

## Monolayers and Multilayers of Conjugated Polymers as Nanosized Electronic Components

GIANNI ZOTTI\* AND BARBARA VERCELLI

*Istituto CNR per l'Energetica e le Interfasi, c.o. Stati Uniti 4, 35127 Padova, Italy*

ANNA BERLIN

*Istituto CNR di Scienze e Tecnologie Molecolari, via C.Golgi 19, 20133 Milano, Italy*

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### CON SPECTUS

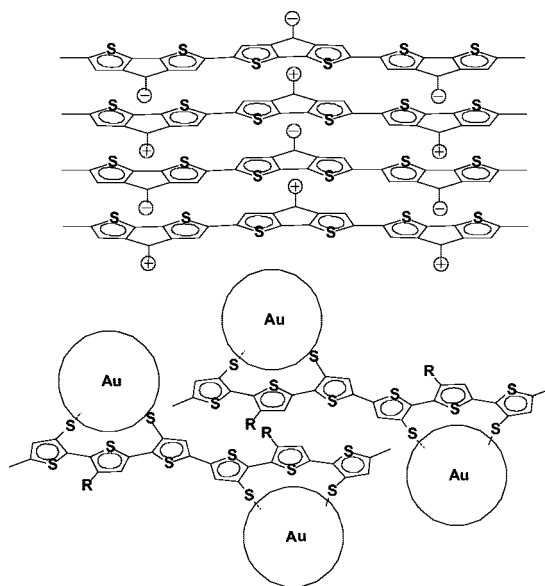
Conjugated polymers (CPs) are interesting materials for preparing devices based on nanoscopic molecular architectures because they exhibit electrical, electronic, magnetic, and optical properties similar to those of metals or semiconductors while maintaining the flexibility and ease of processing of polymers. The production of well-defined mono- and multilayers of CPs on electrodes with nanometer-scale, one-dimensional resolution remains, however, an important challenge. In this Account, we describe the preparation and conductive properties of nanometer-sized CP molecular structures formed on electrode surfaces—namely, self-assembled monolayer (SAM), brush-type, and self-assembled multilayer CPs—and in combination with gold nanoparticles (AuNPs).

We have electrochemically polymerized SAMs of carboxy-alkyl-functionalized terthiophenes aligned either perpendicular or parallel to the electrode surface. Anodic coupling of various pyrrole- and thiophene-based monomers in solution with the oligothiophene-based SAMs produced brush-like films. Microcontact printing of these SAMs produced patterns that, after heterocoupling, exhibited large height enhancements, as measured using atomic force microscopy (AFM).

We have employed layer-by-layer self-assembly of water-soluble polythiophene-based polyelectrolytes to form self-assembled multilayers. The combination of isostructural polycationic and polyanionic polythiophenes produced layers of chains aligned parallel to the substrate plane. These stable, robust, and dense layers formed with high regularity on the preformed monolayers, with minimal interchain penetration. Infrared reflection/adsorption spectroscopy and X-ray diffraction analyses revealed unprecedented degrees of order. Deposition of soluble polypyrroles produced molecular layers that, when analyzed using a gold-coated AFM tip, formed gold–polymer–gold junctions that were either ohmic or rectifying, depending of the layer sequence.

We also describe the electronic conduction of model  $\alpha,\omega$ -capped sexithiophenes featuring a range of electron donor/acceptor units and lengths of additional conjugation. The sexithiophene cores exhibit redox-type conductivity, developing at the neutral/cation and cation/dication levels with values depending the nature of the substitution and the redox system. Extending the conjugation beyond the sexithiophene frame introduces further oxidation processes displaying enhanced conductivity.

Finally, we discuss the ability of CP-based monolayers to coordinate AuNPs. Although thiophene- and pyrrole-based oligomers aggregate toluene-soluble AuNPs, alkyl substitution inhibits the aggregation process through steric restraint. Consequently, we investigated the interactions between AuNPs and polypyrrole or polythiophene monolayers, including those formed from star-shaped molecules. The hindered aggregation provided by alkyl substituents allowed us to adsorb thiol-functionalized oligothiophenes and oligopyrroles directly onto preformed AuNPs. Novel materials incorporating AuNPs of the same size but bearing different conjugated ends or bridges have great promise for applications in electrocatalysis, electroanalysis, and organic electronics.



## Introduction

Since their discovery at the end of the 1970s, conjugated polymers (CPs) have been most widely investigated for bulk applications associated with their conducting properties. The beginning of the 1990s marked a turning point in the field, with an explosion of research on new applications based on the semiconducting properties of neutral oligomeric CPs, such as in electronic devices like field-effect transistors (FETs) and light-emitting diodes (LEDs).<sup>1</sup>

At the beginning of the millennium, a new interest in CPs has originated from their possible use as molecular switches or logic gates in future devices based on nanoscopic molecular architectures.<sup>2</sup> Nanosized CPs appeared particularly interesting in the light of emerging molecular electronics.<sup>3</sup> The widespread development at that time of scanning tunneling and atomic force microscopies has given favorable conditions for significant progress in this field.

CPs as building blocks for synthesis of nanostructured materials and devices<sup>4</sup> are particularly appealing because they exhibit electrical, electronic, magnetic, and optical properties similar to metals or semiconductors while keeping flexibility, ease of processing, and control of electrical conductivity. The electrical conductivity of these polymers can vary from an insulator to almost a metallic state and can be reversibly modulated over 15 orders of magnitude by controlling the dopant type and level.<sup>5</sup> Micro- and nanotechniques such as photolithography, microcontact printing, scanning electrochemical microolithography, and electrochemical dip-pen lithography have been used for fabricating micro- and nanoscale structures from conjugated polymers. The way to real nanocontrol still has much to be done due to limitations in yield, resolution, material type, positioning, and production of high-density arrays.

CP chains are molecular wires that may be driven between the conductive and the insulating state. Understanding of the basic conductivity of these structures is a fundamental prerequisite for the general understanding of the conductive properties of conjugated molecular wires. Therefore the production on electrodes of well-defined mono- and multilayers of CPs is of high importance given their nanometer-size one-dimensional resolution.

Conjugated molecules may form supramolecularly assembled structures.<sup>6</sup> The discovery of how polyconjugated rigid-rod molecules may be ordered on (conducting) surfaces via simple techniques is the goal of our investigations.

In a simplified picture polymeric layers can adopt brush or sandwich conformations. Brush structures may be produced through initiation from well-organized and functional surfaces,

obtained through surface grafting (through anodic coupling)<sup>7</sup> of monomers on self-assembled monolayers (SAMs). Sandwich structures may be formed via electrostatic self-assembly (ESA) of structurally well-defined polymers.

The aim of this Account is to provide an overview of recent work carried out in our laboratories on the preparation of novel CP-based nanometer-size molecular structures on surfaces, supported by synthesis and characterization of new monomers and oligomers with new and promising properties and corroborated by the realization of prototype applicative examples. We will present in the order SAMs, brush-like assemblies, and ESA multilayers of CPs. In this context, we present also results on the conductive properties of the structures, with particular emphasis on the electronic responses of monolayers, and the conductive properties of well-defined oligomeric structures of interest in molecular electronics. Finally we will show results we obtained on combined metal (essentially gold) nanoparticles and CP structures.

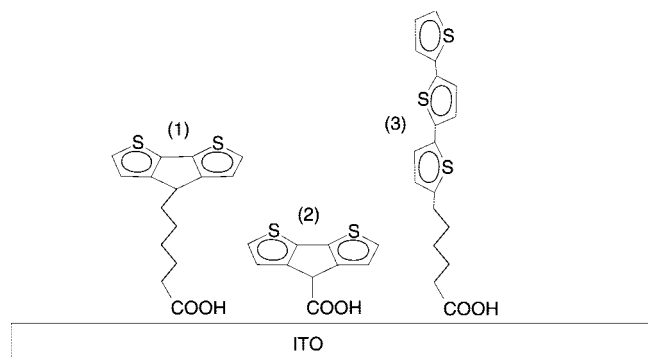
## CP Self-Assembled Monolayers

Organized layers of conjugated polymers or oligomers have attracted much attention for their possible use in many different fields. The conjugated  $\pi$ -electrons form a one-dimensional electron system with electrical and optical properties that may be strongly influenced by interchain interactions.

Self-assembly (SA), a most widely used method for the construction of organized supramolecular structures, has grown to an impressive level. In particular self-assembled monolayers (SAMs) are well documented.<sup>8</sup>

The use of conjugated oligomers or polymers in SAMs is at present valid for optoelectronic applications and for molecular electronics.<sup>9</sup> In particular oligothiophenes, and specifically sexithiophene,<sup>10</sup> have shown in this respect high utility as thin films.

We have produced stable monolayers on transparent indium tin oxide (ITO) electrodes from carboxyalkyl-functionalized bithiophenes and terthiophenes bearing the oligothiophene tail either perpendicularly or linearly linked to the surface-bound carboxyl-terminated alkyl chain (Scheme 1).<sup>11</sup> Electrochemical oxidation of the layer of perpendicular adsorbate **1** produced coupling to a polymer monolayer essentially constituted by thiophene hexamers (Figure 1). In contrast, oxidation of a monolayer of **2** did not produce the polymer. Since the monomeric units in polythiophenes are as a rule *anti*-coupled, it is required that the bithiophenes bend around flexible alkyl chains to allow this conformation. The absence of polymerization from adsorbed **2** may be attributed to the rigid connection to the surface (the long and flexible alkyl

**SCHEME 1.** Oligothiophene Carboxylates on ITO

chain of **1** is absent), which prevents correct alignment of the bithiophene moieties.

With yet another behavior, the linear terthiophene **3** may be oxidatively coupled with 2,2'-bithiophene in solution to polythiophene chains. The SA linear terthiophene **3** may be coupled with itself in solution to produce a one-end surface-grafted monolayer of sexithiophene (**6**) (formula in Scheme 3).

## CP Brush Layers

SAMs may be initiator systems for the preparation of uniform and densely grafted polymer brushes. Controlling the grafting density of the resulting polymer brush by, for example, mixing SAMs allows the preparation of two-component gradients or the construction of complex spatial structures. The latter can be formed by, for example, microcontact printing for structures ranging from 100 nm to several hundred micrometers.

We have used a combination of directed deposition of functionalized areas of SAMs and consecutive surface-initiated polymerization (Figure 2), which allows a superior control of pattern formation and amplification of the patterns by creating polymer-brush layers at predefined sites. Surface defects and topological features of the substrate are covered by the polymer brush producing a higher contrast between chemical and physical properties of functionalized and unfunctionalized areas.

To this end, we have performed the anodic coupling of different pyrrole- and thiophene-based monomers with oligothiophene-based self-assembled monolayers on ITO and gold electrodes.<sup>12</sup> Both monomeric and dimeric molecules have been tested as monomers for coupling with bithiophene-, terthiophene-, 3,4-ethylenedioxythiophene-, and bi-3,4-ethylenedioxythiophene-tailed monolayers. Carboxylate and phosphonate heads were used as hooks to form monolayers on the ITO surface, whereas thiol heads were used for gold. Scheme 2 shows the formulas of the compounds used, surface linkers at the top and monomers at the bottom.

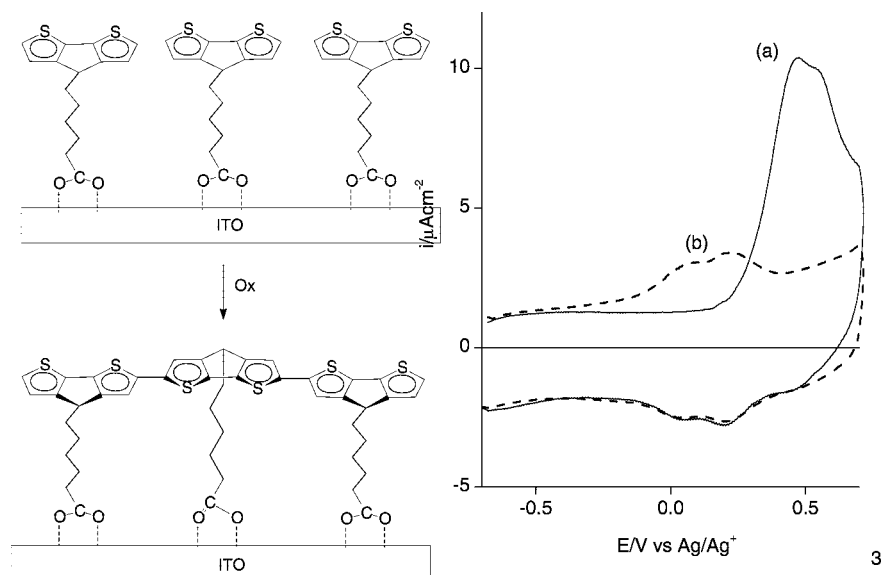
The reactivity to couple, higher for the monomeric than for the dimeric monomers,<sup>7</sup> allows extensive coupling only to the former, in fact to capped pyrrole and 3,4-ethylenedioxythiophene. Considering the coupling site on the surface, terthiophene and bi-3,4-ethylenedioxythiophene couple efficiently with monomers in solution. The practical result is that the best combination for such heterocoupling is terthiophene-headed monolayers and pyrrole- or 3,4-ethylenedioxythiophene-based monomers, as illustrated in Figure 2. In this way, nanometer-size layers of conjugated polymers with nominally normal orientation of the chain to the surface (polymer brush electrodes) have been successfully produced.

The first immediate result of this investigation is that microcontact printing on gold and ITO surfaces produces patterns for which heterocoupling yields strong AFM-measured height enhancements, from nonobserved to clearly evident nanometer-size structures (Figure 3). A second long-term result is the possible use of this heterocoupling approach for the realization of organized structures on electrically addressed surfaces, of particular interest in molecular electronics.

## CP Multilayers by Electrostatic Self-Assembly

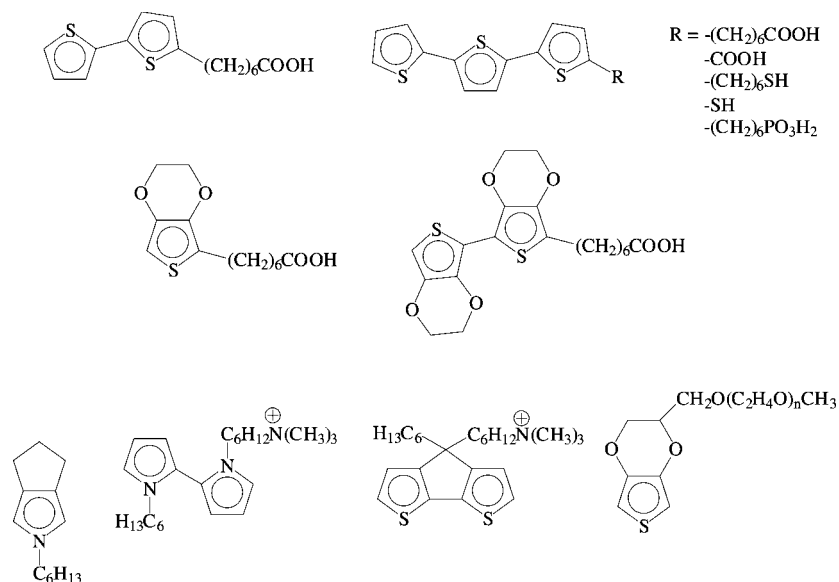
In the course of the last years, the layer-by-layer electrostatic adsorption technique introduced by Decher<sup>13</sup> has been particularly considered as a way to prepare thin, mechanically robust polymer films. This self-assembly method involves the sequential adsorption of polyelectrolytes from dilute solution onto an oppositely charged substrate leading to charge reversal on the surface. The simplicity of the method makes layer-by-layer self-assembly applicable to a wide variety of polyelectrolytes and attractive for a number of potential applications. The formation of multilayer films by this electrostatic self-assembly (ESA) has been extensively reviewed.<sup>14</sup>

**Polythiophene-Based Multilayers.** Polythiophene-based polyelectrolyte multilayers have been layer-by-layer deposited from polymer solution on ITO/glass and gold substrates and characterized by UV-vis spectroscopy, AFM, and cyclic voltammetry.<sup>15</sup> For the first time, isostructural thiophene-based polycations and polyanions **4** and **5** (Scheme 3), alternated reciprocally or with nonelectroactive polyions such as polyallylammonium or polystyrenesulfonate, have been used to produce layers with the polyconjugated chain parallel to the substrate plane. The bolaform amphiphile molecule  $\alpha,\omega$ -bis(carboxyhexyl)sexithiophene (**6**) 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 pro-



**FIGURE 1.** Reaction scheme (left) and cyclic voltammetry (CV, right) of a monolayer of **1** on ITO in acetonitrile + 0.1 M Bu<sub>4</sub>NClO<sub>4</sub> at 0.1 V s<sup>-1</sup>: (a) first scan; (b) last scan.

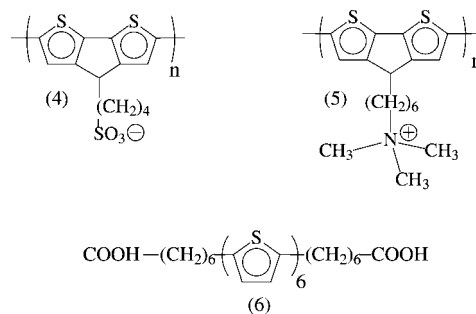
**SCHEME 2.** Pyrrole- and Thiophene-Based Monomers for Brush Layers



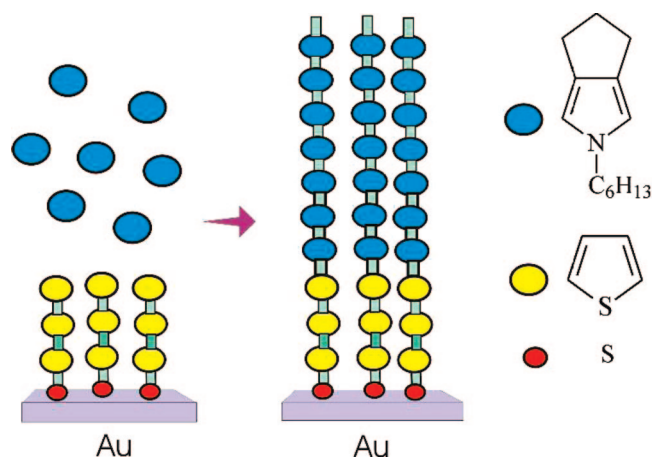
duced up to 20–30 bilayers. The multilayers have been shown to be electroactive, with CV current and optical responses proportional to the number of layers (Figure 4).

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 perpendicular 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.

**SCHEME 3.** Anionic (Sulfonate) and Cationic (Trimethylammonium) Poly(cyclopentadiene)s and  $\alpha,\omega$ -Dicarboxyhexyl-sexithiophene



Subsequently,<sup>16</sup> we have considered the analogous polymers with symmetrical alkylsulfonate (**4b**) and alkylammo-



**FIGURE 2.** Polypyrrole brush formation from terthiophene thiolate on gold.

nium (**5b**) disubstitution (Scheme 4) and the electrostatic self-assembly between them and with other conventional polyions. It was expected that these rigid-rod symmetrical molecules would arrange in layers with superior regularity.

These new water-soluble highly symmetric polycationic and polyanionic polythiophenes, produced by anodic coupling, form stable and dense monolayers on bare ITO and primed-gold surfaces. Electrostatic self-assembly of multilayers occurs with regularity on the preformed monolayers. Films with a minimal interchain penetration are obtained from the polythiophenes due to their chain stiffness. Infrared reflection-adsorption spectroscopy (IRRAS) and X-ray diffraction (XRD) analysis have evidenced in these ESA layers a degree of order not observed in previous polyconjugated multilayers and likely due to a good geometrical matching between anionic and cationic polymers via proper charge density values.

Finally,<sup>17</sup> taking into account the exceptionally high stability and conductivity of poly(3,4-ethylenedioxythiophene) (PEDT),<sup>18</sup> we have produced organosoluble conducting PEDTs bearing short or long oligoethyleneoxide chains (**6b** in Scheme 4). Soluble conducting polymers were produced by anodic coupling. A PEDT bearing a short oligoethyleneoxide chain adsorbs as a stable, conducting, and electroactive monolayer on ITO and glass surfaces. Layer-by-layer alternation of doped PEDTs with poly(sodium-*p*-styrenesulfonate) has given electroactive and robust multilayers with low surface resistivity and fast switchability between the doped and the undoped forms. The first property may be useful for the production of high-quality antistatic layers on insulating surfaces such as glass or quartz. The second may be of interest for the production of efficient electrochromic devices and for contacting efficiently the ITO surface of organic LEDs and photodiodes.

**Polypyrrole-Based Multilayers.** Since for fabrication of micro- and nanoscale structures the production on electrodes of well-defined mono- and multilayers of CPs is of high importance, given their nanometer-size one-dimensional resolution, we have produced SAMs and subsequently ESA multilayers of soluble polypyrroles (Scheme 5) on gold and platinum surfaces.<sup>19</sup> Monolayers are intended not as layers of controlled thickness of bulk material but as molecularly sized regular dispositions of polymer chains on conducting surfaces.

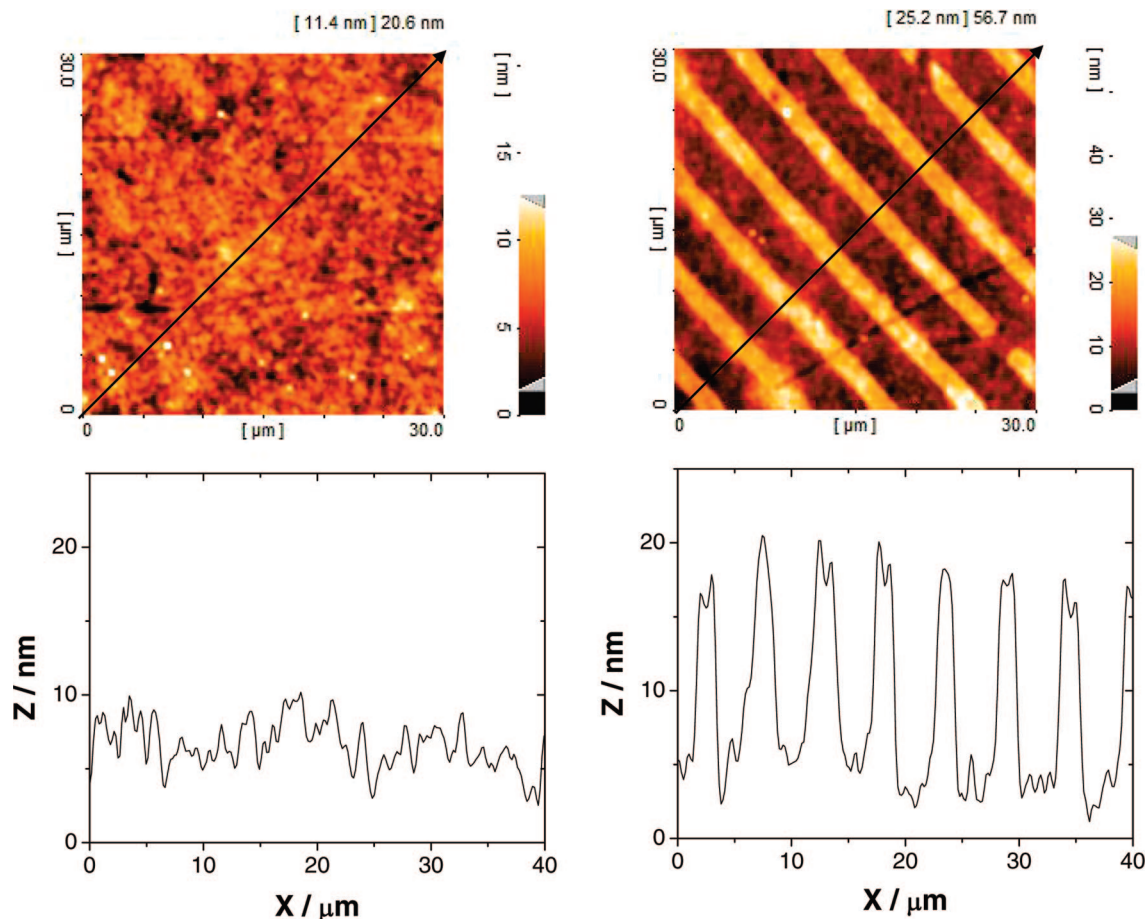
Gold and platinum surfaces were used bare or primed with an anionic 3-mercaptopropylsulfonate or a Nafion layer. Nafion solutions were for the first time reported to form stable, reproducible, and well-characterized monolayers on noble metal surfaces. Polystyrenesulfonate and Nafion were used as polyanions for ESA. ESA proceeds with a growth rate linear with number of bilayers and particularly high with Nafion, which appears to be an efficient primer for all the investigated polypyrroles.

Gold-polymer-gold junctions, obtained 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*-hexyl-cyclopenta[*c*]pyrrole) (**10**). In contrast, gold-polymer-gold junctions rectify current in polypyrrole sulfosuccinate (**7**) (Figure 5a), and alternation of rectifying and ohmic (Simmons) characteristics is observed with progressive ESA (Figure 5b,c).

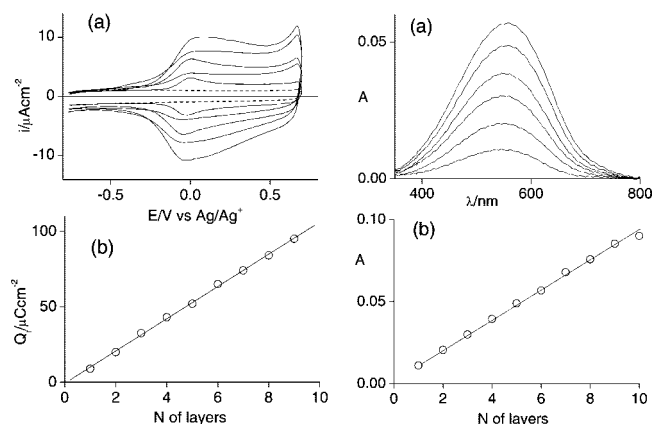
Molecular rectifiers, that is, devices in which molecules allow the passage of a larger current in one bias than in the other, are potential components for memory and logic elements in molecular electronics. We have produced for the first time molecular rectifiers from polypyrrole monolayers.

## Conduction in Thiophene-Based Oligomers

CP mono- and multilayers are quite often based on thiophene oligomers. Oligothiophenes and polythiophenes are in fact used in plastic electronic devices such as organic thin-film metal-insulator-semiconductor field-effect transistors (OFETs)<sup>20</sup> because of their excellent electronic properties, stability under ambient conditions, and ease of chemical modification. In oligothiophenes, the field-effect mobility of carriers is mainly controlled by structural organization of oligomer molecules in the film.<sup>21</sup> Unsubstituted  $\alpha$ -oligothiophenes, the simplest compounds in the family, have been intensively studied since Horowitz et al. demonstrated the high hole mobility of  $\alpha$ -sexithiophene ( $\alpha$ -6T) films.<sup>22</sup> Mobilities as high as  $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  are obtainable from dihexyl-terminated sexithiophene in thin film transistors.<sup>23</sup>



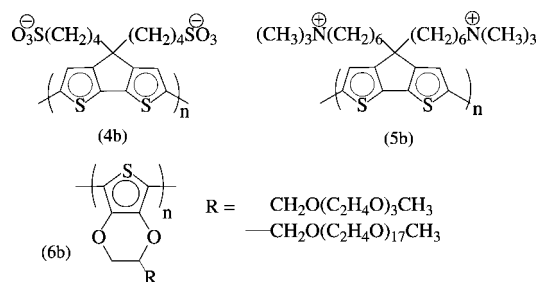
**FIGURE 3.** AFM topography images (top) and section profiles (bottom) of patterns obtained by microcontact printing of terthiophene hexylphosphonate (brighter areas) on ITO (left) before and (right) after coupling with oligoethylenoxy-substituted 3,4-ethylenedioxythiophene.



**FIGURE 4.**  $[4/5]_n$  multilayers on ITO. Left, CV in acetonitrile + 0.1 M  $\text{Bu}_4\text{NClO}_4$ : (a) voltammetric responses and (b) reversible charge vs number of layers. Right, UV-vis spectroscopy (after hydrazine reduction): (a) spectral profiles and (b) absorbance vs number of layers.

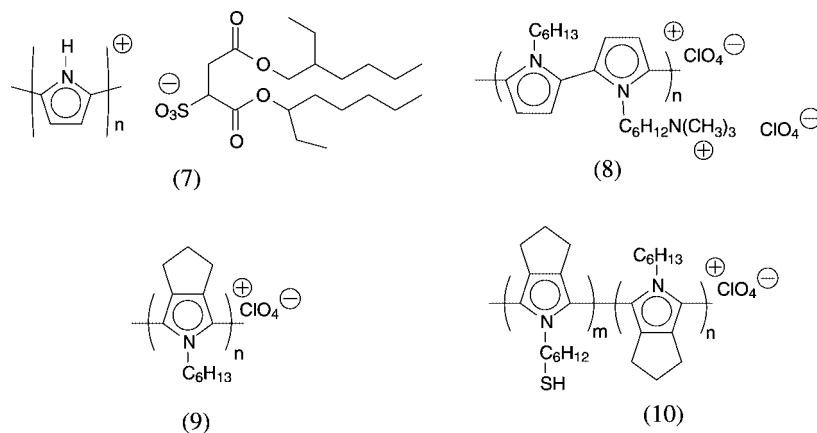
Despite the wide investigation on the conductivity of CPs performed in the past, the conduction in oligothiophenes is still largely unknown. We have therefore dedicated much attention to the conduction in  $\alpha,\omega$ -capped sexithiophenes

#### SCHEME 4. Soluble Polythiophenes



deposited as thin solid films by  $\alpha$ -coupling of the corresponding terthiophenes. This deposition method generally provides the sexithiophene film as a crystalline sample also in the case of insoluble products, and it does this directly on the electrode in a form suitable for magnetic and conductivity investigations. The purpose of our studies was to provide the electronic (electrochemical, magnetic, and conductive) properties of these compounds as thin films. The results are of fundamental importance in the understanding of the basic conductivity of these materials and are particularly useful for the analysis of the conductive properties of conjugated molec-

SCHEME 5. Soluble Polypyrroles



ular wires. It is clear that whereas conduction operating in OFETs is that of the low doping levels, the characteristics of molecular wires may be extended to include the whole available range of doping.

**$\alpha,\omega$ -Capped Sexithiophenes.** The investigations, applied in the past to  $\alpha,\omega$ -methyl-capped sexithiophene,<sup>24,25</sup> have been recently extended in our laboratories to a series of  $\alpha,\omega$ -capped sexithiophenes with different (methyl-, thiol-, cyano-, carboxy-, formyl-, dibromovinyl-, dicyanovinyl-) caps.<sup>26</sup> Substituents with different electron donor–acceptor properties have been used since their presence may give enhanced stability compared with doping. Vinyl substituents like dibromovinyl and dicyanovinyl have been also investigated to check the effect of a conjugation extended beyond the sexithiophene frame.

Among the investigated compounds, there were also carboxy-terminated compounds for grafting to oxide surfaces<sup>27</sup> and thiol-terminated forms for gold grafting.<sup>28</sup> The surface-grafting carboxy- and thiol-terminated forms are particularly interesting in the light of recent molecular electronics.<sup>3</sup> In fact, symmetrical molecular wires with two identical handles are actually investigated as model systems for molecular conduction.<sup>29–31</sup> The insertion of a long conjugated moiety such as the sexithiophene frame is an added value for such studies.

The electrochemically modulated conductivity of electrodeposited thin solid films of the sexithiophenes was investigated by in situ conductivity measurements. The reversible oxidation of sexithiophenes is composed by two separate one-electron steps. Conductivity is redox type and develops at the neutral–cation (neutral–polaron, a) and cation–dication (polaron–bipolaron, b) levels (Figure 6) with values in the range  $10^{-4}$ – $10^{-1}$  S  $\text{cm}^{-1}$  depending on the substitution type.

Whereas differences in electron donor–acceptor properties appear not to be particularly influential, steric and conjugative effects affect conductivity strongly. As a consequence, the cyano moiety, with its effective conjugation and small size, gives the sexithiophene with the best performance in the series.

Conductivity is also much different for the two oxidation states of the sexithiophenes. Thus the conductivity of the second redox couple (b) is roughly 10 times higher than that of the first one (a) so that a sort of empirical “10-fold rule” may be enunciated for these redox neutral–polaron and polaron–bipolaron conductivities.

**Fluorenyl- and Fluorenonyl-Capped Sexithiophenes and Higher Oligothiophenes.** Extending the conjugation beyond the sexithiophene frame with molecular fragments longer than a simple double bond would give novel electronic

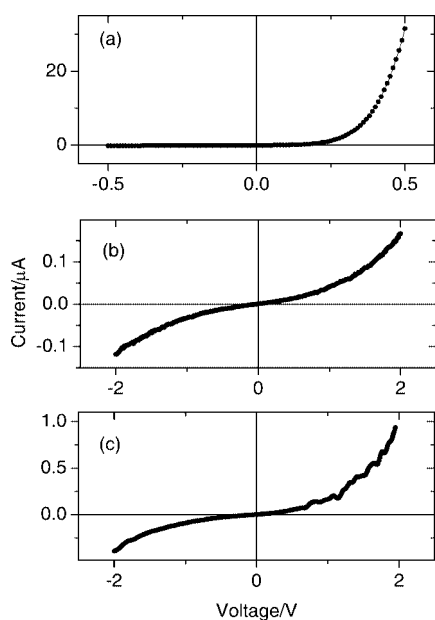
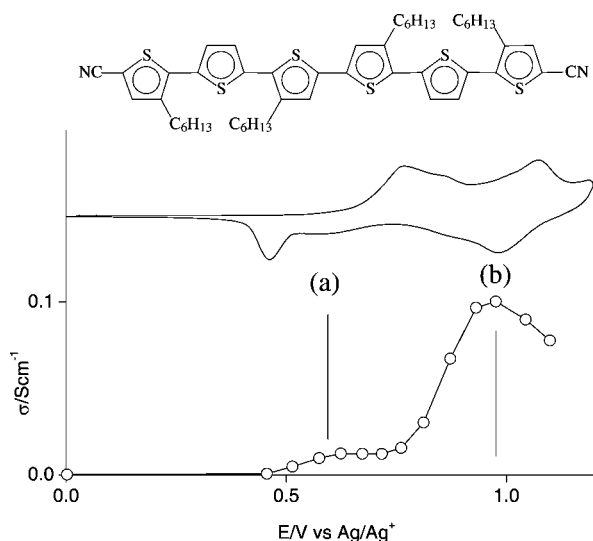


FIGURE 5.  $I$ – $V$  plots for junctions (a) Au/7/Au, (b) Au/7/Nafion/Au, and (c) Au/7/Nafion/7/Au.

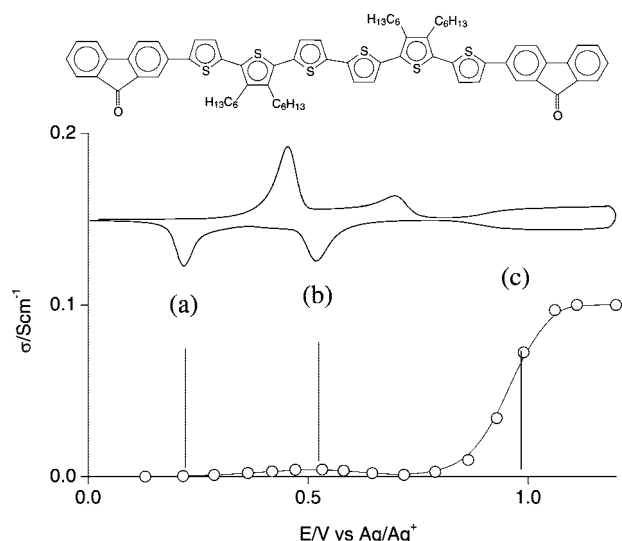


**FIGURE 6.** In situ conductivity vs potential of a tetrahexyl-substituted  $\alpha,\omega$ -dicyano-sexithiophene film in acetonitrile + 0.1 M  $\text{Bu}_4\text{NClO}_4$ . The upper curve is the CV for comparison.

and conductive properties to the molecular wire. The conjugation of  $\alpha,\omega$ -capped sexithiophenes has been significantly extended using fluorene and fluorenone caps.<sup>32</sup> We must recall that a very large amount of research has been devoted to co-oligomers of thiophene and fluorene for OLED applications.<sup>33</sup> Extension of the conjugation of the sexithiophene chain with additional thiophene rings has also been investigated<sup>32</sup> using hexyl-substituted  $\alpha,\omega$ -capped octathiophene, decathiophene, and dodecathiophene. The dodecathiophene is remarkable since it represents the longest regular oligothiophene ever investigated electrochemically in the solid state.

In the fluorenyl- and fluorenonyl-sexithiophenes the reversible oxidation is composed of three separate steps, namely, the two one-electron processes of sexithiophene and a further multielectron process (Figure 7). Conductivity is redox type at the cation–dication (polaron–bipolaron, b) state and metal-like at the subsequent oxidation state (c) with a 20-fold increase at full oxidation. At this stage, capacitive properties are displayed at early doping levels, lower than the one-electron oxidation state.

In the  $\alpha,\omega$ -capped octathiophene, decathiophene, and dodecathiophene, oxidation occurs in a single process with extended capacitive properties absent in the sexithiophene. Conductivity, which increases progressively (by 3 orders of magnitude) with the oligothiophene chain length, is metal-like in all cases. It is noteworthy that in dodecathiophene (with a chain twice as long as that of sexithiophene) the maximum allowed doping charge approaches four electrons per molecule and conductivity, maximized at the two-electron level, decreases linearly from there with charge approaching zero at



**FIGURE 7.** In situ conductivity vs potential of tetrahexyl-substituted  $\alpha,\omega$ -difluorenonyl-sexithiophene films in acetonitrile + 0.1 M  $\text{Bu}_4\text{NClO}_4$ . The upper is the CV for comparison.

the four-electron level. A bipolaron model has been used to account for the observed conductivity in such oligothiophenes.

Comparing the results for the fluorenonyl- and fluorenyl-substituted sexithiophenes with those on the generality of sexithiophenes, we can observe that sexithiophene is in all cases the location of the first two-electron oxidation, further oxidation and related conduction being allowed by the presence of extensively conjugated end moieties.

## Gold–CP Structures

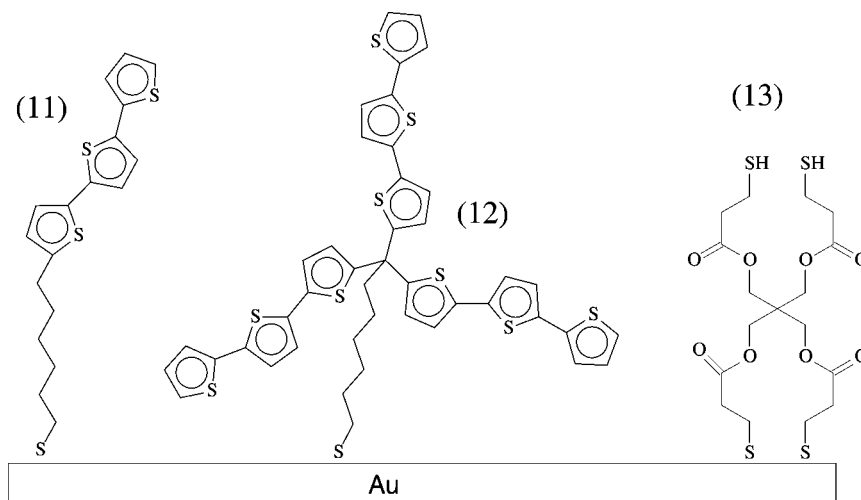
**Star-Shaped Oligothiophenes.** We have recently investigated<sup>34</sup> the ability of CP-based monolayers to coordinate gold nanoparticles (AuNPs) in order to produce novel materials containing this technologically new and attractive form of gold.<sup>35</sup> The use of conjugated chains to link AuNPs is of particular interest for the modulation of conduction, charge transfer, and optical properties of AuNP-based materials.

After it had been reported that terthiophene may be adsorbed on gold surfaces,<sup>36</sup> we investigated the ability of terthiophene-based monolayers for such coordination. Advincula et al. recently reported, but did not characterize, dendrimers functionalized with terthiophene dendrons on their periphery and dendrimer-encapsulated gold nanoparticles.<sup>37</sup> We have therefore considered both a molecule with a single terthiophene end as the gold-interactive moiety and a molecule in which the activity of the moiety is enhanced via the presence in multiple arms, which may be performed with dendrimers.

Whereas the benzene ring, generally used as the core of star molecules, does not allow surface linking with the star ends disposed in a plane parallel to the surface, a four-arm



SCHEME 6. Terthiophenyl-hexanethiol, a Star Tris-terthiophenyl-hexanethiol, and a Tetrathiol on Gold



carbon atom would allow three arms to extend over such a plane and thereby interact mutually. For this reason, we have synthesized the star molecule **12** (Scheme 6) with three terthiophene arms and a hexylthiol linker stemming from the same carbon atom. In this structure, the distance between the end points of the terthiophene arms is ca. 2 nm.

We then investigated the formation of SAMs on gold electrodes of such oligothiophene-armed star-shaped molecules, the surface coupling processes of the monolayers to sexithiophene surface bridges, and the ability of the monolayers to coordinate 5-nm wide gold nanoparticles. Multilayers of this oligothiophene-thiol and gold nanoparticles have also been produced and compared with the analogous structures obtained from the linear terthiophene-thiol (**11**) and a star-shaped nonconjugated tetrathiol (**13**).

Multilayering of oligothiophene-thiol and gold nanoparticles has produced structures that display mechanical strength and electrical conductivity comparable with those of analogous structures from generic polythiols. Moreover, when coupled to sexithiophene, the linkers display a much increased ability to coordinate gold nanoparticles.

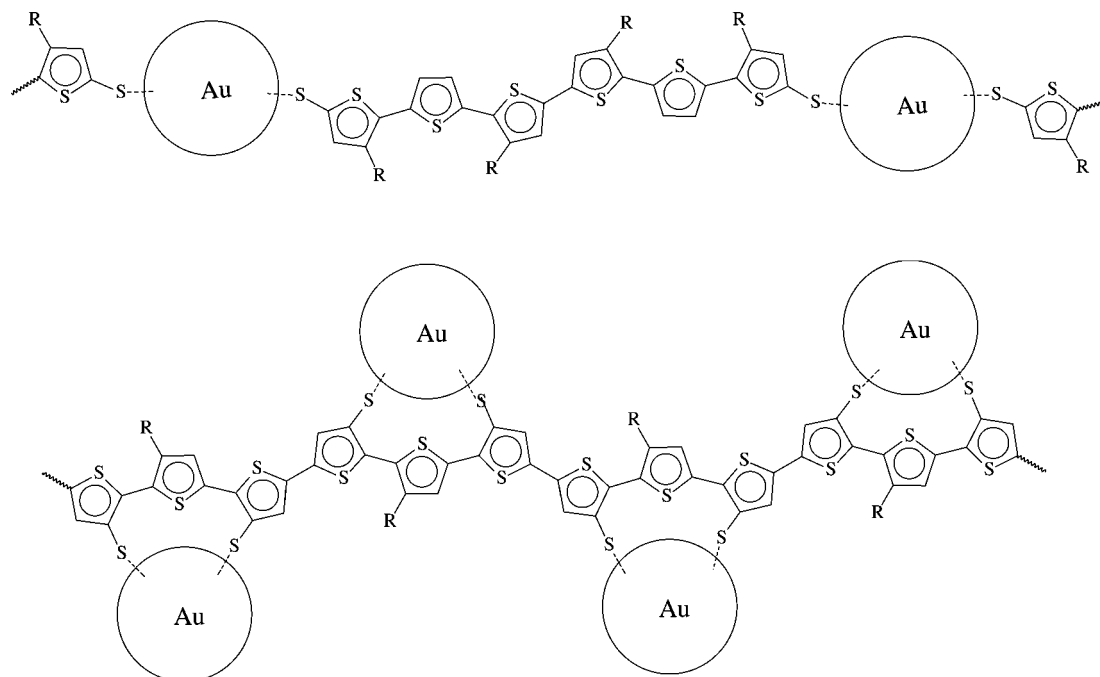
**Gold Nanoparticle Aggregation by Conjugated Heterocyclic Oligomers.** The above-mentioned first and clear evidence of gold nanoparticle coordination to oligothiophenes has opened the way to the direct functionalization of gold nanoparticles with conjugated oligomers in general. In fact, we found that conjugated heterocyclic (thiophene- and pyrrole-based) oligomers aggregate gold nanoparticles weakly capped with a tetraoctylammonium bromide monolayer and dissolved in toluene.<sup>38</sup> The interactions between gold nanoparticles and oligomers were investigated using surface plasmon absorption spectroscopy, FTIR, and TEM. From these studies, it was

concluded that the aggregate formation proceeds in two ways, characterized by a different spacing among the aggregated gold clusters, depending on the linker type and concentration. Terthiophene links to gold with the terthiophene plane parallel to the gold surface and the  $\pi$ -conjugated carbons in line. Such moieties may link two adjacent gold surfaces; that is, a single terthiophene may act as an adhesive sheet between them. For this reason, oligomers bearing bulky substituents do not aggregate gold particles.

Pyrroles too cause aggregation showing clearly that the sulfur atom is not specifically required for aggregation. As in the case of thiophene, also in pyrroles alkylsubstitution introduces steric restraints that may even inhibit the aggregation process completely.

The mechanism of aggregate formation involves in fact two steps, a slow step at low ligand concentrations and a fast step at higher concentrations. Below a critical ligand concentration, gold nanospheres possessing the anchoring adsorbate interlock slowly to yield the aggregates. The formation of a surface plasmon absorption band strongly red-shifted from 525 to ca. 700 nm is attributed to the selective coupling of the plasmon oscillations in tightly interlinked nanospheres. Above the critical concentration, the aggregation is very fast and leads to aggregates characterized by a lower red shift (the band is displayed at ca. 570 nm). From this result, it may be concluded that in the superstructures formed under these conditions AuNPs are less closely spaced. It is possible that at high oligomer concentrations, the linker molecules form more dense layers, possibly via perpendicular (rather than parallel) orientation toward the metal plane.

Two main general conclusions could be drawn. From the pyrrole, thiophene, and 3,4-ethylenedioxythiophene series, it

**SCHEME 7.** Gold Nanoparticles (Top) Bridged to and (Bottom) Pendant from Oligothiophene-thiols

results that the critical concentration decreases as the oligomer length is increased, which points to a higher adsorption constant for the longer oligomers (ca. 1000-fold increased from monomer to dimer). This result is in fact reasonable since longer oligomers provide multiple coordination sites. The second outcome is that the critical concentration increases in the series pyrrole < 3,4-ethylenedioxythiophene < thiophene, which suggests that a higher polarity of the heteroaromatic molecule favors adsorption to gold, as confirmed by the absence of adsorption by phenylenes. 3,4-Ethylenedioxythiophene presents oxygen atoms available for further coordination. It appears that coordination of the heteroatoms to gold is the key factor for adsorption. Considering that the sequence above follows also that of increasing aromaticity, the facile loss of aromaticity accompanying the heteroatom coordination to gold may favor pyrrole over, for example, thiophene.

After obtaining these general results, we undertook a study of the interactions between AuNPs and polypyrrole and polythiophene monolayers with the purpose of producing new and clearly defined structures.<sup>39</sup> The interaction between gold nanoparticles in toluene and polypyrrole or polythiophene monomolecular layers of various types has been investigated. In fact, stable monolayers and multilayers are produced from solution using polypyrrole and poly(3,4-ethylenedioxythiophene) soluble in organic solvents. The conductivities of such gold/polymer multilayers are  $(3-6) \times 10^{-2} \text{ S cm}^{-1}$ ; that is, the values are comparable with those measured for gold nanoparticles linked by short organic bridges.

**Gold Nanoparticles Linked by Pyrrole- And Thiophene-Based Thiols.** In an attempt to produce a stable capping of AuNPs with oligothiophene thiols via the place exchange route, we have added terthiophene-thiol to a toluene solution of AuNPs. The fact that the ruby red color turned immediately blue and the subsequent formation of a dark gold precipitate (much the same way as with terthiophene) indicated that gold clusters are aggregated (instead of being capped) by the thiol. A similar behavior has been shown by compound **11** (see Scheme 6), in which the thiol head and the terthiophene tail are spaced by a long alkyl chain. Yet the aforementioned discovery that hindrance to aggregation is provided by alkyl substitution has opened up the way to the direct adsorption of thiol-functionalized oligothiophenes and oligopyrroles on preformed gold nanoparticles of definite size, thus allowing the facile obtaining of new gold-polymer superstructures.

Novel pyrroliethiol- and thiophenethiol-capped gold nanoparticles have been produced and subsequently linked through electrochemical and chemical coupling.<sup>40</sup> The capping compounds, which form dense self-assembled monolayers on gold electrodes, react in solution with gold nanoparticles to form monodisperse, stable, and soluble thiol-capped gold clusters with the same gold core diameter. These are electrochemically or chemically coupled to polymeric gold clusters linked by conjugated bridges, as pictorially illustrated in Scheme 7. Analogous polymeric clusters have been prepared on gold-modified surfaces via alternation of gold nanoparticles and oligothiophene-based dithiols or

a polythiophene polythiol. The regular growth of the layers is illustrated in Figure 8.

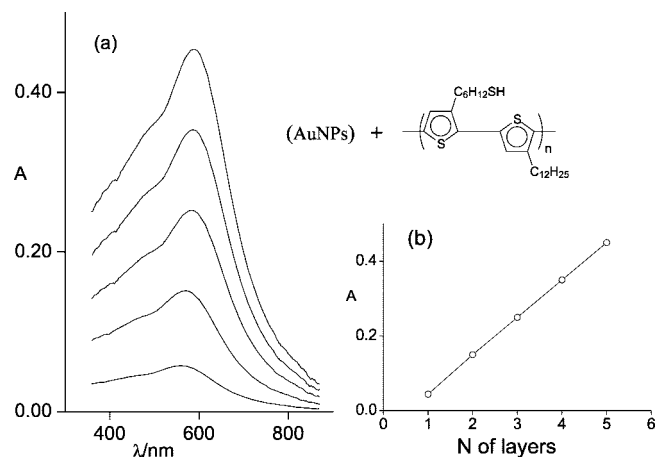
The thiol-capped gold clusters give fast and stable solvo-conductive responses, which parallel the degree of swelling by volatile organic solvents. Their conductivity, in the range  $10^{-7}$  to  $10^{-2}$  S  $\text{cm}^{-1}$ , increases in all cases up to a narrow range of  $2 \times 10^{-2}$  to  $10^{-1}$  S  $\text{cm}^{-1}$  when the polyconjugated ends of the gold clusters are connected to form polyconjugated bridges. Comparison with the literature data on a series of differently linked AuNPs appears to indicate  $10^{-1}$  S  $\text{cm}^{-1}$  as a practical limit to the conductivity in such systems, possibly controlled by the Au–S junctions.

The new materials, in which the gold particles are the same size and bear different conjugated ends or bridges, are expected to open interesting perspectives in the fields of modified electrodes for electrocatalysis and electroanalysis and in organic electronics.

## Conclusions and Outlook

Future developments in this area may be envisaged to occur in three directions. One is the possible use of CPs as catalyst supports because of their relative stability in both acidic and basic media, good electric conductivity, and high specific surface area, to be used, for example, as supports for anode catalysts in methanol fuel cells as in a recent report on polypyrrole with Pt-based nanoparticles.<sup>41</sup> Conductive polymers might be used to disperse and support platinum-based nanoparticles. Using regular platinum nanoparticles embedded in nanosized CPs may result in an efficient charge and fuel transport in methanol fuel cells.

A second development involves CPs and semiconductor nanoparticles, for example, in the rectifying junctions built from polypyrrole layers and CdS nanoparticles.<sup>42</sup> The integration of inorganic semiconductor nanoparticles and organic



**FIGURE 8.** UV–vis (a) spectra and (b) relevant maximum SP absorbance of  $(\text{Au}/\text{PAT})_n$  multilayer growth on gold-primed ITO.

conjugated polymers may lead to composite materials with interesting physical properties and important potential applications in light-emitting diodes, photovoltaics, photorefractions, lasers, and biosensors. Exploiting the cooperative electronic and optical properties of inorganic nanoparticles and conjugated polymers may develop via the construction of appropriate molecular assemblies with an accurate control of the spatial organization. A prime example of a composite material that benefits from morphological structuring is photovoltaic cells. Photovoltaic devices in which the active matrix consists of conjugated polymers may produce high efficiency of optical-to-electrical power conversion.

The last direction, which is the most exciting for its possible contributions to understanding the conductive properties of molecular assemblies, is the investigation of conduction in mono- and multilayers of conjugated oligomers and polymers, particularly at the different redox (doping) levels of the  $\pi$ -system. Such potential-controlled analysis is hopefully greatly rewarding for the development of molecular electronic components with controlled properties.

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## BIOGRAPHICAL INFORMATION

**Gianni Zotti** was born in Padova in 1947. He received his Ph.D. degree from the University of Padova in 1972. In 1973, he joined CNR doing research on the electrochemistry of coordination compounds; then in 1982, he applied his efforts to the photoelectrochemistry of organometallic compounds and to the electrochemical activation of carbon–halogen bonds. In 1984, he first produced conjugated polymer films by the cathodic route, which opened his way to the electrochemistry of conducting polymers. His current interests lie in the development of conjugated polymers and molecular materials with specific electronic properties for application in electronics, photonics, energy conversion, and sensors. He is the author of over 240 publications in international journals.

**Barbara Vercelli** was born in Novara in 1972. She obtained her degree in Chemistry in 1997 at the University of Milan where in 2000 she obtained her Ph.D. degree in Chemical Sciences. Since 2001, she has been doing research at the CNR Institute for Energetics and Interphases IENI-CNR of Padova. Actually she works on electrochemistry of polyconjugated systems and in particular on their use in composite materials with inorganic nanoparticles. Her goal is to realize new materials for organic electronics to be particularly employed in organic solar cells and direct methanol fuel cells. She is author of over 30 publications in international journals.

**Anna Berlin** was born in 1953. She received her Ph.D. degree in Chemistry at the University of Milan in 1977. After working first at Snia Viscosa and then at Dow Lepetit, in 1984 she joined CNR. She is currently interested in the synthesis of organic molecules

and materials with tailored properties for electrochemical, electronic, and photonic applications.

## FOOTNOTES

\*To whom correspondence should be addressed. E-mail: g.zotti@ieni.cnr.it. Tel: (39)049-829-5868. Fax: (39)049-829-5853.

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