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Multiple Adsorption of Polythiophene Layers on ITO/Glass Electrodes and Their Optical, Electrochemical, and Conductive Properties

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Polyelectrolyte multilayers containing electrochemically active polythiophenes have been constructed on ITO/glass substrates using the layer-by-layer adsorption deposition technique. Electrochemically active layers of poly(cyclopentadithienyl-alkylsulfonate), poly(cyclopentadithienyl-alkylammonium), and α,ω-bis(carboxyhexyl)sexithiophene were deposited with nonelectroactive layers of polyallylamine and polystyrenesulfonate. The first sequential adsorption of multilayers in which both the polycation and the polyanion are based on the same polythiophene is reported. UV−vis spectroscopy and cyclic voltammetry indicate a linear dependence of the amount of deposited polymer on the number of deposition cycles. The rate of deposition depends on the oxidation state of the polythiophene being 3 times lower for the oxidized polycationic polymer. Atomic force microscopy characterization of the layers has shown that flat monolayers are deposited with a progressive increase of roughness. Interposition of multiple nonelectroactive layers between the electrode and a single external electroactive polythiophene layer has allowed determination by cyclic voltammetry that each polythiophene layer interpenetrates the confining layers up to a three-layer distance. The conductivities of the multilayers along the surface and perpendicular to it are anisotropic depending on the layer alternation. The photoluminescence properties of the α,ω-bis(carboxyhexyl)sexithiophene multilayers are the same for vacuum-deposited polycrystalline layers.

1. Introduction

Organized multilayers of polyconjugated polymers or oligomers have recently attracted much attention for their possible use in many different fields. The conjugated π-electrons form a one-dimensional electron system with electrical and optical properties which are strongly influenced by interchain interactions. In particular oligothiophenes, and specifically sexithiophene,[1] have shown high ability in light-emitting diodes (LEDs) and field effect transistors (FETs), and regioregular alkylated oligothiophenes[2] display large third-order hyperpolarizabilities useful for nonlinear optical (NLO) devices. These polyconjugated molecules may be assembled in heterogeneous structures with electronic, mechanical, and chemical properties which could not be encountered in homogeneous materials. Superlattice systems and multiple quantum well structures are interesting in high-performance LEDs. Also they are attractive in the use for photovoltaic conversion due to the highly efficient charge separation expected from these segregated structures.

During the past 5 years self-assembly (SA), a most widely used method for the construction of organized supramolecular structures, has grown to an impressive level. In the field of polyconjugated polymers or oligomers, an appreciable number of papers dealing with multilayer SA on electrode surfaces have recently appeared.[3−10] Poly(3-carboxymethylthiophene) was deposited on ITO in alternation with polycationic polyammonium layers up to 5−10 pairs.[3,4] Tetrathiophene diphosphonate has been alternated with zirconium ions in regular multilayers (up to 20 layers).[5] Thiophene-based polymers are most easily self-assembled from solution than polyaniline[6] or polypyrrole,[7] for which

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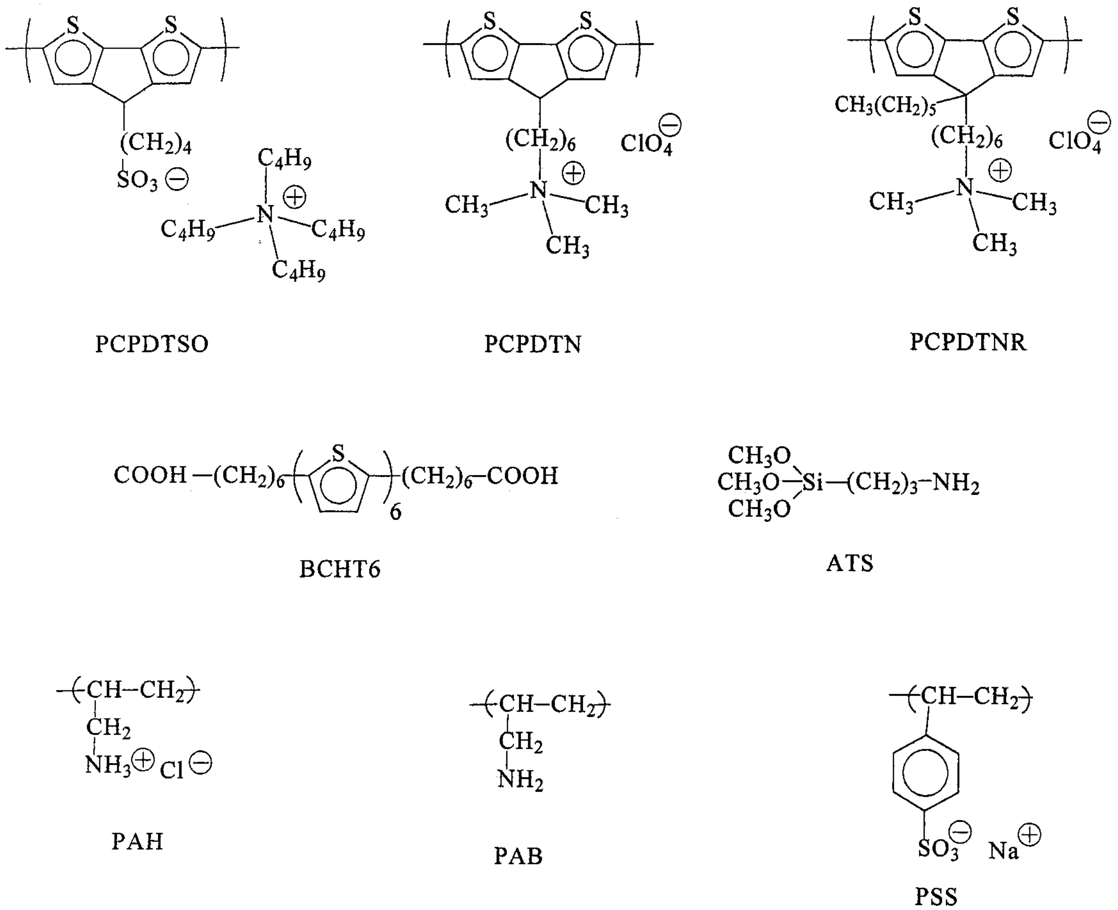
Chart 1



PCPDTSO PCPDTN PCPDTNR

BCHT6 ATS

PAH PAB PSS

reports are given on interpenetrating and/or disordered multilayered sandwiches. SA of multilayers of polyaniline sulfonate (PANI−SO_3) and polyallylamine (PAH) have been investigated with neutron reflectivity techniques.[8] PANI−SO_3 or PPV precursor polymer bilayers have been used on ITO surfaces to improve the LED efficiency.[9] Finally water-soluble poly(*p*-phenylene)s bearing sulfonate and quaternary ammonium functionalizations have been used as multilayers to build efficient blue light emitting diodes.[10]

The electrochemical and conductive properties of such multilayers are largely unknown since in all the above-reported cases no electrochemical characterization was performed. It has been reported that for Langmuir−Blodgett (LB) multilayers the electroactivity decreases quickly as the number of layers is increased disappearing after three to four layers.[11] In contrast in SA multilayers alternating electroactive poly(viologen) (PV) and nonelectroactive polystyrenesulfonate (PSS) layers the electroactivity is displayed without losses after 10 layer pairs.[12] This is due to the fact that LB multilayers are generally more compact and difficult to be permeated by the electrolyte than SA multilayers.[11]

For this reason we have undertaken an investigation of multilayering on ITO/glass electrodes of thiophene-based anionic and cationic polyelectrolytes and the optical, electrochemical, morphological, and conductive properties of the resulting structures. Analogously with the monomeric monolayers previously described,[13] the polymer shape was selected in order to make the axis of the polythiophene chain parallel or perpendicular to the substrate plane. This was made (Chart 1) with the cyclopentadithiophene-based (CPDT) polymers PCPDTSO, PCPDTN, and PCPDTNR, bearing ionic functions along the chain, for the parallel alignment and with α,ω-bis(carboxyhexyl)sexithiophene, which bears the anionic groups at the chain ends, for the perpendicular alignment (ideal structures are illustrated in Schemes 1 and 2 for the CPDT polymers and the sexithiophene, respectively).

The use of planar thiophene-based electroactive chains self-assembled from dilute (low ionic strength) solutions is expected to minimize interpenetration of polymer chains. The α,ω-bis(carboxyhexyl)sexithiophene has been selected since vacuum-evaporated α,ω-dihexylsexithiophene forms ordered films thanks to the aggregating ability of the alkyl and polyaromatic segments of the molecule.[14] For the multilayer deposition the method developed by Decher[15−17] has been used. According to this method, multilayer assemblies are

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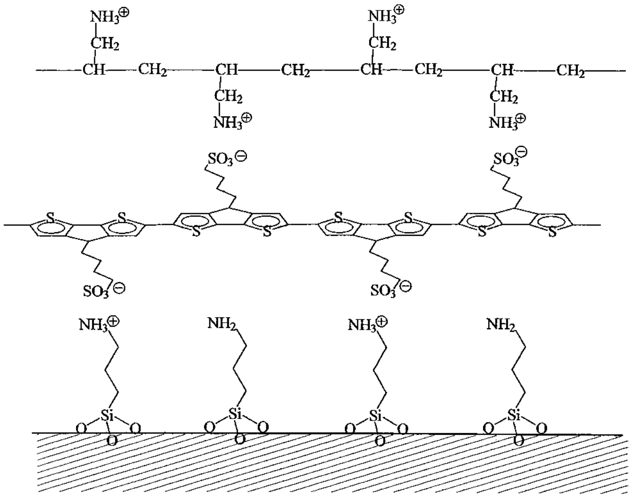
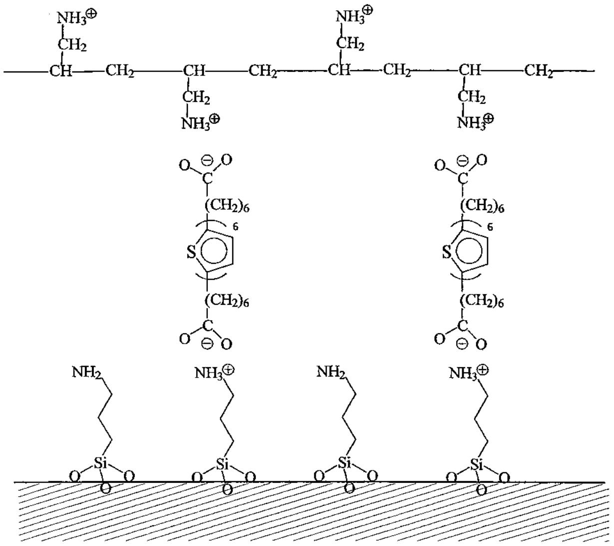
Scheme 1



Scheme 2



prepared by dipping charged substrates alternately into solutions of cationic and anionic polyelectrolytes and/or bipolar amphiphiles (bolamphiphiles). During each dipping process a molecularly thin layer of the corresponding organic polyion is adsorbed at the substrate, the surplus charge reversing the charge of the substrate (charge overcompensation)[18] so that in the subsequent dipping process a polyion of opposite charge can be adsorbed. The layer-by-layer adsorption results in molecular assemblies that are alternately composed of cationic and anionic compounds and exhibit a thickness in the nanometer range.

2. Experimental Section

Chemicals and Reagents. Poly(tetrabutylammonium 4-(4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithien-4-yl)butanesulfonate) (PCPDTSO),[19] poly({6-(4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithien-4-yl)hexyl}-trimethylammonium perchlorate) (PCPDTN),[20] poly({6-(4-hexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithien-4-yl)hexyl}trimethylammonium perchlorate) (PCPDTNR),[20] poly(4-hexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene) (PCPDTC6),[21] and α,ω-bis(carboxyhexyl)sexithiophene (BCHT6)[13] were produced as previously reported. Acetonitrile was reagent grade (Uvasol, Merck) with a water content <0.01%. The supporting electrolyte tetrabutylammonium perchlorate (Bu_4NClO_4) was previously dried under vacuum at 70 °C.

The polycation poly(allylamine hydrochloride) (PAH) (M_w = 15 000, DP = ca. 200) and the polyanion poly(sodium-*p*-styrenesulfonate) (PSS) (M_w = 100 000, DP = ca. 500) were purchased from Aldrich and used as received. Poly(allylamine) base (PAB) was produced in solution by PAH neutralization with NaOH.

(3-Aminopropyl)trimethoxysilane (ATS) was purchased from Fluka. Chlorobenzene and all other chemicals were reagent grade and used as received.

SA Method for Multilayer Deposition. ITO/glass electrodes were 1 × 4 cm indium tin oxide one-side-coated glass sheets (10 Ω square^{-1}, Balzers, Liechtenstein). The ITO microstructure consists of grains ca. 100 nm long with an amorphous phase along the grain boundaries. The ITO/glass electrodes were cleaned with acetone and dried prior to use.

Multilayers were built on both the ITO and the glass surfaces of the ITO/glass electrodes after silanization with ATS according to the literature.[15,16] In detail, the clean ITO/glass substrate was immersed for 1 h in 5% ATS solution in nitrogen-degassed dry toluene and then washed with dry toluene and dried.

The effective ATS functionalization was tested via amidization (25 °C, 1 h) with 1% 3,5-dinitrobenzoyl chloride in acetonitrile containing a few drops of 2,6-lutidine as proton scavenger.[22] The one-electron reduction of the nitrobenzene moiety in acetonitrile at $E° = -1.25$ V vs Ag/Ag$^+$ was used to evaluate the degree of ATS functionalization. The relevant charge was 50 μC cm^{-2}, i.e., close to that of a ferrocene monolayer,[23] which allows the statement that the degree of ATS functionalization corresponds closely to one monolayer.

The buildup of the multilayers was performed according to the methodology introduced by Decher,[15−17] i.e., by dipping the ITO/glass electrodes alternatively into the aqueous solutions of polyanion and polycation, the former being adsorbed as the first layer. Immersion times were 30 min for the first layer and 15 min for all subsequent layers. Between the two immersion steps, the substrate was washed (with Milli-Q-water unless otherwise stated) for 1 min and dried in air.

The regularity of the multilayer buildup was monitored by UV−vis spectroscopy; the relevant absorbance data are given as measured, i.e., for the sum of the ITO and glass sides. As confirmation that the polymer adsorbs up to the same level at both sides of the electrode, electrochemical overoxidation of the multilayer electrode at 2 V followed by reduction at −2.0 V, which bleaches the polymer material, causes a 50% decrease of the absorbance.

The concentrations of the polyion solutions were kept low (typically 10^{-4}−10^{-3} M) to avoid the formation of films thicker by charge shielding or possible coiling of polymer chains.[18,24]

Apparatus and Procedure. Electrochemical experiments were performed at 25 °C under nitrogen in three electrode cells in acetonitrile + 0.1 M Bu_4NClO_4. The reference electrode was silver/0.1 M silver perchlorate in acetonitrile (0.34 V vs SCE). The voltammetric apparatus (AMEL, Italy) included a 551 potentiostat modulated by a 568 programmable function generator and coupled to a 731 digital integrator.

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Electronic spectra were taken with a Perkin-Elmer Lambda 15 spectrometer, IR spectra on a Perkin-Elmer 2000 FTIR spectrometer. Matrix-assisted laser desorption ionization (MALDI) mass spectra were taken on a Reflex TOF spectrometer (Bruker) using 2,5-dihydroxybenzoic acid as matrix. Front-face luminescence spectra were run with a Spex Fluorolog 2 spectrofluorimeter; given the high noise from glass, silica plates (1 × 1 cm) were used as substrate.

Measurements of the sheet resistance of the multilayers were performed on the glass side with the four-probe technique using a Keithley 220 programmable current source and a Keithley 195A digital multimeter. The perpendicular resistance was measured with a two-probe technique on the ITO side of a half-covered sample between the bare ITO surface and the multilayer-coated ITO surface contacted by a spring-pressed platinum minispherical probe; calibration of the apparatus was performed with poly(*N*-methylpyrrole)ClO_4 films of known conductivity and thickness.

Atomic force microscopy (AFM) measurements were performed on 1 × 1 cm glass sections mounted on ca. 1.5 cm diameter steel disks with adhesive tabs. Experiments were conducted in air at ca. 295 K using a Digital Multimode STM equipped with tapping mode etched silicon tips (TESP, force or spring constant, 20−100 N m^{-1}; nominal tip curvature radius, 5−10 nm, cantilever length, 125 μm) and "J" type scanner ($x-y$ range, 125 μm; z range, 5 μm). The AFM was operated in tapping mode at scan rates from 1 to 1.5 Hz.

3. Results and Discussion

3.1. Synthesis of Polythiophene Solutions. Polythiophene solutions were prepared according to the following general procedure. The polymers were deposited at a 2 × 5 cm platinum sheet electrode by potentiostatic oxidation at 0.65 V of a 10^{-2} M solution of the relevant monomer in acetonitrile + 0.1 M electrolyte (Bu_4NClO_4, unless otherwise stated) following the literature prescriptions (see Experimental Section). After the passage of the required amount of charge (typically 2 C) the deposit was washed in acetonitrile and dried (except PCPDTNR, see below). It was then dissolved in 20 mL of the appropriate solvent (except BCHT6, see below). We will consider the individual cases in the following subsections.

PCPDTSO. The polymer deposit was dissolved in water to give a clear dark blue solution. This solution could be used as such (oxidized) or be reduced with an excess (few drops) of hydrazine, which turned immediately the color to violet ($\lambda_{max} = 570$ nm). Given an extinction coefficient ϵ of 1.2 × 10^4 M^{-1} cm^{-1} obtained from the same CPDT polymers,[21] the typical polymer concentration resulted to be ca. 8 × 10^{-4} M of CPDTSO repeat units. The PCPDTSO solutions were brought to pH = 2 with perchloric acid in order to allow adsorption on the primed electrode.

PCPDTN. Hydrazine treatment of this polycationic polymer deposit, besides reducing it to the neutral state, substitutes the perchlorate with the hydroxyl anion therefore making the polymer soluble in ethanol. Thus the hydrazine-treated polymer deposit is subsequently dried and dissolved in ethanol to give a clear dark blue solution. The maximum absorption occurs at 590 nm. A typical solution was 3 × 10^{-4} M in CPDTN repeat units. A similarly concentrated aqueous solution was prepared by neutralization of the ethanol solution of the hydroxide with HCl followed by ethanol evaporation to dryness and dissolution of the residue in water.

PCPDTNR. Since in this case the polymer is soluble in acetonitrile, the polymer solution was prepared by exhaustive potentiostatic oxidation of the monomer in acetonitrile + 0.1 M $LiClO_4$. The electrolyzed solution was evaporated, and the electrolyte was removed by washing with water and evaporating the solution to a dark blue solid. A typical 10^{-3} M solution in acetonitrile was prepared and used as such (oxidized) or after reduction with hydrazine (reduced). The maximum absorption of the reduced solution occurs at 590 nm as for PCPDTN.

BCHT6. The sexithiophene deposit, after reduction with hydrazine, was recrystallized from boiling chlorobenzene. The deposition of BCHT6 on the ATS-primed ITO/glass (see below) has been performed from its solution in boiling chlorobenzene followed by washing in boiling chlorobenzene.

Table 1. Optical (ΔA) and Electrochemical (ΔQ) Deposition Rates for the Investigated Multilayers

multilayer type	$\Delta A \times 10^3$/ bilayer^{-1}	$\Delta Q/\mu C\ cm^{-2}$ bilayer^{-1}
PCPDTSO/PAH	25	50
PCPDTSO(ox)[a]/PAH	20	40
PCPDTN/PSS	20	40
PCPDTNR/PSS	20	40
PCPDTNR(ox)[a]/PSS	6	12
PCPDTSO/PCPDTN	40	80
BCHT6/PAB	65	100

[a] Polythiophene in the oxidized state.

3.2. Multilayer Deposition. Multilayer deposition was performed on ATS-primed ITO/glass (see Experimental Section) alternating the polyconjugated polymer solution with the counterpolyion solution. The resulting structures are ideally illustrated in Schemes 1 and 2 for the CPDT polymers and the sexithiophene, respectively. Since the ATS-primed surface is able to coordinate polyanions, the alternating deposition procedure was preceded, in the case of the polyconjugated polycations (PCPDTN and PCPDTNR), by a first monolayer of PSS produced from a 10^{-3} M PSS solution (pH = 2 by $HClO_4$). In the following subsections the individual multilayer types are reported while optical growth rates are summarized in Table 1.

PCPDTSO/PAH Multilayers. Multilayer deposition was performed by alternating reduced PCPDTSO with PAH, the latter in 10^{-3} M concentration. Figure 1a shows the UV−vis spectrum of the polymer multilayer characterized by the peak-shaped absorption at 570 nm. In Figure 1b the absorbance of the neutral polymer is plotted vs the number of dipping cycles. The relationship is linear with slope 25 × 10^{-3} per PCPDTSO/PAH bilayer; the intercept is slightly positive due to a higher coverage degree of the first layer. Spectroscopically linear deposition was achieved up to at least 30 bilayers.

PCPDTN/PSS and PCPDTNR/PSS Multilayers. Multilayers were obtained alternating reduced PCPDTN or PCPDTNR with PSS, the latter in 10^{-3} M concentration at pH = 2 by $HClO_4$. Also the UV−vis spectra of these multilayers show a clear peak at 570 nm. The relationship of absorbance and number of bilayers is linear with a slope of 20 × 10^{-3} bilayer^{-1}, both for the hydroxide and chloride solutions of PCPDTN and for reduced PCPDTNR; in this case the intercept is zero.

Multilayers from Oxidized or Neutral PCPDTSO and PCPDTNR. The deposition of PCPDTSO/PAH

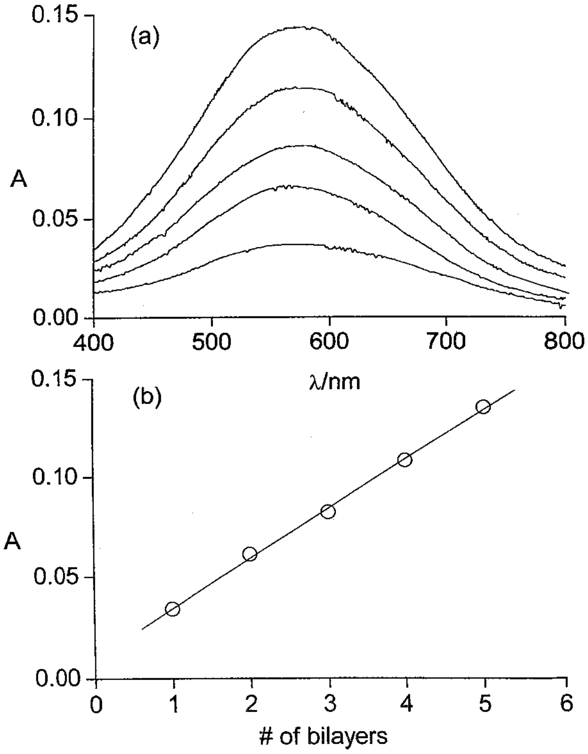

Figure 1. (a) UV−vis spectra of (PCPDTSO/PAH)$_n$ multilayers ($n = 1-5$) on ITO/glass and (b) plot of absorbance vs n.

multilayers has been performed at different oxidation states of the polythiophene in order to check possible differences in the growth rate due to the charged state of the polythiophene backbone. To this end a solution of the as-prepared (oxidized) polymer in methanol (5×10^{-4} M) has been used before and after reduction with hydrazine. The UV−vis spectrum of the polymer multilayer from the oxidized solution displays the long wavelength tail typical of the conducting material. Treatment with hydrazine in acetonitrile leads the multilayered polymer immediately to the neutral state with a peak-shaped absorption at 570 nm. The latter is the same displayed by multilayers formed from the reduced solution. The optical growth rate ($\Delta A = 20 \times 10^{-3}$ bilayer^{-1}, measured at 570 nm on reduced samples) is the same from both oxidized and reduced solutions and comparable with that from the acidic water solution previously described. From these results the redox state of the PCPDTSO backbone appears to be noninfluent on the amount of charge overcompensation.

Deposition of PCPDTNR/PSS multilayers was also performed from both oxidized and reduced solutions. The relationship of absorbance (as reduced) and number of bilayers is linear with slopes of 6×10^{-3} and 20×10^{-3} bilayer^{-1} for the oxidized and reduced solutions, respectively. In this case the dependence from the oxidation state of the polymer is clearly evident. The reversible cyclic voltammetric charges (see following section) are in the same ratio thus confirming the optical analysis. A likely explanation for the different deposition rates is that electrostatic balance is attained at a lower degree of coverage for the oxidized polymer due to its higher charge density. The opposite result, i.e., a higher coverage degree for the oxidized state of PCPDTSO than for its reduced state, is not obtained possibly due to the fact that the reduced polymer already attains the maximum allowed coverage.

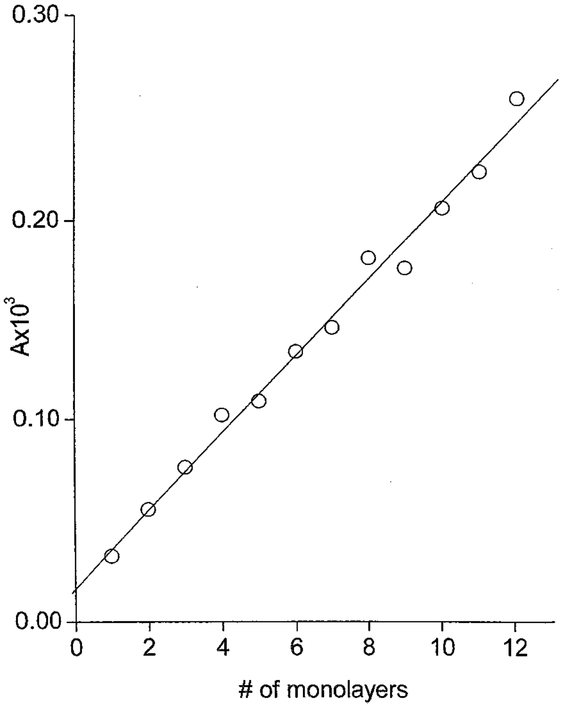

Figure 2. Plot of absorbance vs number of layers n for (PCPDTSO/PCPDTN)$_n$ multilayer ($n = 1-6$) on ITO/glass.

PCPDTSO/PCPDTN Multilayers. A case of particular interest in multilayering is the alternation of polycationic and polyanionic polythiophenes which has been possible in our case. The two polymers contain the same polythiophene backbone and bear the ionomeric moiety at the same position separated by a short alkyl chain (four and six methylene groups for CPDTSO and CPDTN, respectively). It is therefore expected that a commensurate deposition occurs. Multilayer deposition has been performed alternating reduced PCPDTSO and PCPDTN solutions.

The maximum absorbance increases linearly with the number of monolayers (Figure 2). The slope is 40×10^{-3} bilayer^{-1}, i.e., exactly twice the value for bilayers of the individual components.

BCHT6/PAB Multilayers. Dipping the ATS-primed ITO/glass in boiling chlorobenzene solution of BCHT6 for 1−2 min produces a monolayer in a very reproducible fashion. The UV−vis spectrum (lowest in Figure 3a) shows a clear peak at 395 nm with an intensity of 60×10^{-3} absorbance unit. The vibronic structure at lower energy indicates the crystalline nature of the deposit.[25] As a whole the spectrum resembles strictly that of crystalline sexithiophene.[25]

Multilayer deposition has been performed alternating BCHT6 with 10^{-2} M PAB solution. Figure 3 gives the spectra and the absorbance plotted vs the number of dipping cycles. The relationship is linear with slope of 65×10^{-3} bilayer^{-1}.

3.3. Electrochemistry of Multilayers. In general the cyclic voltammetric (CV) response of the multilayers here described does not develop at the first scan, but some scans are required to activate the whole multilayer. Typically samples of up to 10 bilayers require 2−3

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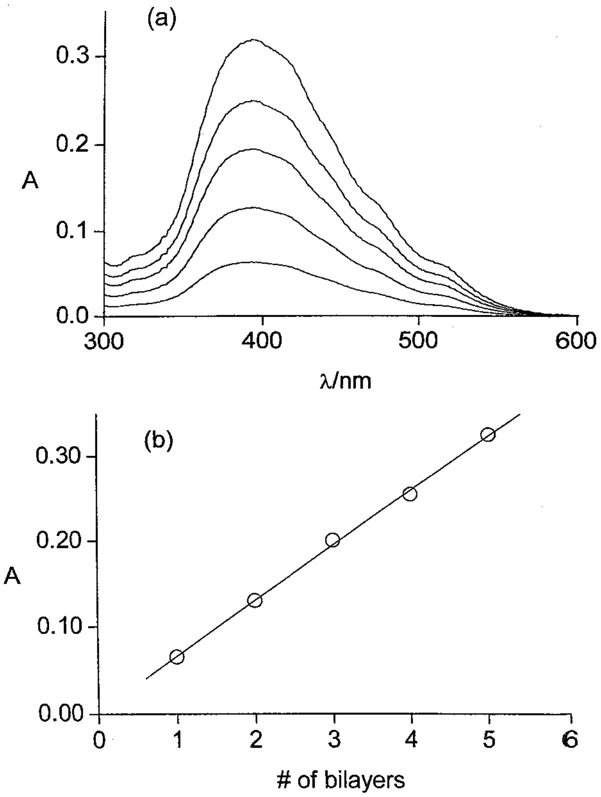

Figure 3. (a) UV−vis spectra of (BCHT6/PAB)$_n$ multilayers (n = 1−5) on ITO/glass and (b) plot of absorbance vs n.

CV cycles at 0.02 V s^{-1} in order to develop a stable response. Thus the as-prepared layers appear to be quite compact and electrolyte-free before the electrochemical stress. This fact is in line with the robustness of the multilayers which stand sticky-tape tests, as commonly found in this type of multilayering. The CV reversible response is perfectly stable to potential cycling (no loss of electroactivity is observed in, e.g., a (PCPDTSO/PAH)$_5$ multilayer after 25 scans at 0.02 V s^{-1}); moreover the cycled multilayers are as resistant to the sticky-tape test as the as-prepared ones, which indicates that solvent swelling and electrolyte permeation are also reversible. In the following the characteristics of the individual multilayer type are described; the electrochemical growth rates are summarized in Table 1.

The CV at the PCPDTSO multilayer electrode in acetonitrile + 0.1 M Bu_4NClO_4 shows two redox processes at $E° = -0.3$ and 0.2 V, as in the bulk polymer.[19] The response is proportional to the scan rate (Figure 4) and to the number of bilayers (Figure 5). The reversible charge Q_r, measured at a switching potential $E_\lambda = 0.7$ V, is 50 μC cm^{-2} bilayer^{-1}.

Also the CV at the PCPDTN and PCPDTNR multilayer electrode shows a twin response at $E° = -0.3$ and 0.1 V as in the bulk polymer[20] with the peak currents linear with scan rate. The charge Q_r is linear with the number of bilayers (ca. 40 μC cm^{-2} bilayer^{-1}, at E_λ = 0.7 V). The reversible charge of the PCPDTSO/PCPDTN multilayer is ca. 40 μC cm^{-2} monolayer^{-1}, compatible with the previous results.

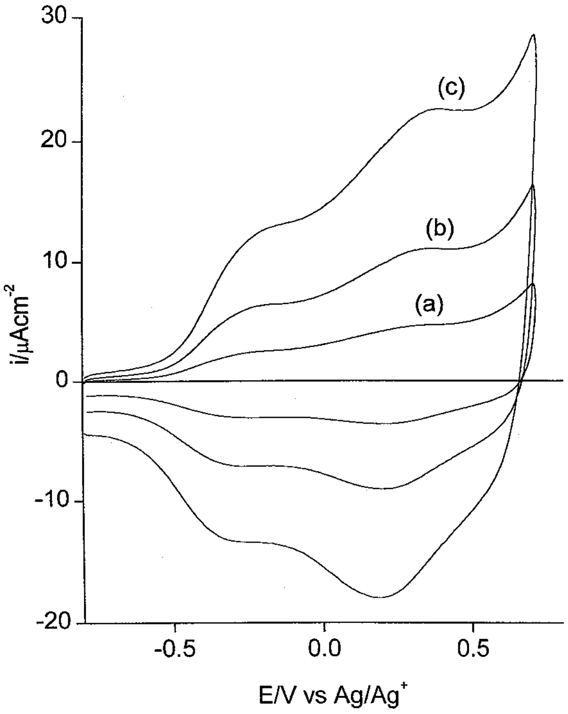

Figure 4. CV of (PCPDTSO/PAH)$_6$ on ITO/glass in acetonitrile + 0.1 M Bu_4NClO_4. Scan rate: (a) 0.02; (b) 0.05; (c) 0.1 V s^{-1}.

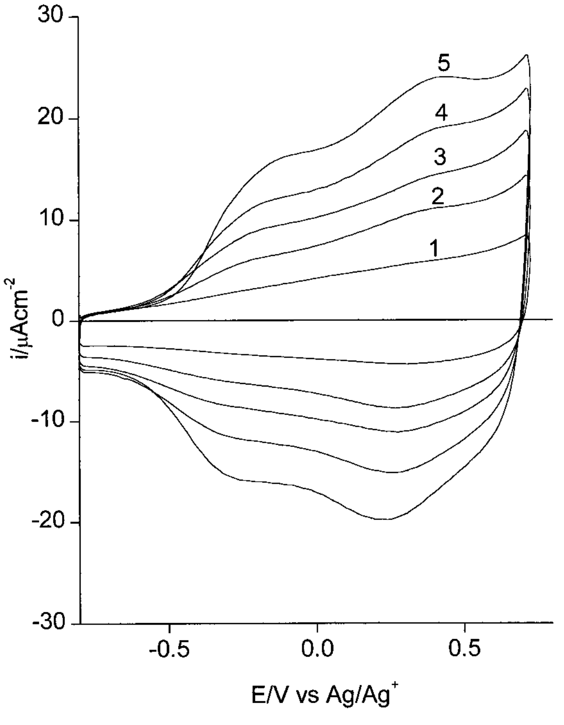

Figure 5. CV of (PCPDTSO/PAH)$_n$ multilayers (n = 1−5) on ITO/glass in acetonitrile + 0.1 M Bu_4NClO_4. Scan rate: 0.1 V s^{-1}.

Electrochemical quartz crystal microbalance (EQCM) analysis has shown that one electron per repeat unit is exchanged at $E_\lambda = 0.7$ V,[26] and on this occasion we have confirmed this result for the generality of CPDT-based polymers. Thus it appears that for the CPDT-based polymers a coverage degree of (4−5) × 10^{-10} mol cm^{-2} monolayer^{-1} is obtained corresponding to a molecular area (per repeat unit) of ca. 0.4 nm^2.

For PCPDTSO/PAH, PCPDTN/PSS, and PCPDTNR/PSS multilayers the extinction coefficient of the CPDT

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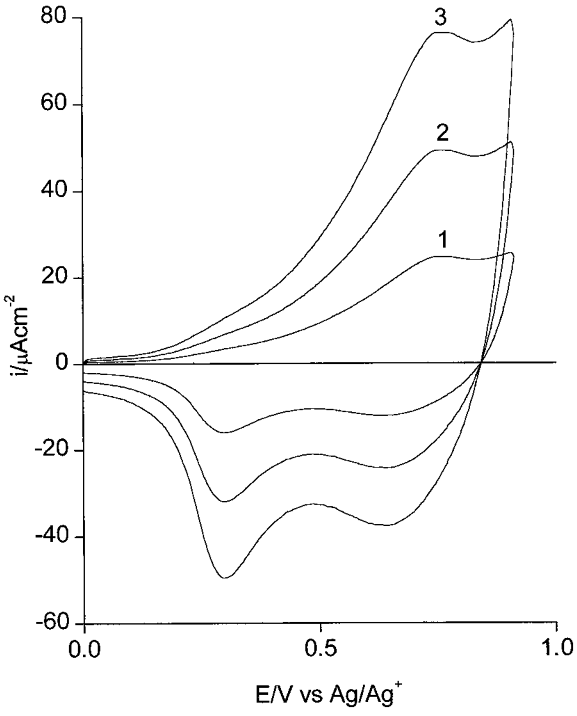

Figure 6. CV of $(BCHT6/PAB)_n$ multilayers ($n = 1-3$) on ITO/glass in acetonitrile + 0.1 M Bu_4NClO_4. Scan rate: 0.1 V s^{-1}.

polymer has allowed determination that the absorbance increase rate corresponds to a coverage of (8−10) × 10^{-10} mol cm^{-2} $bilayer^{-1}$ (as repeat units). The optically measured value is therefore twice the electrochemical value. This discrepancy may be explained by a preferential parallel orientation of the polymer chains along the electrode surface with consequent apparent increase of the absorption coefficient.[27]

As reported before the ATS-primed ITO/glass substrate covers with a very reproducible monolayer in a boiling chlorobenzene solution of BCHT6. This monolayer is oxidized in a CV cycle centered at $E° = 0.5$ V with Q_r = ca. 100 μC cm^{-2} at $E_\lambda = 0.9$ V. The CV at the BCHT6 multilayer electrode (Figure 6) shows that the response is essentially linear with the number of bilayers and scan rate and compatible with the electroactivity of all the bilayers. The charge Q_r is linear with the number of bilayers (ca 100 μC cm^{-2} $bilayer^{-1}$, as for the monolayer). Given a two-electron reversible oxidation of the sexithiophene,[28] this value corresponds to 5 × 10^{-10} mol cm^{-2} $bilayer^{-1}$, compatible with a compact monolayer.

From the extinction coefficient of 6 × 10^4 M^{-1} cm^{-1} for sexithiophene,[29] the absorbance increase rate corresponds to 5.5 × 10^{-10} mol cm^{-2} $bilayer^{-1}$. The electrochemical and optical results are therefore practically the same, which means that in this case a random orientation of the sexithiophene chains is produced. The coverage is identical with that reported for tetrathiophene diphosphonate multilayered with zirconium ions.[5]

The molecular area in the BCHT6 layers is 0.32 nm^2, which is reasonably comparable with the value of 0.28 nm^2 calculated for tetrathiophene.[30] The thickness of a monolayer of the sexithiophene, calculated on the basis of a density of 1.5 g cm^{-3} (as for T6),[31] is 2.5 nm. It must be considered that a value of 3.5 nm was measured for ordered films of the strictly similar α,ω-dihexylsexithiophene.[14]

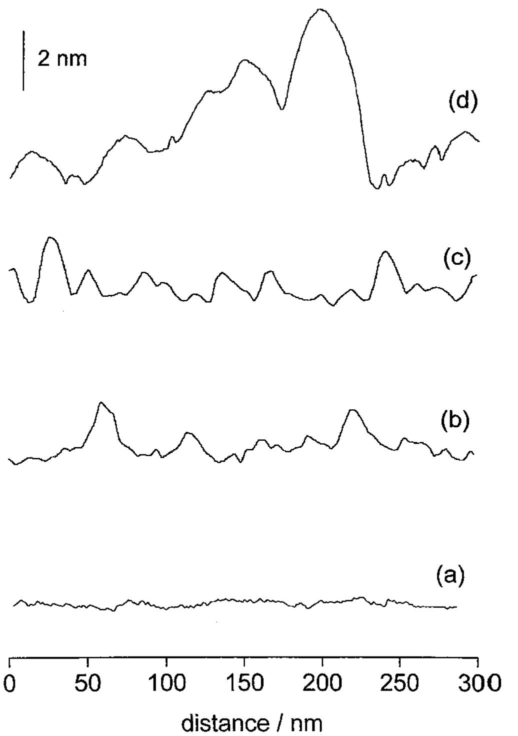

Figure 7. AFM profiles for (a) glass, (b) + ATS, (c) + BCHT6, (d) + PAB. Root mean square roughness: (a) 0.1; (b) 0.5; (c) 0.55; (d) 1.8 nm.

3.4. Atomic Force Microscopy Analysis of Multilayers. Since the ITO side of the ITO/glass electrode is not suitable for this type of analysis, we have imaged and compared the surfaces of glass substrates as such, ATS-primed, monolayered at the ATS-primed surface and multilayered. Topographic images of 0.3 × 0.3 μm^2 dimension have been obtained, and the relevant profiles are given in Figures 7−9. As shown in Figure 7a, the blank substrate is very flat with low slopes ca. 0.1 nm high and 100 nm apart. The hills increase in height to ca. 0.5 nm when the substrate is reacted with ATS (Figure 7b), but morphological changes are minor. Also the adsorption of BCHT6 onto a primed substrate results in a surface morphology and roughness similar to that seen for the primer layer (Figure 7c). On the contrary a large number of spherical particles giving a 2 nm roughness are present in the PAB layer (Figure 7d) and multilayers.

The deposition of BCHT6 over PAB occurs as a cover with frequent cracks appearing as dark dots in the micrograph (Figure 8). The profile shows sharp height drops at their edges of 2.5 nm, a distance corresponding to the calculated BCHT6 monolayer thickness and to the optically determined value (see before).

The main change in surface morphology is associated with the formation of the PAB layers, in which the coiled

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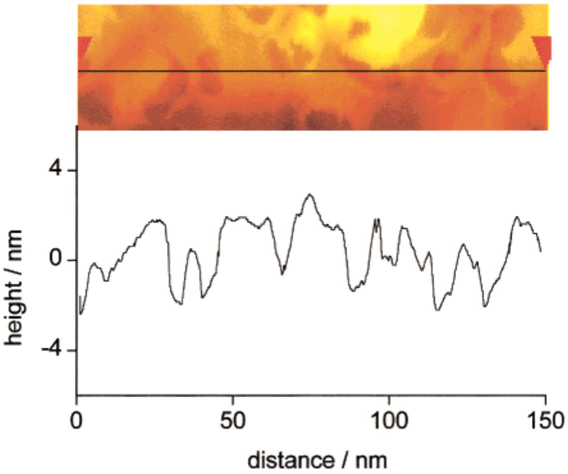

Figure 8. AFM (a) micrograph and (b) profile for ATS + BCHT6 + PAB + BCHT6 multilayer.

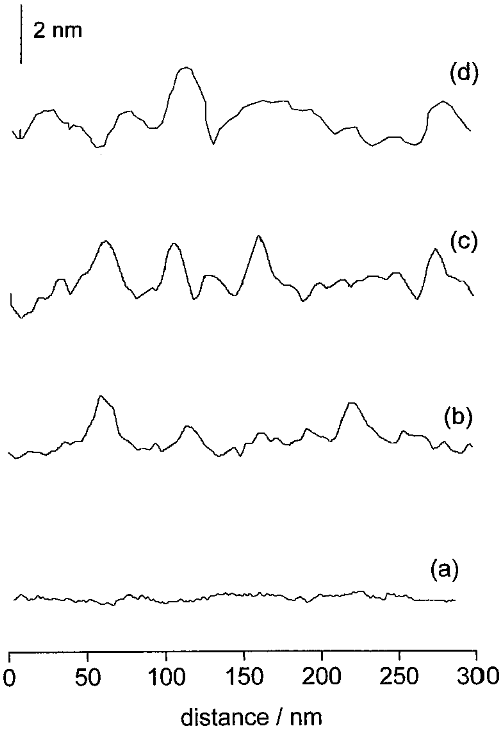

Figure 9. AFM profiles for (a) glass, (b) + ATS, (c) + PCPDTSO, (d) + PCPDTN. Root mean square roughness: (a) 0.1; (b) 0.5; (c) 0.6; (d) 0.6 nm.

structure of the polyamine is likely to be responsible for the increased size of the structures. This is not the case with the PCPDTSO/PCPDTN multilayers (Figure 9). The first PCPDTSO layer increases the roughness to 0.6 nm only (Figure 9c) and the subsequent PCPDTN layer keeps this roughness almost unchanged (Figure 9d). In any case after five bilayers the roughness increases to ca. 1 nm, reflecting a progressive (albeit not dramatic) disorganization, as commonly found in multilayering.[32] In SA multilayers of polyaniline sulfonate (PANI$-$SO$_3$) and polyallylamine (PAH),[8] it has been shown that though layer separation is kept up to at least 40 bilayers the intralayer organization decreases progressively.

The fortuitous presence of a pinhole in a PCPDTSO/PCPDTN bilayer electrode has allowed a clear-cut measurement of the thickness of the layer which is 3.5 nm, including the primer layer. Given the latter a 0.6 nm thickness,[33] the bilayer is ca. 3 nm thick, i.e., the value calculated assuming a reasonable density of 1.5.

3.5. The Multilayer Structure. According to UV$-$vis spectroscopic and electrochemical data (see Experimental Section) the multilayer formation occurs in a similar way on both the ITO-covered and free glass surfaces, both of which are in fact primed. The dependence of absorbance and reversible charge on the number of layers is in all cases linear, which indicates regularity of the subsequent deposition and charge overcompensation. This means also that the layer lying on the ATS monolayer does not differ significantly from the subsequent ones. The fact that the first and the subsequent layers are alike may be explained by matching of the charge with the amine (first) and polyamine (subsequent) layers, with complete charge overcompensation.

The amount of adsorbed CPDT repeat units is almost the same, i.e., (4$-$5) $\times 10^{-10}$ mol cm^{-2} layer^{-1}, independent of the polymer type. This value is the same for a ferrocene monolayer (4.5×10^{-10} mol cm^{-2}),[23] which points to a high packing of the polymer chains in a parallel arrangement. Also in the case of the sexithiophene the coverage (5×10^{-10} mol cm^{-2} layer^{-1}) is comparable with that of ferrocene.

Polyammonium and polysulfonate multilayers, in particular PDDA/PSS multilayers (PDDA is polydiallyldimethylammonium chloride), have been recently investigated in detail by radioanalytical methods.[24] The most interesting result is that the outer surface charge density for both the polyammonium and the polysulfonate layers is ca. 4×10^{-10} mol cm^{-2} vs 9×10^{-10} mol cm^{-2} for the total charge of a polymer monolayer (ca. 50% compensation). Though this value cannot be taken as a rule, the results account clearly for the high degree of overcompensation encountered also in our cases.

The nature of mutual interaction between the polymer layers is electrostatic, with the formation of ion pairs between interwoven chains.[18] Though the strength of a single bond is not high, the presence of so many bridges makes the interaction so strong that no dissolution occurs in any solvent and that the mechanical strength is high. In the case of the α,ω-bis(carboxyhexyl)-sexithiophene a single bond is formed by the thiophene and the amine or polyamine layer in order to account for the overcompensation of charge.[15] Nonetheless such an interaction is so strong that a covalent (amide) bond was suggested to be formed. In fact treatment of a PAB film on a platinum substrate with 10^{-3} M 7-(2,2′-bithien-5-yl)heptanoic acid in boiling chlorobenzene produce the appearance in the IR reflection$-$absorption spectrum of the carbonyl band at 1560 cm^{-1}, typical of the carboxylate anion. Thus the nature of the bond is once more electrostatic (ammonium$-$carboxylate ion pairing) and the reason for the layer stability is the strong intermolecular interactions between the sexithiophene molecules. Furthermore the terminal carboxylic acid groups are able to interact strongly with each other through H-bonding, as recently shown for carboxyl-terminated SA layers on gold.[34]

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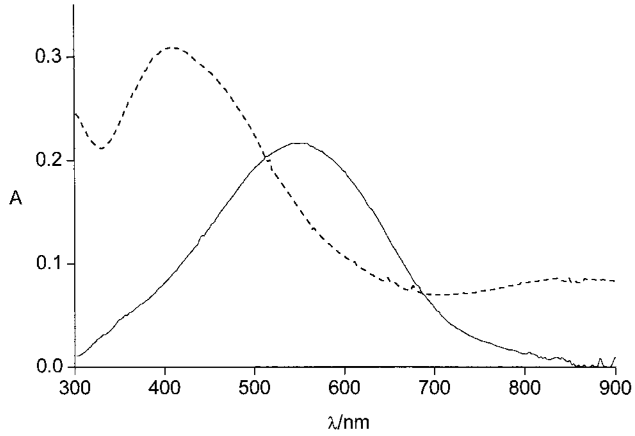

Figure 10. UV−vis spectra of (PCPDTSO/PCPDTN)$_6$ on ITO/glass: (—) neutral and (- - -) I_2-doped.

The disposition of the polyconjugated chains is in principle parallel (for the CPDT polymers) or perpendicular (for the sexithiophene) to the surface plane. The high coverage degree, and hence charge overcompensation,[18] and the enhanced optical absorption for the CPDT polymers agree with the expected parallel alignment of the chains to the surface. On the contrary the absorbance data for the sexithiophene are compatible with a quasi-parallel (or disordered) alignment of the sexithiophene chains in a polycrystalline structure, despite the molecular geometry (linear rod) and the one-end grafting. This suggests that folding of the sexithiophene rigid rod along the flexible hexyl chains in fact occurs.

In the following section we will consider the conductivity and photoluminescence (i.e., the electron transport) properties of the investigated multilayers.

3.6. Conductivity of the Multilayers. The four-point conductivity was measured on the glass side of the multilayered electrode to obtain the multilayer sheet resistance. The PCPDTSO/PAH layers were produced in the oxidized state and were therefore conducting, whereas for the PCPDTSO/PCPDTN and BCHT6/PAB (reduced) multilayers I_2-doping was preliminarily required. I_2-doping changes the color of the multilayers to brown (Figure 10). The reversibility of the doping has been checked by dedoping with hydrazine, which regenerates the pristine material. The appearance of a long flat absorption in the low-energy range is characteristic of the doped oligothiophene, whereas the strong maximum at 400 nm is peculiar for I_2-doped polythiophene.[35]

In a thick (PCPDTSO/PAH)$_{30}$ multilayer the measured sheet resistance and the calculated thickness (2 nm per PCPDTSO/PAH bilayer) assigned the conductivity a value of 0.03 S cm^{-1}. This value is the same for the polymer cast from water solution.[19] Particularly interesting is the comparison with multilayers alternating conducting and insulating bilayers. In the (PCPDTSO/PAH/PSS/PAH)$_{15}$ multilayer the resistance is almost doubled, as expected for a 1:1 alternation of conducting and insulating bilayers.

The perpendicular resistance of (PCPDTSO/PAH)$_{30}$ and (PCPDTSO/PAH/PSS/PAH)$_{15}$ multilayers corresponds to conductivities of 0.01 and 4×10^{-4} S cm^{-1}, respectively. Thus it appears that the anisotropy is low (ca. 3) for alternating conducting and insulating monolayers but is significantly high (ca. 40) when an insulating bilayer is interposed between conducting bilayers. It must be reminded that a recent investigation on the conductivity of polypyrrole LB multilayers[36] has shown a much higher anisotropy with values of 20 and 3×10^{-6} S cm^{-1} for the parallel and perpendicular conductivities, respectively. This difference may be due to the more compact structure and higher order of LB layers.

I_2-doped (PCPDTSO/PCPDTN)$_6$ and (BCHT6/PAB)$_3$ multilayers display sheet resistances corresponding to calculated conductivities of 0.06−0.07 S cm^{-1} for both structures. These conductivities are in reasonable agreement with those of I_2-doped penta- and heptathiophenes (0.01−0.2 S cm^{-1}).[37]

3.7. Electron Transfer from the Electrode to a Polythiophene Monolayer. The construction of the multilayers has given us the opportunity to evaluate the electron transfer rate from the electrode to the polythiophene monolayer and hence the conductive properties between adjacent conducting polymer layers. We have done this by interposing a progressively increased number of PAH/PSS bilayers between the primer and an outer PCPDTSO layer. Hereafter in this section the primer layer and the outer thiophene sulfonate layers will be included in the number of alternate ammonium−sulfonate bilayers.

The outer PCPDTSO layer, whose presence was confirmed by the UV−vis absorption, displays the CV of the single bilayer unchanged up to four bilayers (six interposed monolayers) if a scan rate of 0.1 V s^{-1} is used. At five bilayers the oxidation peak potential is positively shifted (by ca. 0.15 V) whereas the response at six bilayers is further shifted to give a featureless slope. From the potential shift at the five-bilayer sample the electron-transfer rate k_0 has been evaluated as ca. 0.1 s^{-1}.[38] This latter value corresponds, both in proteins[39] and in alkane chain surface tethered ferrocene,[40] to a hopping distance of ca. 2.5 nm from the electrode.

The theoretical thickness of a single PAH/PSS bilayer, assuming a density of 1, is 1.5 nm. In fact the reported thickness of a single PAH/PSS bilayer is ca. 5 nm,[41] with a partition of 2.0 and 3.5 nm, respectively,[42] but these values were evaluated for high ionic strength (2 M NaCl). In salt-free solution like ours, the thicknesses are considerably lower. It has been shown that for a PSS monolayer the thickness is ca. 1 mg m^{-2} if produced in salt-free solution but 15 mg m^{-2} for growth in 0.1 M NaCl[24] (thicknesses of 1 and 15 nm, respectively, vs a calculated value of 0.9 nm, assuming a density of 1). Thus in our case we may assume a bilayer thickness of

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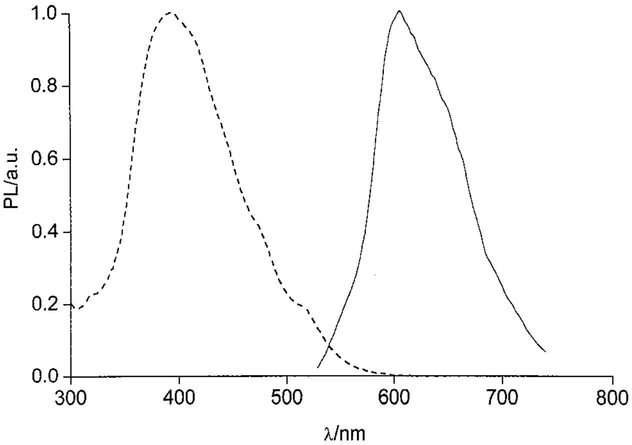

Figure 11. Photoluminescence (—) and absorption (- - -) spectra of a BCHT6/PAB multilayer on silica.

ca. 1.5 nm so that the 2.5 nm distance of charge hopping occurs in a five-bilayer sample of ca. 7.5 nm thickness, with a penetration of the outer PCPDTSO layer to ca. three bilayers below. This result is comparable with that obtained with PAH/PSS multilayers.[18]

The k_0 value of 0.1 s^{-1} allows an evaluation of the perpendicular conductivity σ in such multilayers using the proportionality of maximum redox conductivity σ and k_0, $\sigma = 0.25(a^2k_0)(ne^2/kT)$, where a is the hopping distance (2.5 nm), n the density of carriers (ca. 1.6×10^{21} cm^{-3}), and the other symbols have their usual meaning.[43] The calculated conductivity (ca. 10^{-11} S cm^{-1}) shows that at this distance (ca. 7.5 nm) between conducting layers a very efficient insulation exists.

3.8. Photoluminescence of Sexithiophene Multilayers. The photoluminescence (PL) properties of our sexithiophene multilayers have been investigated, given their importance for possible application in LEDs. The PL of a BCHT6/PAB multilayer displays a maximum at 605 nm (Figure 11) similar to that of sexithiophene.[44] The response of a four-bilayer sample is comparable, both in position and intensity, with that of a 20 nm thick vacuum-evaporated sample of BCHT6 (the quantum yield is ca. 10^{-3} as normally found in sexithiophenes),[44] which displays a comparable absorbance. Moreover the response increases linearly with the number of bilayers. All these results indicate that the inclusion of the sexithiophene in the multilayered structure is not adverse to the photoluminescence properties. This result, which differs from the results obtained with poly(3-carboxylmethylthiophene)/polyamine multilayers[6] and is on the contrary in agreement with that obtained with oligothiophene-based zirconium phosphonate multilayers,[45] is accounted for by the high separation of chromophores in adjacent layers.

Conclusions

Polythiophene-based polyelectrolyte multilayers have been layer-by-layer deposited from polymer solution on ITO/glass substrates and characterized by UV−vis spectroscopy, AFM, and cyclic voltammetry. For the first time cyclopentadithiophene-based polycations and polyanions, alternated reciprocally or with nonelectroactive polyions, have been used to produce layers with the polyconjugated chain parallel to the substrate plane. The bolaform amphiphile molecule α,ω-bis(carboxyhexyl)sexithiophene was alternated with polyallylamine to produce multilayers with the conjugated chain formally perpendicular to the substrate plane. Robust regularly alternated multilayers of the two types have been produced up to 20−30 bilayers. The multilayers have been shown to be electroactive, with current responses proportional to the number of layers, after the as-prepared compact and electrolyte-free layers have been solvent permeated by cyclic voltammetry.

The possibility of forming layers with reduced or oxidized polythiophene backbones has allowed determination of the dependence of the growth rate on the oxidation state of the polythiophene and the conductive properties of the layers, both along the layer plane and perpendicularly to it. Charge transport between the electrode and the layers has been investigated by cyclic voltammetry, whereas photoluminescence spectroscopy has allowed assessment of the influence of the layers on the carrier photogeneration in comparison with the vacuum-deposited polycrystalline material.

This investigation, which follows a previous paper on the monolayer formation from analogous polythiophenes,[13] provides basic tools for the construction and the investigation of organized polyconjugated structures on electrodes.

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