Polypyrrole Self-Assembled Monolayers and Electrostatically Assembled Multilayers on Gold and Platinum Electrodes for Molecular Junctions

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Self-assembled monolayers (SAMs) and electrostatically assembled multilayers of some soluble polypyrroles (including a thiol-functionalized polypyrrole) were produced on gold and platinum electrodes. Gold and platinum surfaces were used either bare or primed with an anionic monolayer of 3-mercaptopropylsulfonate or Nafion. Poly(sodium-*p*-styrenesulfonate) and Nafion were used as polyanions for electrostatic self-assembly (ESA). The layers were investigated by cyclic voltammetry, infrared reflection absorption spectroscopy, quartz crystal microbalance, and atomic force microscopy (AFM). ESA proceeds with a growth rate that is linear with the number of bilayers and particularly high (stored charge 30−60 μC cm^{-2} bilayer^{-1}) with Nafion, which appears to be the primer for all the investigated polypyrroles. Gold−polymer−gold junctions, formed by contact between a polypyrrole SAM on gold and a gold-coated AFM tip, rectify current in polypyrrole sulfosuccinate, whereas they are ohmic with Simmons characteristics in poly(*N*-hexylcyclopenta[*c*]pyrrole). In the former case alternation of rectifying and ohmic characteristics is observed with progressive ESA.

1. Introduction

Conducting polymers (CPs) are actually developing as materials for synthesis of nanostructured materials and devices.[1] They are particularly appealing because they exhibit electrical, electronic, magnetic, and optical properties similar to those of metals or semiconductors while keeping flexibility, ease of processing, and modifiable electrical conductivity. The electrical conductivity of these polymers can vary from an insulator to the almost the metallic state and can be reversibly modulated over 15 orders of magnitude by controlling the dopant type and level.[2]

While the properties of CPs offer many advantages, application of these materials for high-density nanoarrays is limited. Photolithography,[3] microcontact printing,[4] scanning electrochemical microlithography,[5] and electrochemical dip-pen lithography[6] have been used for fabricating micro- and nanoscale structures from CPs, but there are still limitations in yield, resolution, material type, positioning, and production of high-density arrays.

Nanosized CPs are particularly interesting also in the light of recent molecular electronics.[7] In fact, CP chains are molecular wires which may be driven between the conductive and the insulating states. An understanding of the basic conductivity of these structures is a fundamental prerequisite for the general understanding of the conductive properties of conjugated molecular wires.

For all these purposes, of high importance is the production on electrodes of well-defined mono- and multilayers of CPs, given their nanometer-size one-dimensional resolution.

Monolayers of polythiophenes, in particular polyalkylthiophenes, are in fact found in the literature.[8,9] Multilayers are produced in general by the layer-by-layer electrostatic adsorption (electrostatic self-assembly, ESA) technique introduced by Decher and Hong[10] and recently reviewed.[11] ESA of CPs, particularly thiophene-based polymers, is well-represented.[12]

Layers from polypyrroles are comparatively rare. Electroactive poly(*N*-alkylpyrrole) monolayers on gold are produced by the electrochemical oxidation of pyrrole-terminated self-assembled *N*-alkanethiol monolayers only in dry electrolyte media.[13] Gold surfaces bearing alkyl self-assembled

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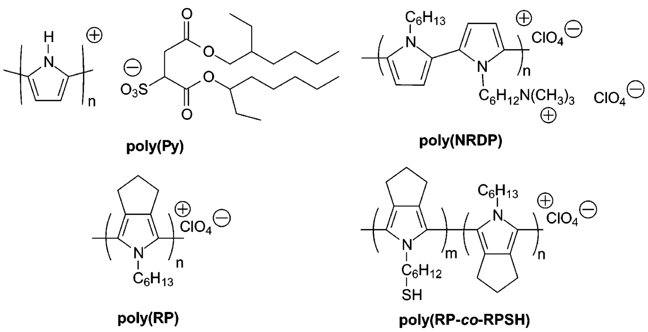
Chart 1



monolayers (SAMs) promote polypyrrole layer deposition from pyrrole,[1] and p-doped polypyrrole has been produced as layers of controlled thickness by direct adsorption from a diluted polymerization solution[14] (polymerization-induced adsorption).[15] In both these cases, however, the deposit thickness extends beyond the monolayer.

Our goal was that of producing well-defined SAMs and subsequently electrostatically assembled multilayers of polypyrrole and poly(*N*-alkylpyrrole) on gold and platinum surfaces. Monolayers are intended not to be layers of controlled thickness of bulk material but to be molecularly sized regular dispositions of polymer chains on conducting surfaces.

To this end we have used two approaches, namely, (i) adsorption of soluble polymers and (ii) thiol-linking (to gold) of thiol-modified soluble polypyrrole. As examples of the two approaches we may recall that polythiophene monolayers have been produced on gold (i) by adsorption of soluble poly(3-octylthiophene)[9] and (ii) by sulfide linking of thiol-functionalized soluble polyalkylthiophenes.[8]

The used polypyrroles, shown in Chart 1, are the parent polypyrrole poly(Py) (as a sulfosuccinate), the fully alkyl substituted poly(RP), and a *N*-alkyl substituted polypyrrole bearing tetralkylammonium terminal moieties poly(NRDP) (as the perchlorate salts). All these soluble polymers are used in the p-doped state so that they are polycationic with the positive charge delocalized over the polyconjugated backbone. Of them poly(NRDP) bears extra nondopant positive charges. Poly(RP-*co*-RPSH) is the soluble polymer with thiol units for covalent linking to the gold surface.

Among polyanions used for ESA, we selected poly(sodium-*p*-styrenesulfonate) (PSS) as a typical hydrophilic ionomer and Nafion as a hydrophobic polyanionic source. Nafion, a copolymer of tetrafluoroethylene and sulfonyl fluoride vinyl ether, is one of the most interesting solid polymer electrolytes for technological and scientific research. It is used as an ionomeric permselective membrane for a variety of electrochemical applications including fuel cells, water electrolyzers, chlor−alkali cells,[16] and electrochromic devices.[17] Moreover, it should be remembered that redox properties,[18] electrical capacitance,[19] potentiometric responses,[20] and permeation of liquid-phase olefins of polypyrrole−Nafion electrodes and membranes have been the subject of investigation in the past.

Thin polypyrrole layers (not monolayers) were used in the past to build rectifying junctions with silicon[21] or CdS[22] nanoparticles. In this paper we report also some metal−polymer−metal junctions, where the polymer is a monolayer of polypyrrole, that rectify current. The junction is formed by mechanical contact between a SAM on gold and a gold-coated atomic force microscopy (AFM) tip, developing these junctions as new systems for molecular electronics.

2. Experimental Section

2.1. Chemicals and Reagents. All melting points are uncorrected. All reactions of air- and water-sensitive materials were performed under nitrogen. Air- and water-sensitive solutions were transferred with double-ended needles. The solvents used in the reactions (Fluka) were absolute and stored over molecular sieves. Acetonitrile was reagent grade (Uvasol, Merck) with a water content of <0.01%. The supporting electrolyte tetrabutylammonium perchlorate (Bu_4NClO_4) and all other chemicals used for the characterizations were reagent grade and used as received.

2,4,5,6-Tetrahydrocyclopenta[*c*]pyrrole and the monomer 2-hexyl-2,4,5,6-tetrahydrocyclopenta[*c*]pyrrole (RP) were prepared as described in the literature.[23]

Poly(2-hexyl-2,4,5,6-tetrahydrocyclopenta[*c*]pyrrole) (poly(RP); doping level 0.15)[23] and poly([6-(1′-hexyl-1′*H*-[2,2′]bipyrrol-1-yl)-hexyl]trimethylammonium) tetrafluoborate (poly(NRDP; doping level 0.33)[24] were prepared as in the literature and used in acetonitrile solution at a 10^{-3} M concentration.

Soluble polypyrrole di(ethylhexyl)sulfosuccinate (poly(Py); doping level 0.33) was prepared according to the literature,[25] and the solutions used for monolayer formation were 0.1% in $CHCl_3$ and 0.01% in acetone.

3-Mercaptopropylsulfonate (MPS), hexadecanethiol (C16SH), PSS ($M_w = 100\,000$), and Nafion (5% solution in lower aliphatic

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alcohols + 10% water, 1200 equiv weight) were purchased from Aldrich. PSS was used as a 10^{-2} M solution whereas Nafion was diluted in EtOH to the concentration of 1%.

2-(6-Bromohexyl)-2,4,5,6-tetrahydrocyclopenta[c]pyrrole. A soluton of 2,4,5,6-tetrahydrocyclopenta[*c*]pyrrole (130 mg, 1.21 mmol) in dimethylformamide (DMF; 6 mL) was added dropwise to a suspension of NaH (60 mg, 1.37 mmol) and 1,6-dibromohexane (349 mg, 1.43 mmol) in DMF (6 mL). The reaction mixture was stirred overnight. Water was added, and the resulting mixture was extracted with hexane. The organic phase was washed with water and dried (Na_2SO_4), and the solvent was evaporated. Flash chromatography of the residue (silica gel, petrol ether/CH_2Cl_2, 8:2) afforded the title compound as an oil (211 mg, 65% yield). Anal. Calcd for $C_{13}H_{20}BrN$: C, 52.19; H, 7.01; N, 6.09%. Found: C, 52.07; H, 6.93; N, 6.01. ^1H NMR ($CDCl_3$) δ 1.43 (m, 4H), 1.81 (m, 4H), 2.30 (m, 2H), 2.62 (t, 4H), 3.39 (t, 2H), 3.79 (t, 2H), 6.29 (s, 2 H).

6-(5,6-Dihydro-4H-cyclopenta[c]pyrrol-2-yl)hexane-1-thiol (RPSH). A mixture of 2-(6-bromohexyl)-2,4,5,6-tetrahydrocyclopenta[*c*]-pyrrole (544 mg, 2.01 mmol), thiourea (169 mg, 2.21 mmol), and ethanol (12 mL) was refluxed for 16 h. The solvent was evaporated under vacuum, a solution of KOH (124 mg, 2.21 mmol) in water (15 mL) was added, and the mixture was refluxed for 2.5 h. The reaction mixture was extracted with ether. The organic phase was washed with water and dried (Na_2SO_4), and the solvent was evaporated. Flash chromatography of the residue (silica gel, petrol ether/CH_2Cl_2, 8:2), afforded the title compound as an oil (250 mg, 55% yield). Anal. Calcd for $C_{13}H_{21}NS$: C, 69.90; H, 9.48; N, 6.27. Found: C, 69.73; H, 9.32; N, 6.12. ^1H NMR ($CDCl_3$) δ 1.36 (m, 5H), 1.67 (m, 4H), 2.29 (m, 2H), 2.49 (t, 2H), 2.60 (t, 4H), 3.79 (t, 2H), 6.29 (s, 2 H). HREIMS calcd, 222.1316; found, 222.1310.

Electrosynthesis of RP-co-RPSH Copolymers. RP-*co*-RPSH copolymers were prepared as follows. Solutions of RPSH (1 or 2 $\times 10^{-3}$ M) and RP (4×10^{-3} M) in acetonitrile (25 mL) + 0.1 M $NaClO_4$ were electrolyzed at 0.8 V. After the passage of 2.5 F mol^{-1} the solvent was evaporated and the polymers were separated from the electrolyte by $CHCl_3$−water extraction. The resulting products were dried, dissolved in acetonitrile, washed with hexane (to remove nonreacted monomer), and dried.

2.2. Apparatus and Procedure. *Electrochemistry.* Experiments were performed at 25 °C under nitrogen in three-electrode cells. The counter electrode was platinum; unless otherwise stated the reference electrode was a silver/0.1 M silver perchlorate in acetonitrile (0.34 V vs the saturated calomel electrode). The voltammetric apparatus (AMEL, Italy) included a 551 potentiostat modulated by a 568 programmable function generator and coupled to a 731 digital integrator.

The electrochemical investigation was performed in acetonitrile + 0.1 M Bu_4NClO_4 at a scan rate of 0.1 V s^{-1} (unless otherwise stated).

Surface Preparation. Gold and platinum electrodes were 1×4 cm^2 sheets. They were treated for 1 min with hot mixed chromic acid ($K_2Cr_2O_7$ in 96% H_2SO_4), then carefully washed with Milli-Q water, and dried. Gold electrodes were used as such or after being immersed in a 10^{-3} M ethanol solution of MPS[26] or C16SH overnight (15−16 h), rinsed with ethanol, and dried. This treatment produces a uniform negatively charged (Au/MPS) or hydrophobic (Au/SC16) gold surface.

Multilayer Deposition. The buildup of the multilayers was performed according to the methodology introduced by Decher and Hong,[10] that is, by dipping the electrodes alternatively into the solutions of the two polymers. Immersion times were 5 min. After each immersion step the substrate was carefully washed (two steps) and dried in air.

IRRAS. Fourier transform infrared (FTIR) spectra were taken in reflection−absorption mode on a Perkin-Elmer 2000 FTIR spectrometer. Infrared reflection absorption spectroscopy (IRRAS) spectra of the layers were taken with a grazing incidence reflection unit (Specac). All spectra were recorded with 2 cm^{-1} resolution at an angle of incidence of 80° relative to the surface normal. Ten cycles were run for each spectrum, and weighted subtraction of the background at the end of the series of measurements was applied. No gas purging of the chamber was necessary.

QCM. Quartz crystal microbalance (QCM) analyses were performed with a platinum-coated AT-cut quartz electrode (0.2 cm^2), resonating at 9 MHz, onto which the polymers were deposited. The oscillator circuit was homemade, and the frequency counter was an Agilent model 53131A. Data were collected by a microcomputer with a homemade analyzing software by which frequency changes $\Delta\nu$ were monitored as mass changes Δm.

AFM. AFM images were obtained using a Digital Instruments Dimension 3100 atomic force microscope with NanoScope Software and MikroMasch noncontact silicon cantilevers in tapping mode.

CP-AFM. The AFM tips used for the bulk resistance measurements were plateau-style tips purchased from Pacific Nanotechnology.

Silicon substrates and AFM tips were coated with metal using a Balzers thermal metal evaporator at a pressure of 10^{-6} Torr. Tips were coated with 100 nm of Au at a rate of 0.1 nm s^{-1} after the deposition of a 5 nm Cr adhesion layer. Template stripped flat substrates were made according to the literature.[27] First, 500 nm of Au was deposited onto a clean Si wafer. One square centimeter pieces of Si were then glued to this layer using epoxy, with the polished side to the Au surface. This sandwich structure was then baked at about 120 °C for 1 h or until cured. Substrates were pried away using a razor blade or tweezers, cleaving the Au/Si interface.

Current−voltage measurements were made using a modified multi-mode atomic force microscope (Digital Instruments). Junctions were formed by bringing Au-coated AFM tips into contact with SAMs on Au substrates. A Keithley 236 source/measure unit was used to apply a voltage to the AFM tip, and the substrate was grounded through a Keithley 6517 DC ammeter. For a typical data-taking session with a single Au-coated tip, at least five $I-V$ traces per SAM were measured.

3. Results and Discussion

3.1. Nafion Monolayers on Gold and Platinum. For this investigation gold electrodes were used bare or modified with MPS or C16SH (see Experimental Section) to produce uniform negatively charged or hydrophobic electrode surfaces. To our surprise we found that also Nafion solutions modify the noble metal surfaces with a strongly adsorbed monolayer.

Langmuir−Blodgett (LB) layers of Nafion have been recently deposited on dodecanethiol-primed gold.[28] Multilayers of about 1 $\mu g\ cm^{-2}\ layer^{-1}$ (ca. 10^{-9} mol cm^{-2} in terms of sulfonate moieties) were measured by QCM. LB layers on silicon are about 1.3 nm $layer^{-1}$ thick and are constituted by 34 nm diameter grains.[29]

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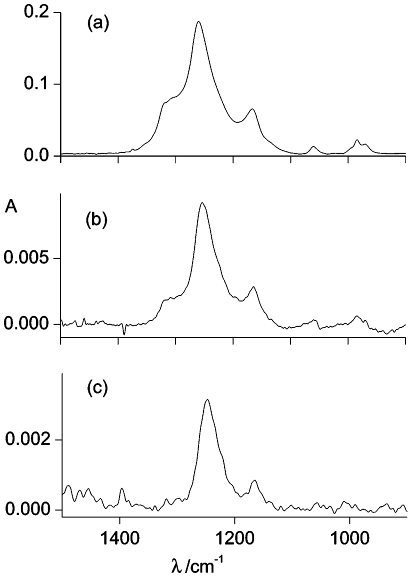

Figure 1. IRRAS spectra of (a) a thick Nafion layer and (b, c) Au/Nafion monolayers from (b) 1% and (c) 0.1% ethanol solutions.

We have found by IRRAS analysis that Nafion monolayers are formed from 1% ethanol solution on bare gold at the same level as on C16SH-primed gold. The layers are very stable, and only prolonged treatment with a hot chromic mixture can detach the layer completely. Also, platinum forms similar monolayers so that the interaction of Nafion with gold is not specific.

The interaction of a Nafion membrane with a platinum electrode has been recently investigated by infrared spectroscopy.[30] As found in that analysis, the IRRAS spectrum of the Nafion monolayer (Figure 1b) displays strong bands at 1320, 1250, and 1160 cm^{-1}. A weak multiplet centered at 985 cm^{-1} is due to C−O−C modes.[30] The bands at 1250 and 1160 cm^{-1}, due to the antisymmetrical (A) and symmetrical (S) stretching modes of $-CF_2-$ moieties,[30] have the same intensity ratio as in the bulk polymer (Figure 1a) whereas the band at 1320 cm^{-1}, due to A stretching mode of the sulfonate moieties, is about 50% lower (the corresponding S band at 1060 cm^{-1} is weak). A and S bands exhibit transition dipole moments which are perpendicular and parallel to the axis of the moiety, respectively. Thus, they may be oriented perpendicular or parallel to the electrode plane and they are, therefore, useful for a determination of the molecular orientation of the polymer layer by using the so-called surface selection rule for IR spectroscopy at metal surfaces.[31] The correspondence of the monolayer spectrum with the bulk spectrum for the $-CF_2-$ modes indicates no particular orientation of the polymer chains whereas on the contrary the decreased intensity of the sulfonate A-band indicates a preferential perpendicular orientation of these functional groups.

QCM has evaluated a surface mass of 1.0 ± 0.1 μg cm^{-2} in substantial agreement with the result in the literature for LB films.[28] When a density of 1.58 g cm^{-3} is used,[32] the thickness is about 6 nm. A recently evidenced picture for Nafion colloids[33] corresponds to elongated particles made of packed and aligned backbone chains with the pendant sulfonate groups located at the periphery. The diameter of these cylindrical aggregates is 3−5 nm.[33] The value compared with the monolayer thickness suggests that a layer of cylindrical aggregates is formed on the gold surface.

AFM (Figure 2) has shown a surface regularly covered by 25−30 nm wide domains with a thickness of 4 nm (by rastering), in appreciable agreement with the estimated value. The roughness is 0.7 nm.

We have investigated the dependence of Nafion coverage from the Nafion concentration in the film-forming solution. The result, shown in Figure 3, is that the isotherm shows two levels of adsorption (below and above 0.5% Nafion concentration) corresponding to 0.4 and 1.0 μg cm^{-2}, respectively. The FTIR spectrum at the first level (from 0.1% concentration, Figure 1c) shows that the intensity of the sulfonate A-band has decreased further to almost disappear. Thus the layer produced at low concentration is oriented whereas the thicker layer obtained at higher concentrations appears to have randomly distributed sulfonate ends.

It has been recently shown by IRRAS[30] that the interaction of platinum with Nafion resembles that with a sulfuric acid solution. On bare and clean noble metal surfaces, van der Waals interactions are large as a result of the polarizability of the metallic electrons, and this allows adsorption of both polar and nonpolar adsorbates. Yet the metal samples used in this report are not produced under ultradry conditions so that they are in fact coated by some adsorbed water,[34,35] and this makes the surface hydrophilic. On this surface Nafion is strongly adsorbed, and we will show in this report that it presents itself as the best candidate for the adsorption of all the soluble polypyrroles here investigated.

The Nafion monolayer from the 1% ethanol solution has been used for surface adsorption of polypyrroles as reported below.

3.2. Copolymerization of RPSH and RP. Recently a polymeric SAM, chemisorbed onto a gold surface via multiple thiol or disulfide groups grafted on the polymer backbone, has been reported.[36] As compared to organothiol SAMs, this polymeric SAM shows improved stability because of cooperative binding via multiple thiol−gold or disulfide−gold bonds.

To produce an analogous polypyrrole layer while reducing the occurrence of cross-linking by disulfide bridging, we have produced copolymers of RPSH with RP. Because RPSH is irreversibly oxidized at $E_p = 0.72$ V, that is, the same potential as that of RP,[23] RPSH−RP copolymerization will produce copolymers with a composition similar to that of the electrolytic batch.

Bulk copolymers were prepared with added RP in a 2:1 or 4:1 ratio to RPSH as reported in Experimental Section

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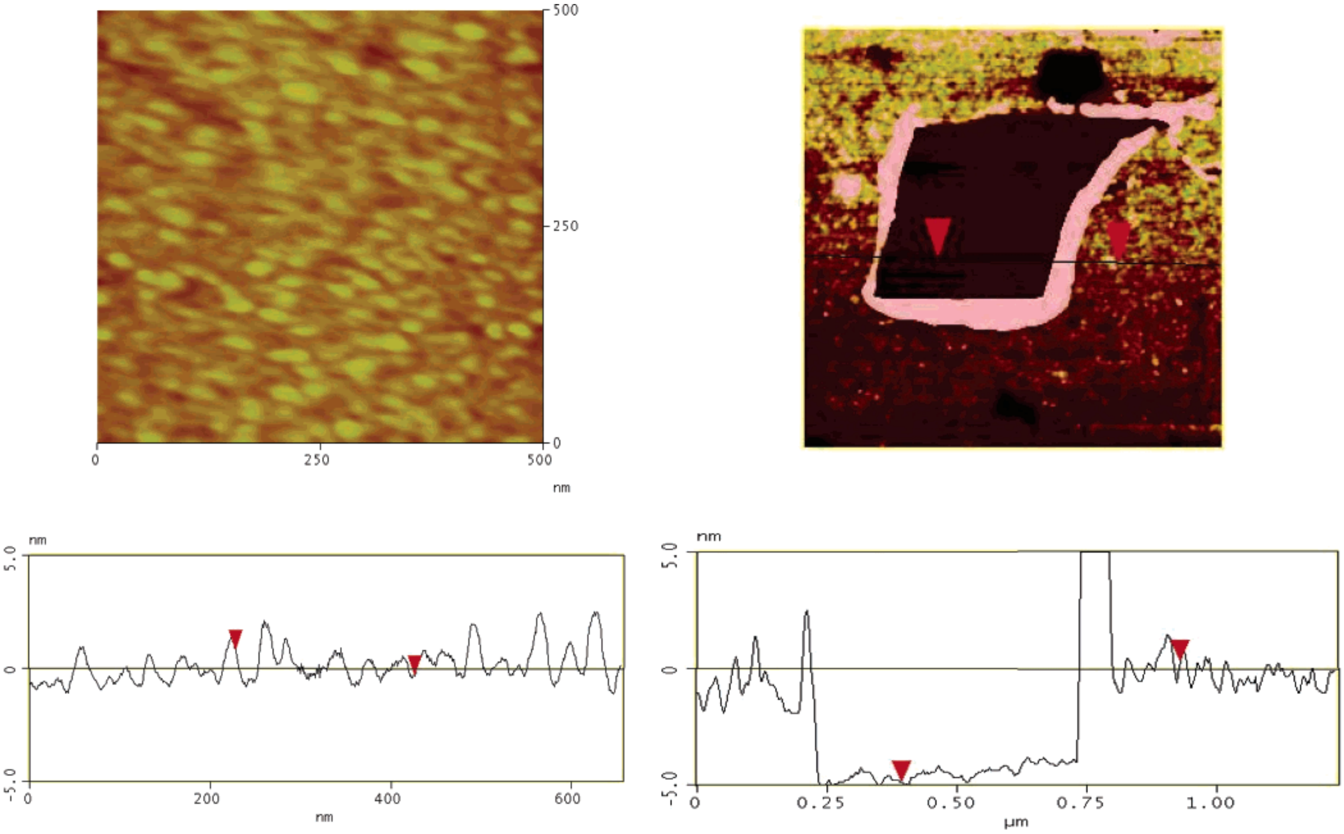

Figure 2. AFM topography images (upper) and section profiles (lower) of Au/Nafion monolayers on gold. Right: rastered layer.

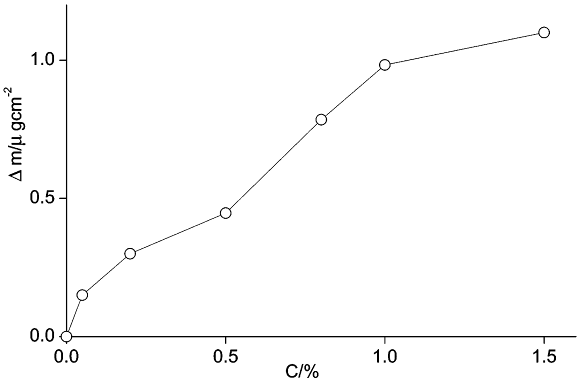

Figure 3. QCM mass vs Nafion concentration (%) for Au/Nafion monolayers.

following the procedure used for poly(RP).[23] The copolymers are fully soluble in $CHCl_3$ and acetonitrile and partially soluble (20−50%) in ethanol.

The homopolymer poly(RP) displays the same UV−vis spectrum of both copolymers which indicates that the polymers possess the same degree of conjugation (namely, the same length of the conjugated backbone) of the homopolymer. The integrated S 2p (thiol) and N 1s (pyrrole) peaks in the X-ray photoelectron spectra of the copolymers has indicated that the 4:1 copolymer is in fact $(RP)_6$−RPSH whereas the 2:1 copolymer is $(RP)_{2.5}$−RPSH. The difference may be attributed to a slightly higher reactivity to coupling of the RP monomer.

The copolymers are not indefinitely stable because in the runs of multiple days irreversible cross-linking of the thiol moieties insolubilizes the polymer. Thus copolymer solutions for forming monolayers were freshly prepared and used within 1 day before their ability to graft to gold as electroactive layers (see below) was lost.

Table 1. Redox Charges (μC cm^{-2}) for Polypyrrole SAMs at Different Electrode Surfaces

polypyrrole	Au	Au/MPS	Au/Nafion
poly(Py)	30	10	35
poly(RP)	0	0	60
poly(RP-*co*-RPSH)	50		
poly(NRDP)	0	20	70

3.3. Polypyrrole SAMs. Adsorption of polypyrroles on the electrode was performed as follows. The electrodes were immersed in the polypyrrole solution for 5 min, then they were carefully washed with the same solvent, dried, and cyclic voltammogram (CV) analyzed from −1.0 to 0.0 V (for poly(Py)) or to 0.8 V (for the others, which are *N*-alkyl substituted polypyrroles) in acetonitrile + 0.1 M Bu_4NClO_4. In the first case the redox charge, evaluated according to the published electrochemical QCM method,[37] corresponds to about 0.35 electrons (pyrrole ring)$^{-1}$ whereas in the *N*-alkyl substituted polypyrroles the value is 0.50 electrons (pyrrole ring)$^{-1}$.[38]

The values of reversible-charge surface density, as a measure of the degree of coverage, obtained for the monolayers of the different polypyrroles, are summarized in Table 1.

In the case of poly(Py), when $CHCl_3$ was used as the solvent no adsorption at all was recorded on bare Au or Pt

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(37) Zotti, G.; Zecchin, S.; Schiavon, G.; Groenendaal, L.; *Chem. Mater.* **2000**, *12*, 2996.

(38) Zotti, G.; Zecchin, S.; Schiavon, G.; Vercelli, B.; Berlin, A.; Dalcanale, E.; Groenendaal, L. *Chem. Mater.* **2003**, *15*, 4642.

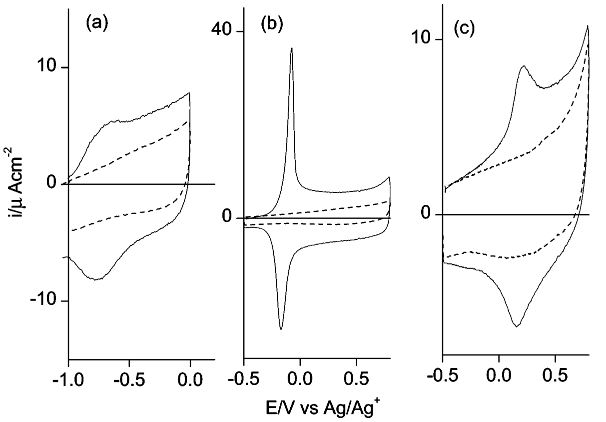

Figure 4. CV of (a) Au/poly(Py); (b) Au/Nafion/poly(RP); and (c) Au/MPS/poly(NRDP) monolayers in acetonitrile + 0.1 M Bu_4ClO_4. Scan rate: 0.1 V s^{-1}.

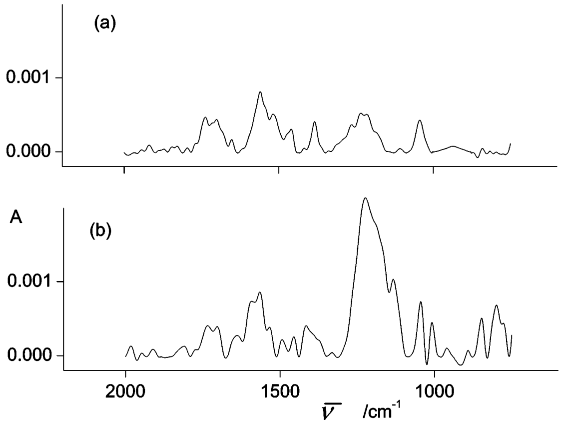

Figure 5. IRRAS spectra of (a) Au/poly(Py) and (b) Au/poly(Py)/PSS monolayers.

electrodes; moreover, neither anionic (Au/MPS) nor lipophilic (Au/SC16) surfaces gave any adsorption. Significant adsorption is obtained when passing from $CHCl_3$ to the polar solvent acetone. The CV (Figure 4a) is centered at $E° = -0.65$ V, as regularly found with polypyrrole with sulfonate counteranions such as, for example, tosylate.[39] In this case the coverage is high on the bare Au and Pt electrodes (stored charge 30 μC cm^{-2}); on the contrary MPS priming of Au decreases the amount of adsorption by 50−70%. It, therefore, appears that the interaction is not mainly electrostatic but is likely to involve direct adsorption on the conductor of the polypyrrole sulfosuccinate ion pair, either through the polypyrrole backbone or the sulfosuccinate counteranion. IRRAS analysis reported below has helped in suggesting which is the right disposition. The failed adsorption from $CHCl_3$ solution is accounted for by swelling of the alkyl side chains of the succinate anion which prevents the interaction with the metal surface. On a monolayer of Nafion the poly(Py) coverage is increased to 35 μC cm^{-2}.

Adsorption of soluble hydrophobic poly(RP) does not occur at all at any electrode surface, Au/MPS and Au/SC16 included. A way of forming a stable monolayer could have been that of creating a hydrophobic yet polyanionic surface, which has been obtained by priming the bare gold surface with Nafion. After this treatment the electrode adsorbs a conspicuous and very reproducible poly(RP) monolayer as shown by the CV (Figure 4b) at $E° = -0.12$ V with a reproducible redox charge of 60 μC cm^{-2}.

Self-assembly (SA) of poly(RP-*co*-RPSH) on gold from a 10^{-3} M solution of both $(RP)_6$−RPSH and $(RP)_{2.5}$−RPSH copolymers results in monolayers with the same redox response at $E° = -0.10$ V and the same reversible charge of 50 μC cm^{-2}.

SA of poly(NRDP) was first attempted on bare gold and on Au/MPS. Of these only the latter forms appreciable layers, which show the redox response of the polymer (Figure 4c) at $E° = 0.15$ V[24] and are very reproducible giving a reversible charge of 20 μC cm^{-2}. The formation of monolayers on the negatively charged surface confirms that strongly localized charges, such as those on tetralkylammonium moieties, are effective whereas charges delocalized over the polymer backbone are too weak for this purpose. As a consequence SA on Au/Nafion has given the record coverage of 70 μC cm^{-2}.

3.4. IRRAS Spectroscopy of the Poly(Py) Layer. The IRRAS spectrum of a Au/poly(Py) monolayer is shown in Figure 5a. The spectrum displays bands at 1720 cm^{-1} (carbonyl stretching of succinate ester) and 1220 and 1050 cm^{-1} (stretching of the sulfonate moiety) and a band at 1560 cm^{-1} due to the oxidized polypyrrole. After PSS treatment the spectrum (Figure 5b) records a scarce loss of succinate anion, evidenced by a moderate decrease of the carbonyl band, and the acquisition of PSS showing the strong sulfonate bands at 1220, 1040, and 1010 cm^{-1}.

Because PSS adds externally to polypyrrole, the result appears to indicate that the polypyrrole sulfosuccinate ion pair is adsorbed to the metal substrate via the sulfosuccinate moiety. Simple molecular modeling shows that the sulfosuccinate anion is flat with the two carbonyl moieties exposed to adsorption. Moreover, density functional theory calculations have recently shown that the ester moiety adheres with noticeable strength to gold.[40] The consequences in electrical junctions are quite significant, as reported below.

3.5. AFM Spectroscopy of Monolayers. AFM on flat templated gold substrates before and after monolayering has shown that the microscope tip follows the underlying gold surface with unchanged roughness (0.2 nm) as expected from uniform monolayers.

Only in the case of poly(Py) (Figure 6), that is, the polymer with the more bulky counteranion, a modest increase (from 0.2 to 0.4 nm) of the roughness is observed. The image shows round domains about 10 nm wide, and soft rastering has allowed the evaluation of a thickness of about 1 nm.

3.6. Comments on Monolayering. For SA of polypyrroles, all p-doped and hence bearing positive charges on the polyconjugated backbone, both the negative charge on the metal surface and the nature of the polymer chain are of utmost importance.

Surface-localized anion charges, such as those present in MPS-primed gold, are effective only when strongly localized

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(40) David, M.; Roman, T.; Dino, W. A.; Nakanishi, H.; Kasai, H.; Ando, N.; Naritomi, M. *J. Phys.: Condens. Matter* **2006**, *18*, 1137.

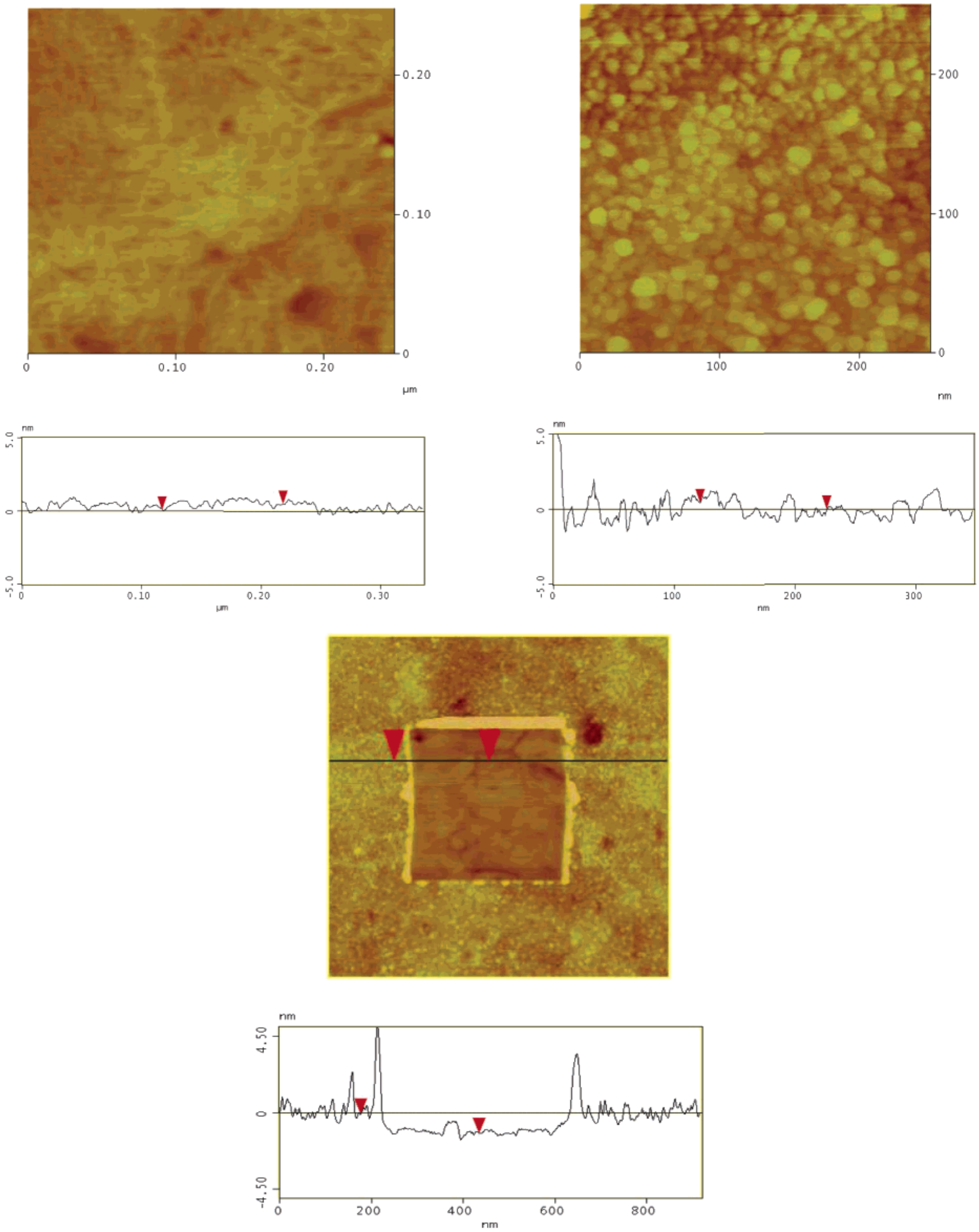

Figure 6. AFM topography images (upper) and section profiles (lower) of Au/poly(Py) monolayers on gold (top right). Top left: bare gold. Bottom: rastered layer.

positive charges are present in the polymer such as in the case of poly(NRDP). In other cases the charge is of less or no importance. Thus, poly(Py) adsorbs nicely on bare gold whereas on negatively charged gold SA is someway hindered.

Similarly SA of the hydrophobic poly(RP) does not occur on negatively charged gold. Instead it is allowed by a hydrophobic Nafion layer, which is a clear example of the dominance of the apolar–polar characteristics of the polymer chain in controlling the SA process.

From Table 1 (and Table 2 for multilayers, see below) it is clearly shown that poly(Py) layers store approximately 50% of the charge stored by the others. This is mainly due to the fact that measured charges of poly(Py) correspond to 0.35 electrons (pyrrole ring)$^{-1}$ whereas in *N*-alkyl substituted polypyrroles 0.50 electrons (pyrrole ring)$^{-1}$ are involved. Taking this into account polypyrrole monolayer coverages are essentially the same ($9-12 \times 10^{-10}$ mol cm^{-2}, in terms of pyrrole rings) for all the polymers used in this investigation.

Table 2. Redox Charges (μC cm^{-2} Bilayer^{-1}) for ESA Polypyrrole−Polyanion Multilayers at Different Electrode Surfaces

surface	polypyrrole	PSS	Nafion
Au	poly(Py)	40	20
Au/poly(RP-*co*-RPSH)	poly(RP)	0	40
Au/MPS	poly(NRDP)	10	40
Au/Nafion	poly(Py)		30
Au/Nafion	poly(RP)		60
Au/Nafion	poly(NRDP)		60

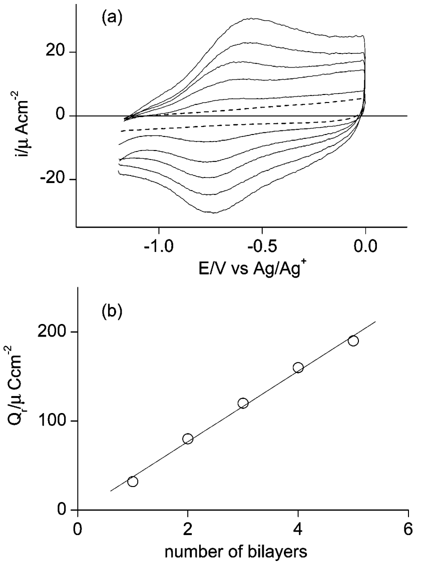

Figure 7. (a) CV of poly(Py)/PSS multilayers on Au in acetonitrile + 0.1 M Bu_4ClO_4. Scan rate: 0.1 V s^{-1}. (b) Plot of reversible charge vs number of bilayers.

3.7. Polypyrrole ESA Multilayers. The results from alternating PSS or Nafion and the different polypyrroles on various polypyrrole-modified surfaces are summarized in Table 2.

ESA of PSS and poly(Py) on Au/poly(Py) (Figure 7) proceeds regularly with a linear growth with a slope of 40 μC cm^{-2} bilayer^{-1}, that is, about the same value of the primer layer. The CVs are centered at $E° = -0.65$ V as for the monolayer because the counteranion is in any case a sulfonate. ESA with Nafion gives also a linear growth with a lower slope (20 μC cm^{-2} bilayer^{-1}).

Alternating PSS and poly(RP) on Au/poly(RP-*co*-RPSH) does not give any growth. It appears that the positively charged yet hydrophobic poly(RP) chains do not interact strongly enough with the hydrophilic PSS anionic chains. Instead ESA is successful using the hydrophobic Nafion counteranion. In this case the charge increases linearly with the number of bilayers (Figure 8) with an increase of 40 μC cm^{-2} bilayer^{-1}. The redox potential of the first layer, that is, poly(RP-*co*-RPSH)−ClO_4 ($E° = -0.075$ V), is shifted cathodically (to $E° = -0.125$ V) for the subsequent layers because of the stabilizing effect of sulfonate anions. In fact, it has beem confirmed that upon substitution of perchlorate with Nafion the first poly(RP-*co*-RPSH)−ClO_4 layer changes its potential (with a negative shift of 50 mV) without changing its reversible charge.

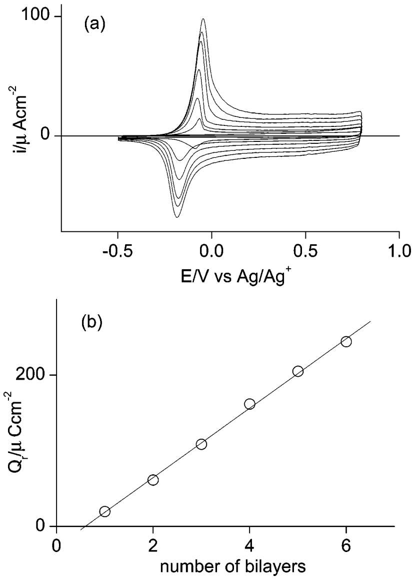

Figure 8. (a) CV of poly(RP)/Nafion multilayers on Au/poly(RP-*co*-RPSH) in acetonitrile + 0.1 M Bu_4ClO_4. Scan rate: 0.1 V s^{-1}. (b) Plot of reversible charge vs number of bilayers.

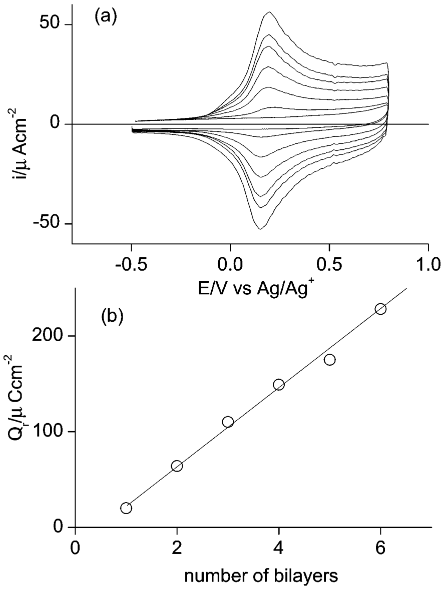

Figure 9. (a) CV of poly(NRDP)/Nafion multilayers on Au/MPS in acetonitrile + 0.1 M Bu_4ClO_4. Scan rate: 0.1 V s^{-1}. (b) Plot of reversible charge vs number of bilayers.

ESA of poly(NRDP) on the Au/MPS/poly(NRDP) layer has been obtained with both PSS and Nafion (Figure 9). The linear increase is 10 μC cm^{-2} bilayer^{-1} for PSS, that is, half the value of the primer layer. With Nafion the growth is 40 μC cm^{-2} bilayer^{-1}, that is, twice the value of the primer layer. This result comes either from a better interaction of a lipophilic chain than of a hydrophilic chain or from a different distribution of the sulfonate end groups in the two polymers.

ESA from Au/Nafion with Nafion as the counteranion is successful in all cases. Au/[Nafion/poly(RP)]$_n$ grows in a perfectly linear fashion with a slope of 60 μC cm^{-2} bilayer^{-1} (as for the first layer), and the same happens for Au/[Nafion/poly(NRDP)]$_n$. Au/(Nafion/poly(Py))$_n$ grows with a lower slope (30 μC cm^{-2} bilayer^{-1}) in agreement with the lower doping charge (due to the lower switching potential, see above).

All the described multilayers are stable to repetitive CV cycling and are robust enough to stand the typical scotch-tape stripping tests.

Table 3. Resistance of Au/Polypyrrole/Au Junctions

junction	resistance (Ω)
Au/Nafion/poly(RP)/Au	2×10^9
Au/poly(Py)/Nafion/Au	7×10^7
Au/poly(Py)/Nafion/poly(Py)/Au	2×10^7
Au/decanethiol/Au	2×10^7

The use of Nafion as a surface primer and anionic ionomer has allowed the regular multilayering of all types of soluble polypyrroles, which makes it the ideal material for the building of such multilayer structures.

3.8. Electrical Characterization of Polypyrrole Layers. Gold-coated AFM tips were used as a nanoscale spring-loaded top contact. This electrode was brought into contact with SAMs on Au under an appropriate applied load, and a voltage sweep was applied to the tip while the substrate was held at the ground. We have compared the current−voltage ($I-V$) characteristics with those of a decanethiol SAM taken as a reference. Resistance values are summarized in Table 3.

The tips we used are plateau-style tips which are regular AFM tips truncated perpendicularly to the z axis, resulting in a structure that has a micrometer-sized plateau used to create larger area contacts to the SAMs. The tip is not atomically flat over the entire plateau, but the resulting contact area is hundreds of times larger than in the case of contacts made with standard AFM tips. Because asperities vary from tip to tip, the contact area can vary significantly between tips. For that reason all the measurements were performed with the same plateau tip which was tested before and after each measurement session with the reference Au/decanethiol monolayer (Figure 10c). The $I-V$ curves for these junctions are practically the same over at least three potential cycles and over three test points.

The investigation has been focused on the two most different polypyrroles here investigated, namely, the twisted-chain and lypophilic N-alkyl substituted poly(RP) and the flat-chain plain poly(Py).

Au/Nafion/Poly(RP)/Au. Figure 10a shows the dependence of current on voltage for the Au/Nafion/poly(RP)/Au junction. This sigmoidal trace is similar in shape to $I-V$ characteristics observed for alkylthiol SAMs.

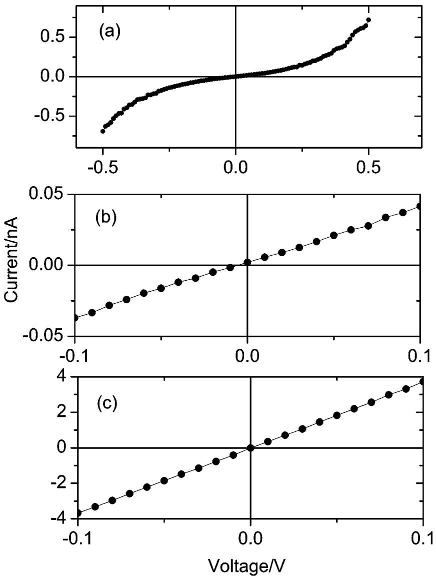

Figure 10. $I-V$ plots for the junctions (a, b) Au/Nafion/poly(RP)/Au and (c) Au/SC10/Au.

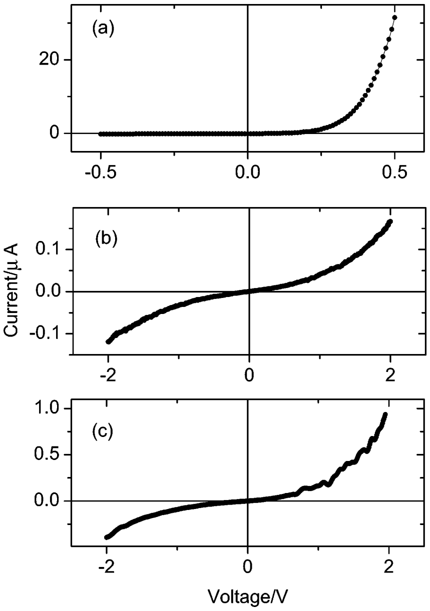

Figure 11. $I-V$ plots for the junctions (a) Au/poly(Py)/Au; (b) Au/poly(Py)/Nafion/Au; and (c) Au/poly(Py)/Nafion/poly(Py)/Au.

The line fits the Simmons equation for tunneling through a rectangular barrier.[41] Though it is well-known that the Simmons model is only a crude approximation for nonresonant tunneling in molecular junctions,[41] the reasonable fit provides qualitative support for nonresonant tunneling as the transport mechanism.

This system is highly resistive as can be seen by the resistance measured at the linear section of the $I-V$ curve (low-amplitude voltage sweep, Figure 10b). For comparison the Au/decanethiol monolayer (Figure 10c) shows a 100-fold lower resistance. In any case it is conductive compared with a plain Nafion monolayer, for which currents of some pico-amperes, corresponding to the instrumental limit, are obtained (blocking contact). Co-penetration of the polymers is responsible for the observed conductivity.

Au/Poly(Py)/Au. In the Au/poly(Py)/Au junction (Figure 11a) the shape of the $I-V$ curves corresponds to a rectifying behavior. The junction rectifies current in the forward direction (positively biased AFM tip).

Good fit with the Schottky equation is obtained. The rectification ratio is rather high, that is, 150 at 0.5 V bias.

After adding a Nafion layer, the resulting Au/poly(Py)/Nafion/Au junction changes to a sigmoidal shape (Figure 11b) that can be fitted with the Simmons equation. The resistance (7×10^7 Ω) is seriously decreased compared with that of the Au/Nafion/poly(RP)/Au junction (2×10^9 Ω). A further addition of poly(Py) (Au/poly(Py)/Nafion/poly(Py)/Au; Figure 11c) restores partially the rectification aspect (the rectification ratio is 2 at 1 V bias) and causes a further decrease of resistance.

We have checked the effect of inverting the bilayer sequence in Au/poly(Py)/Nafion/Au, that is, considering the

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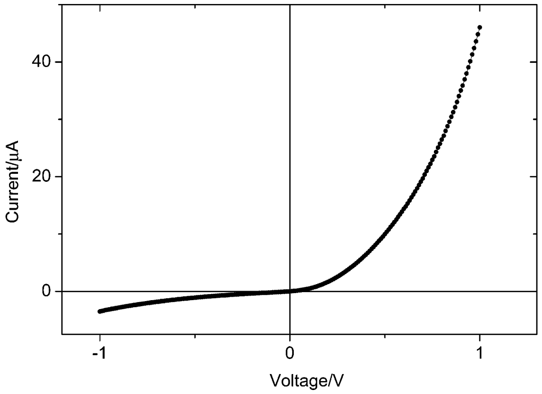

Figure 12. $I-V$ plot for the junction Au/Nafion/poly(Py)/Au.

Au/Nafion/poly(Py)/Au junction. This system (Figure 12) presents a rectifier shape, and the rectification ratio is 10 at 0.5 V bias. Thus the sequence determines the type of junction.

Rectifier. The junctions studied here do not contain a donor−acceptor (D−A) pair, but nonetheless they may rectify current; the observation that they are rectifiers confirms that a D−A pair is not essential for rectification. Recent work has shown that rectifying metal−insulator−metal junctions can be fabricated using molecules that do not contain donor−acceptor compounds.[42]

Apart from the D−A case, other processes are responsible for asymmetrical conduction, that is, rectification in "metal−organic−metal" assemblies.[7c] One is due to Schottky barriers at the "metal−organic" interfaces but appears to be ruled out in our case because the junction of polypyrrole polysulfonate and gold is clearly ohmic.[43] A second situation occurs if the part of the molecule whose molecular orbital must be accessed during conduction (the polypyrrole chain in our case) is placed asymmetrically within a "metal−molecule−metal" sandwich, for example, because of the presence of a long alkyl sulfonate spacer such as the sulfosuccinate in our case. As confirmation of this situation, a subsequent Nafion anionic half-layer compensates the asymmetry and relieves the rectification.

4. Conclusions

Soluble polypyrroles (including thiol-functionalized polypyrrole) were used for the first time to produce SAMs and electrostatically assembled multilayers on gold and platinum electrodes.

Gold and platinum surfaces were used bare or primed with an anionic MPS or a Nafion layer. Nafion solutions are for the first time reported to form stable and well-characterized monolayers on noble metal surfaces, and the result is of high interest in particular for fuel cell applications.

Polystyrenesulfonate and Nafion were used as polyanions for ESA. ESA proceeds with a growth rate linear with the number of bilayers and particularly high with Nafion, which appears to be an efficient primer for all the investigated polypyrroles.

Gold−polymer−gold junctions, formed by mechanical contact between a polypyrrole SAM on gold and a gold-coated AFM tip, are ohmic with Simmons characteristics in the case of poly(*N*-hexylcyclopenta[*c*]pyrrole). Instead, gold−polymer−gold junctions rectify current in polypyrrole sulfosuccinate, and in this case alternation of rectifying and ohmic characteristics is observed with progressive ESA.

Molecular rectifiers, that is, devices in which molecules allow the passage of a larger current in one bias than in the other, are potential components for memory and logic elements in molecular electronics. We have produced for the first time molecular rectifiers from polypyrrole monolayers.

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