peak intensities after the adsorption of C16SH, indicating partial desorption of the ferrocenyl dendrimers in the course of the C16SH adsorption. This result reflects the relatively weak interaction between the Au substrate and the ferrocene-terminated dendrimers. This behavior contrasts with our previous findings that have shown a high level of stability for amine-terminated PAMAM dendrimers on Au surfaces.[46] In the case of the PPI—Fc_X dendrimers, most of the adsorption energy is probably associated with interactions between interior tertiary amines and the Au substrate. After coadsorption of C16SH, however, the adsorption stability of the dendrimers in the mixed monolayer is greatly enhanced, and the mixed monolayers are robust enough to survive a series of successive electrochemical experiments while maintaining their surface coverage (vide infra).

Cyclic voltammograms of PPI—Fc_X ($X = 8$, 16, and 32)/ C16SH-modified Au electrodes are shown in Figure 2. A symmetrical, nearly reversible redox wave, corresponding to the terminal ferrocenyl groups of PPI—Fc_X in the mixed monolayer, is centered at +0.41 V. The presence of a single anodic wave suggests that all the ferrocenyl groups are independent and equivalent.[39] Moreover, for all generations of the ferrocenyl dendrimers, the $E_{1/2}$ values remain essentially constant, indicating that all the ferrocenyl redox centers are located in the same microenvironment,

Table 1. Ellipsometric Thickness and Dendrimer Coverage of PPI−Fc$_X$/C16SH Mixed Monolayers

dendrimer	theoretical diameter (nm)	ellipsometric thickness (nm)		surface coverage (mol/cm^2, ×10^{-11})	
		PPI−Fc$_X$ only	PPI−Fc$_X$/C16SH	calculated[a]	measured[b]
PPI−Fc$_{32}$	4.6	1.5 ± 0.2	2.2 ± 0.2	0.91	0.59 (65%)[c]
PPI−Fc$_{16}$	3.8	1.0 ± 0.2	1.7 ± 0.1	1.65	0.73 (44%)
PPI−Fc$_8$	2.8	1.0 ± 0.1	1.7 ± 0.2	2.45	1.22 (50%)

[a] The values were calculated assuming a hexagonal close-packed array of an ideal-sphere PPI−Fc$_X$ with a given diameter. [b] Measured by voltammetry. [c] Percentage of the coverage calculated for a full monolayer of PPI−Fc$_X$.
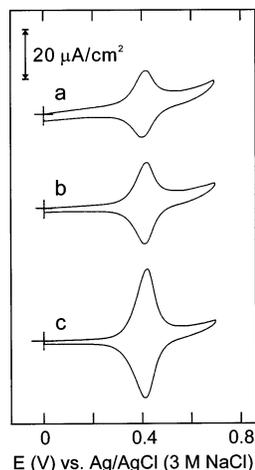
Figure 2. Cyclic voltammetry of Au electrodes modified with mixed monolayers of PPI−Fc$_X$ and C16SH: (a) mixed monolayer of PPI−Fc$_8$ and C16SH; (b) mixed monolayer of PPI−Fc$_{16}$ and C16SH; (c) mixed monolayer of PPI−Fc$_{32}$ and C16SH. The scan rate was 100 mV/s, and the electrolyte solution was aqueous 1.0 M HClO$_4$.

that is, on the peripheries of the dendrimers.[47] A plot of scan rate versus anodic peak current ($i_{p,a}$) is nearly linear between 20 and 500 mV/s (data not shown). The peak splittings (ΔE_p) between the anodic and cathodic peak potentials ($E_{p,a}$ and $E_{p,c}$, respectively) are close to the theoretical value of zero for a reversible electron transfer to a surface-confined redox species (ΔE_p = 18, 18, and 26 mV for PPI−Fc$_{32}$/C16SH, PPI−Fc$_{16}$/C16SH, and PPI−Fc$_8$/C16SH, respectively). From these results, we conclude that the ferrocenyl dendrimers are confined to the electrode and that the ferrocenyl groups undergo independent, reversible electron-transfer processes with the electrode surface.[48]

The surface coverage of the ferrocenyl dendrimers in PPI−Fc$_X$/C16SH-modified electrodes was estimated by integration of the charge under the anodic waves in Figure 2.[43] The results are given in Table 1. The surface coverage values are calculated using the exposed geometrical area of the electrodes, assuming a roughness factor of 1.2 and assuming that all the surface-confined ferrocene groups are redox active. The latter assumption is reasonable for surface-confined, redox-active dendrimers,[38] but we have previously shown that it might not be true for dendrimers in bulk solution.[49] The measured dendrimer coverages for Fc$_{32}$/C16SH, Fc$_{16}$/C16SH, and Fc$_8$/C16SH are (0.59, 0.73, and 1.22) × 10^{-11} mol/cm^2, respectively, which corresponds to 65%, 44%, and 50% of the theoretical coverage expected for a full monolayer of the corresponding dendrimer.[38] If we assume the electrode surface is fully covered with PPI−Fc$_X$ and C16SH, then we can conclude that about 50% of
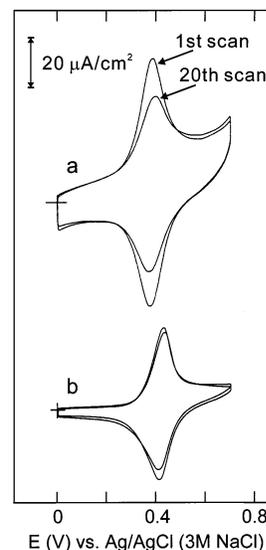
Figure 3. Effect of repetitive electrochemical cycling on the stability of Au electrodes modified with (a) a PPI−Fc$_{32}$-only monolayer and (b) a mixed monolayer consisting of PPI−Fc$_{32}$ and C16SH. The 1st and 20th voltammetric scans between 0 and 0.7 V are shown. The scan rate was 100 mV/s, and the electrolyte solution was aqueous 1.0 M HClO$_4$.

the Au surface in the PPI−Fc$_X$/C16SH mixed monolayer is occupied by C16SH. This value is in good agreement with C16SH surface coverage estimated by the relative intensities of the methyl peaks in the FTIR-ERS spectra discussed earlier.

Ellipsometric measurement of PPI−Fc$_X$/C16SH mixed monolayers provides insight into the conformational structure of the adsorbed dendrimers (Table 1). The average ellipsometric thickness of PPI−Fc$_{32}$-only monolayers was measured to be 1.5 ± 0.2 nm, which is significantly smaller than the ideal-sphere diameter (4.6 nm) of PPI−Fc$_{32}$. A similar trend was also observed for PPI−Fc$_{16}$ and PPI−Fc$_8$. This discrepancy between measured and theoretical diameters can be explained by structural distortion of the surface-confined dendrimers. It is well-known that dendrimers form a flattened structure upon surface adsorption.[46,50,51] Moreover, the PPI dendrimers used in this study are expected to be especially flexible because the dendritic scaffold is primarily composed of alkylamine groups.[52]

The effect of coadsorbed C16SH on the stability and permeability of PPI−Fc$_X$/C16SH mixed monolayers was investigated by cyclic voltammetry (Figure 3). There are two important points. First, $i_{p,a}$ for an electrode modified with the PPI−Fc$_{32}$-only monolayer decreases significantly after successive voltammetric scans (40% decrease after

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Scheme 2

a: electrode
b: monolayer
c: solution
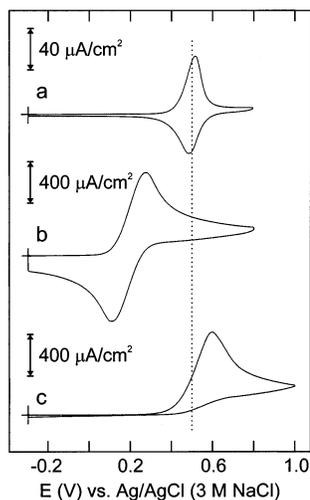
Figure 4. Cyclic voltammograms demonstrating current rectification at a Au electrode modified with a PPI−Fc$_{32}$/C16SH mixed monolayer: (a) an electrode modified with a PPI−Fc$_{32}$/C16SH mixed monolayer in a solution containing no K$_4$Fe(CN)$_6$; (b) a naked electrode in a solution containing 3.0 mM K$_4$Fe(CN)$_6$; (c) an electrode modified with a PPI−Fc$_{32}$/C16SH mixed monolayer in a solution containing 3.0 mM K$_4$Fe(CN)$_6$. The scan rate was 200 mV/s, and the buffered (0.18 M CH$_3$COONa and 0.1 M CH$_3$COOH, pH = 4.8), aqueous electrolyte solution contained 0.1 M NaClO$_4$. The dashed line denotes $E_{1/2}$ for the PPI−Fc$_{32}$/C16SH mixed monolayer.

20 scans), indicating partial desorption of the ferrocenyl dendrimers (Figure 3a). However, after coadsorption of C16SH, adsorption stability of the ferrocenyl dendrimers is greatly enhanced, probably because of the hydrophobic C16SH pocket that prevents water from assisting dendrimer desorption from the Au surface (Figure 3b). Second, the capacitive charging current of the dendrimer-only monolayer is larger than that of the mixed monolayer. This indicates that PPI−Fc$_{32}$-only monolayers are more permeable to electrolyte ions and solvent than PPI−Fc$_{32}$/C16SH mixed monolayers. These findings clearly indicate that the coadsorbed C16SH layer plays an important role in stabilizing dendrimer-containing monolayers and in preventing direct approach of ions to the electrode surface.

Electrochemical Rectifying Behavior of Ferrocenyl Dendrimer/Alkanethiol Mixed Monolayers. On the basis of the results presented so far and previous reports of surface-confined dendrimers,[38,46,50,51] we conclude that the ferrocenyl dendrimers are flattened on the Au electrode surfaces and that coadsorbed C16SH effectively covers the naked Au interstices between dendrimers. We believed that this conformation of the composite monolayer, coupled with the intrinsic compactness of the PPI dendrimers, suppresses direct access of redox molecules to the electrode surface, which is an essential condition for proper performance of electrochemical current rectifying devices.[19] However, the electrode should be electrically coupled to the solution via the peripheral ferrocenyl groups on the dendrimers to permit electron-transfer mediation between redox probe molecules in solution and the electrode surface.

Figure 4 shows a series of voltammograms that confirm the ability of PPI−Fc$_X$/C16SH mixed monolayers to support electrochemical rectification. Figure 4a shows a typical cyclic voltammogram of a Au electrode modified with the PPI−Fc$_{32}$/C16SH mixed monolayer in a 0.1 M aqueous NaClO$_4$ solution. The cyclic voltammogram exhibits a single redox peak at 0.50 V corresponding to the surface-immobilized ferrocenyl groups (note that this potential is slightly more positive than the corresponding
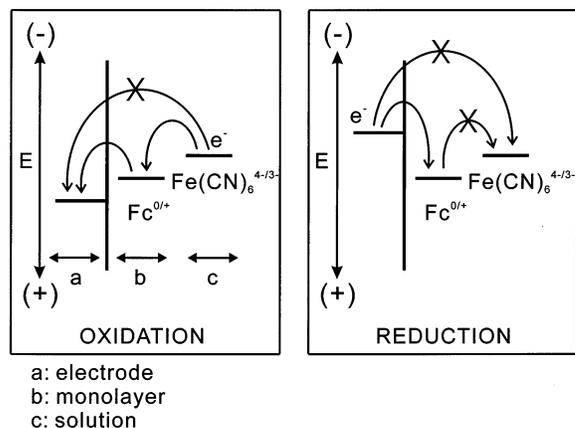
peak in Figure 2; this is a consequence of the change in electrolyte solution). A cyclic voltammogram obtained at a naked Au electrode immersed in an aqueous 3 mM Fe(CN)$_6^{4-}$ electrolyte solution is shown in Figure 4b (note the change in current scale). The voltammogram in Figure 4c was obtained at a Au electrode modified with the PPI−Fc$_{32}$/C16SH mixed monolayer in an aqueous 3 mM Fe(CN)$_6^{4-}$ solution. There are three important features in this latter voltammogram. First, no voltammetric feature corresponding to the oxidation of Fe(CN)$_6^{4-}$ is observed at the expected potential (0.19 V, Figure 4b), suggesting that the PPI−Fc$_{32}$/C16SH mixed monolayer effectively prevents penetration of Fe(CN)$_6^{4-}$. Second, $i_{p,a}$ for the peak at 0.60 V, which is near the oxidation potential of the dendrimeric ferrocenyl groups (Figure 4a), is similar to that observed for Fe(CN)$_6^{4-}$ at the naked Au electrode (Figure 4b). We conclude that the anodic current peak in Figure 4c corresponds to the mediated oxidation of Fe(CN)$_6^{4-}$ by surface-immobilized ferricenium groups. Most likely, electrons are shuttled between the solution and the electrode via electron hopping between ferrocenyl and ferricenium groups on the periphery of the dendrimer. Third, when the potential scan is reversed, no cathodic peak corresponding to reduction of Fe(CN)$_6^{3-}$ is observed. The observation of unidirectional current is characteristic of electrochemical rectification. The forward reaction (oxidation in this case) is thermodynamically favorable because surface-immobilized ferricenium is capable of oxidizing solution-phase Fe(CN)$_6^{4-}$. The reverse reaction, however, does not occur because it involves the thermodynamically uphill electron transfer from ferrocene to Fe(CN)$_6^{3-}$. Scheme 2 summarizes the energetics for the mediated electron-transfer reactions.

It is noteworthy that a Au electrode modified with the PPI−Fc$_{32}$-only monolayer in an aqueous Fe(CN)$_6^{4-}$ solution yields voltammetric behavior similar to that found for a naked Au electrode (Figure 4b). This result suggests that the PPI−Fc$_{32}$-only monolayer is permeable to the redox solutes and that the presence of C16SH is necessary for proper functioning of the dendrimer-based rectifier.

To confirm that the voltammetric feature in Figure 4c arises from the current rectifying capability of the PPI−Fc$_{32}$/C16SH mixed monolayer, we carried out two additional electrochemical experiments.

The first series of voltammograms shows the dependence on Fe(CN)$_6^{4-}$ concentration of the rectifying behavior of the PPI−Fc$_{32}$/C16SH mixed monolayer (Figure 5). The voltammograms were obtained for Fe(CN)$_6^{4-}$ concentrations ranging from 0 to 10 mM. The anodic peak current clearly increases with increasing concentration of Fe(CN)$_6^{4-}$, and its magnitude is well correlated to the
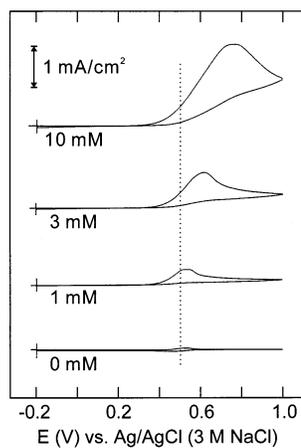
Figure 5. Cyclic voltammetry of a Au electrode modified with a PPI−Fc$_{32}$/C16SH mixed monolayer in an electrolyte solution containing the indicated concentrations of K$_4$Fe(CN)$_6$. The scan rate was 200 mV/s, and the buffered (0.18 M CH$_3$COONa and 0.1 M CH$_3$COOH, pH = 4.8), aqueous electrolyte solution contained 0.1 M NaClO$_4$. The dashed line denotes $E_{1/2}$ for the PPI−Fc$_{32}$/C16SH mixed monolayer.
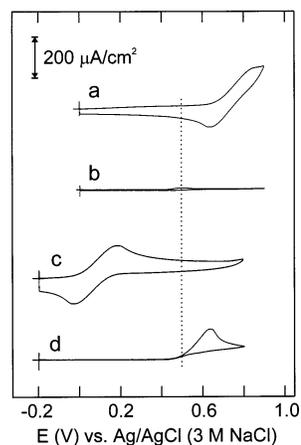
Figure 6. Cyclic voltammetry of Au electrodes in aqueous electrolyte solutions containing 0.01 M Na$_2$SO$_4$ and (a) 1.0 mM [Fe(bpy)$_3$](ClO$_4$)$_2$ or (c) 1.0 mM [Co(bpy)$_3$](ClO$_4$)$_2$. Cyclic voltammetry of Au electrodes modified with PPI−Fc$_{16}$/C16SH mixed monolayers in aqueous electrolyte solutions containing 0.01 M Na$_2$SO$_4$ and (b) 1.0 mM [Fe(bpy)$_3$](ClO$_4$)$_2$ or (d) 1.0 mM [Co(bpy)$_3$](ClO$_4$)$_2$. The scan rate was 100 mV/s. The dashed line denotes $E_{1/2}$ for the ferrocene groups in the PPI−Fc$_{16}$/C16SH mixed monolayer.

concentration of Fe(CN)$_6^{4-}$. This experiment provides clear evidence that the voltammetry observed in Figure 4c results from Fe(CN)$_6^{4-}$ oxidation mediated by the ferrocenyl dendrimer in the mixed monolayer.

In the second experiment, we performed cyclic voltammetric experiments using Fe(bpy)$_3^{2+}$ and Co(bpy)$_3^{2+}$ as solution-phase redox molecules, because they have different formal potentials and ionic charges compared to Fe(CN)$_6^{4-}$. The cyclic voltammogram in Figure 6b was obtained at a Au electrode modified with a PPI−Fc$_{16}$/C16SH mixed monolayer and immersed in a 1 mM aqueous Fe(bpy)$_3^{2+}$ electrolyte solution. The absence of voltammetric features for the Fe(bpy)$_3^{2+}$ oxidation near its formal potential (0.75 V) indicates that direct oxidation at the electrode surface is effectively blocked by the PPI−Fc$_{32}$/C16SH mixed monolayer. Note that the small peak at 0.50 V (Figure 6b) corresponds to the oxidation and reduction of the surface-confined, ferrocene-terminated dendrimers. Current rectifying behavior was not observed in the Fe(bpy)$_3^{2+}$ solution, because ferrocenium is not a
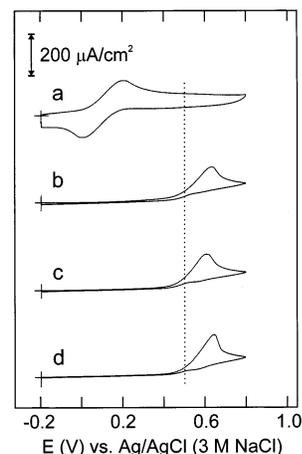
Figure 7. Effect of dendrimer generation on rectification. Cyclic voltammetry of Au electrodes modified with the following mixed monolayers: (b) PPI−Fc$_8$/C16SH, (c) PPI−Fc$_{16}$/C16SH, and (d) PPI−Fc$_{32}$/C16SH. The voltammogram in (a) was measured at naked Au electrodes. The electrolyte solutions contained 1.0 mM [Co(bpy)$_3$](ClO$_4$)$_2$ and 0.01 M Na$_2$SO$_4$. The scan rate was 100 mV/s. The dashed line denotes $E_{1/2}$ for the PPI−Fc$_{32}$/C16SH mixed monolayer.

sufficiently strong oxidant to oxidize Fe(bpy)$_3^{2+}$; that is, the formal potential of Fe(bpy)$_3^{2+}$ oxidation is more positive than that of ferrocene oxidation. Figure 6d corresponds to the same experiment, but in a 1 mM aqueous Co(bpy)$_3^{2+}$ solution. This voltammogram shows typical rectifying behavior (compare with the voltammetric response of Co-(bpy)$_3^{2+}$ obtained at a naked electrode, Figure 6c), suggesting that current rectification at these dendrimer-based mixed monolayers is a general phenomenon, regardless of the chemical identity of the bulk-phase redox molecules.

Figure 7 presents the effect of dendrimer generation on electrochemical rectification. Because all three generations of ferrocenyl dendrimers have the same redox potential (Figure 2), it is not surprising that oxidation of Fe(CN)$_6^{4-}$ turns on at the same potential independent of dendrimer generation. This result leads us to conclude that the ferrocene groups are in a similar microenvironment and are available to mediate electron transfer regardless of generation.

Summary and Conclusions

This paper describes the use of two-component monolayers consisting of redox-active ferrocenyl dendrimers and *n*-hexadecanethiol as an electrochemical rectifying device. The two-component monolayers are prepared by direct adsorption of ferrocene-functionalized PPI dendrimers, followed by adsorption of C16SH. Results obtained using FTIR-ERS and cyclic voltammetry suggest that the ferrocenyl dendrimer surface coverage in the two-component monolayer is about 50% of the theoretical coverage expected for a full monolayer regardless of dendrimer generation. Because of the excellent blocking properties of the ferrocenyl dendrimer/C16SH mixed monolayer, we achieved electrochemical current rectification; that is, oxidation of solution-phase Fe(CN)$_6^{4-}$ proceeds exclusively via electron transfer mediated by the ferrocenyl groups appended to the dendrimers.

Although there have been many previous examples of electrochemical rectification, the system described here is noteworthy because of the interesting physical and chemical properties of the dendrimers. Specifically, the dendrimer interiors can contain various sorts of catalysts and reporter probes, many different types of functionalities

can be appended to each dendrimer, and the number of peripheral groups on the dendrimers can be easily tailored to accomplish specific tasks. Finally, the range of dendrimer sizes ($\sim$1$-$10 nm) is well matched to the range necessary to connect molecular systems to electronic devices.