New Insights on the Interaction between Thiophene Derivatives and Au Surfaces. The Case of 3,4-Ethylenedioxythiophene and the Relevant Polymer

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1. INTRODUCTION

It is well ascertained that the interface between metal and organic components plays a major role in determining the overall properties of these systems.1−10 In particular, the electrical conduction and the adhesion of the organic components are particularly affected by interfacial properties. As a consequence, investigations dealing with the interface are of the utmost importance for the development of many devices. In spite of this, relatively little attention has been paid to the investigation of the adsorption and possible reactivity of some of the most important aromatic molecules. In particular, the adsorption of derivatives which constitute the basis of conducting polymers is poorly investigated, so that the actual nature of the interface is basically unknown. In most studies the molecules at the buried interface are implicitly assumed to maintain the same structure and properties as those in the bulk of the organic film, although often without acquiring any experimental evidence.

In this respect, the noble metal Au constitutes the supposedly inert substrate of choice for many applications, for example, in electronic devices and in electrochemical sensors. However, the results reported in the literature, about the higher or lower stability of thiophene molecules, principally unsubstituted, on Au substrates are not always in agreement with one another, also due to the different experimental conditions adopted by the different authors.11−18 As an example, unsubstituted thiophene was adsorbed at low temperature on a Au(111) single crystal from the vapor phase in ultrahigh vacuum conditions:11 the authors observed the desorption of the molecules without any decomposition reactions at a temperature significantly lower than room temperature. On the other hand, STM showed different domains ascribed to thiophene molecules when the adsorption process was carried out from a dilute ethanolic solution on a Au polycrystalline surface at room temperature,12,13 and some authors reported that the adsorption of unsubstituted thiophene in similar conditions leads to the formation of ultrathin films of chemisorbed thiophene.16,17 Sako and co-workers,15 however, showed the decomposition of unsubstituted thiophene upon adsorption on polycrystalline Au.

ABSTRACT: The nature of the interface between electrogenerated poly(3,4-ethylenedioxythiophene) and the Au substrate is studied in detail. In particular, the adsorption of the relevant monomer, namely, 3,4-ethylenedioxythiophene, is investigated and compared with that of other thiophene derivatives. Different deposition procedures have been adopted: very thin films of the thiophene derivatives have been obtained through chemisorption processes from vapor and liquid phases, on Au polycrystalline substrates, Au nanoparticles possessing different size, and a Au(111) single crystal. Different techniques, operating both in situ and ex situ, have been employed for the characterization of these deposits, that is, X-ray photoemission and surface-enhanced Raman spectroscopy. The results show that the poly(3,4-ethylenedioxythiophene)/metal interface is far from being simply constituted by unreacted molecules in contact with the substrate; rather, the formation of oligothiophene species and sulfur atoms at the interface has been ascertained.
In many applications, thiophene derivatives and their oligomeric and/or polymeric species are used in the form of thin films on Au, with thicknesses ranging from that of a single monomolecular layer, as in the case of self-assembled monolayers, up to a few micrometers. Moreover, composites in which Au nanoparticles (NPs) are embedded inside polythiophenes have emerged as innovative materials for developing (electro)catalytic and sensor devices.25

In the present paper, we focus our attention on 3,4-ethylenedioxythiophene (EDOT, Chart 1) and some of its derivatives, namely, the dimer (bi-EDOT), 3,4-ethylenedioxy-2,2′:5′,2″-terthiophene (TET), 4-(2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl-methoxy)-1-butanesulfonic acid (SO3-EDOT), and the relevant polymer (PEDOT). Specific interest for PEDOT is due to its particularly interesting properties, such as high electric conductivity, low oxidation potential, and high stability in the oxidized form, low band gap, and even optical transparency in the visible region.19 As a consequence, PEDOT is widely employed in many applications, such as organic light emitting diodes, thin film transistors, antistatic coatings, electroluminescent and electrochromic devices, capacitors, photovoltaic cells, and even sensors; some devices are already on the commercial stage.19,20

Our approach to the study of the adsorption of EDOT and other thiophene derivatives (Chart 1) on Au is based on the use of high-resolution synchrotron X-ray Photoemission Spectroscopy (XPS), under various experimental conditions, that is, adsorption from aqueous solution and vapor phase on Au(111) single crystal substrates, on Au polycrystalline substrates, and on the surface of Au NPs possessing different sizes. In addition, PEDOT has been electrogenerated on Au polycrystalline surfaces. XPS has been selected as the principal investigation technique thanks to the possibility to gain information on the structure and bonding of molecular species at surfaces through the core level binding energies. The conclusions drawn from these investigations have been confirmed and complemented by Surface-Enhanced Raman Spectroscopy (SERS). When the adsorption process was carried out from solution, water was preferred as the solvent medium since it is most widely used as an environmental-friendly solvent in many organic electronics applications [see, for example, ref 19].

The results evidence that Au is actually far from being inert with respect to thiophene derivatives. In particular, 3,4-ethylenedioxythiophene and its derivatives undergo unexpected reactions on Au, leading to molecular dissociation. The results gained on simple thiophene derivatives, namely, thiophene and 3-methylthiophene, and on sodium 2-mercaptoethanesulfonate (MESNa) have been employed to give a rationale to the spectroscopic features of PEDOT and to understand the nature of the PEDOT/Au interface. It is found that a thin buffer layer of reacted EDOT molecules is formed between PEDOT and the underlying Au substrate.

2. EXPERIMENTAL METHODS

2.1. Au Polycrystalline Substrate. Au polycrystalline films (200 nm thick), grown on a flat glass support coated by a 2 nm thick Cr buffer layer (Universal Sensors), were cleaned with piranha solution (96% H2SO4/30% H2O2 3:1 mixture). Then the substrates were immersed in a 10 mM EDOT (Aldrich) aqueous solution. The vessels used for the film preparation were protected from exposure to light and stored at room temperature. The resulting EDOT films were rinsed in ultrapure water immediately after removal from the solution and quickly inserted into the UHV chamber for analysis. The Au polycrystalline substrates were not thermally treated, for example, by flame annealing, to be as close as possible to the actual preparation conditions of the substrates in many applications. Hence, in our cases, not surprisingly, Atomic Force Microscopy (AFM) images (Figure S-1, Supporting Information) did not exhibit large Au(111) terraces, at variance with what happens for thermally treated Au substrates.

2.2. Au(111) Single-Crystal Substrate. The Au(111) single-crystal surface (Matek) was cleaned by subsequent cycles of sputtering (Ar+ ions at 500 eV) and annealing (at 400 °C), resulting in the absence of contaminants, as evidenced by photoemission: in particular, the C 1s core level peak was absent after the cleaning procedure. A few milliliters of EDOT were inserted into a vacuum-sealed glass tube connected to the UHV chamber through a leak valve. Several pumping cycles were applied before exposure of the clean Au surface to EDOT, bi-EDOT, and TET vapors. In addition, the walls of the small vacuum chamber used for exposure were preliminarily saturated with each thiophene derivative. The glass tube containing the EDOT vapors was kept at room temperature during exposure, while in the case of bi-EDOT and TET the tube was heated at 115 °C. The substrate was kept at room temperature during all exposures. The vacuum chamber was baked-out at the end of each exposure, to minimize cross-contamination phenomena.

2.3. Au NPs. Au NPs (14 and 3.5 nm) have been chemically synthesized according to two different procedures based on the use of citrate− and chloride ions− as the encapsulating agents, respectively. In both cases, the Au NPs were precipitated adding 5 mL of a 1 M NaCl solution to 500 mL of the Au NP solution. The resulting precipitate was centrifuged and washed five times with ultrapure water to eliminate the excess encapsulating agent and NaCl. The precipitate was then treated with piranha solution (H2SO4 96% w/w + H2O2 30% w/w 3:1; note that this mixture is dangerous as it violently reacts with organics; 20 mL per 50 mg of Au NPs) to eliminate the traces of the encapsulating agent adsorbed on the metal NPs, centrifuged, and washed five times with ultrapure water. A freshly prepared 1 M NaBH4 solution (20 mL per 50 mg of Au NPs) was used to reduce the Au NP
After the polymerization, the thin films were thoroughly rinsed by overlapped potential versus time polymerization curves. Supporting Information), leading to reproducible results as testified by overlapped potential versus time polymerization curves. The electrodes crystalline electrode has been dipped for 5 min in a 10 mM NaBF4 as supporting electrolyte. Au polycrystalline substrates current density) from a 10 mM EDOT solution containing 0.1 M NaBF4 at room temperature. No coalescence, that is, merging of individual NPs into bigger metal cores, was seen in Transmission Electron Microscopy (TEM) images (not shown). An aliquot of solid Au NPs (ca. 40 mg) was dispersed in 10 mL of a 10 mM EDOT solution. After 24 h dipping, the Au NPs were centrifuged and washed five times with ultrapure water and dried in air. The resulting powder was deposited on a carbon tab and characterized through XPS and Near Edge X-ray Absorption Fine Structure (NEXAFS).

2.4. Electrogenerated PEDOT Thin Films. PEDOT thin films were electrosynthesized under galvanostatic conditions (0.4 mA cm−2 current density) from a 10 mM EDOT solution containing 0.1 M NaBF4, as supporting electrolyte. Au polycrystalline substrates similar to those used for the deposition of EDOT from the aqueous phase were employed. Different deposition times were employed, namely, 0.03, 0.06, 0.25, 1, 3, 10, and 160 s (Figure S-2, Supporting Information), leading to reproducible results as testified by overlapped potential versus time polymerization curves. After the polymerization, the thin films were thoroughly rinsed with ultrapure water and dried in air.

To verify if the adsorbed layer is desorbed during the first instants of the PEDOT electrogeneration process, a Au polycrystalline electrode has been dipped for 5 min in a 10 mM EDOT aqueous solution containing 0.1 M NaBF4. The electrode was then removed from the EDOT solution, thoroughly rinsed with ultrapure water, and inserted in an electrochemical cell containing only the supporting electrolyte. A +1.0 V potential step was applied for 10 s. Finally, the electrode was thoroughly rinsed with ultrapure water and dried in air.

2.5. Characterization of the Au Surfaces. The thickness of the dried polymeric coating deposited for 160 s on a Au polycrystalline surface was investigated by means of AFM employing a CP Park Autoprobe instrument in tapping mode. A NSG-11 tip from NT-MDT with a 11.5 N/m typical force constant was used. These measurements were ascertained to be reliable since AFM images evidenced that the polymer film was quantitatively removed by carefully scratching the surface with a plastic tip. Photoemission and X-ray absorption experiments were performed in the ultra-high vacuum (UHV) end station of the BEAR beamline at the synchrotron radiation laboratory (Elettra) in Trieste, Italy. Photoemission measurements from the Au 4f, C 1s, and S 2p core levels were performed at normal emission with a hemispherical deflection analyzer (66 mm mean radius) driven at constant pass energy, with 500 eV energy resolution. The value of the photon energy (hν = 184 eV for Au 4f, hν = 385 eV for C 1s, hν = 260 eV for S 2p) was chosen to maximize the surface sensitivity and increase the photoabsorption cross section with respect to conventional Al and Mg Kα excitation sources. The emission lines from the Au 4f levels were acquired at each photon energy and were taken as an energy reference for the alignment of the spectra on the binding energy scale (Au 4f7/2 = 84.0 eV). Care was taken to minimize X-ray induced damage by applying a low intensity photon flux and by monitoring the time evolution of the spectra in subsequent scans. All measurements were performed at room temperature.

The SERS spectra were recorded on a Nicolet Nexus 870 FT-IR spectrometer equipped with a FT Raman module. A Nd:YAG near-infrared (NIR) laser (λ = 1064 nm) and a Ge detector operating at liquid-nitrogen temperature were used. The SERS measurements were carried out in a homemade cell with a glass window. All the measurements were made using a 180° back-scattering geometry and a spectral resolution of 4 cm−1. Before the adsorption of EDOT, SO3-EDOT, thiophene, and 3-methylthiophene molecules on the Au polycrystalline surfaces, these adsortates were polished using diamond paste (0.25 μm), cleaned by 50 repeated voltammetric cycles in 0.5 M H2SO4 (suprapure grade), at a 0.1 V/s potential scan rate, between 0.0 and +1.2 V, Hg/HgSO4, and Na2SO4(sat) reference electrode, and subsequently electrochemically roughened according to the procedure reported in ref 27. Finally, they were once more submitted to potential cycling in 0.5 M H2SO4 according to the procedure described above. Two different kinds of adsorption experiments were carried out. In the first, the process was followed by inserting the Au substrates into the cell containing ultrapure water; then, the substance under study was introduced into the cell by means of a microsyringe, and a series of spectra was acquired. Alternatively, the Au surface was dipped for 5 min in a dilute aqueous solution of the substance under study; then, the surface was thoroughly rinsed with ultrapure water and finally inserted into the cell. A short dipping time guarantees the adsorption of a tiny amount of species on the Au substrate; in our case, the Raman spectra exhibit significant peaks, leading to the conclusion that our experimental setup is sensitive enough to detect such a small amount of material. To achieve suitable signal-to-noise ratio and to reduce the time required for the measurement, allowing us to follow the adsorption process, 64 scans per spectrum were acquired, and the laser power was kept at 1 W.

2.6. Chemicals. All the chemicals were from Aldrich, except for SO3-EDOT and TET, which were synthesized according to refs 28 and 29, respectively. The EDOT was freshly vacuum distilled before use. All aqueous solutions were prepared with Millipore water, 18 MΩ cm resistivity.

3. RESULTS

EDOT Adsorbed from Solution on Au Polycrystalline Surfaces. When EDOT is adsorbed from aqueous solutions, the photoemission spectra of the S 2p core levels (Figure 1) show three different spin—orbit split doublets. The position of the S 2p3/2 peaks is reported in Table 1. These components can be ascribed to thiophene (at 163.6 eV), thiolate/poly-S species (at 162.1 eV), and S atoms adsorbed on Au substrate (at 161.4 eV), respectively. The peaks associated with the thiophene species show slightly larger broadening, which can be related to different bonding configurations at the surface. Additional features, located at higher binding energy (at 167.0 and 168.5 eV), are ascribed to the presence of oxidized sulfur species. The C 1s level spectra, recorded before and after EDOT adsorption from aqueous solution on polycrystalline Au, respectively, are shown in Figure 2. It should be noticed that the bare substrate exhibits traces of contamination, as expected for samples that were not prepared and handled in ultra-high vacuum. Furthermore, no flame annealing was applied to the substrate before deposition, to approach the real preparation conditions used in various applications as much as possible. After adsorption, the C 1s spectrum exhibits a relatively broad and asymmetric peak that is scarcely compatible with the expected line-shape for the EDOT molecule: in particular, three partially overlapped singlets of equal
respectively.

The 10 mM aqueous phase on polycrystalline Au (24 h dipping time), Au vap., and Au sol. refer to electrogenerated Sthioph to thiophene ring sulfur, and Sox to the formation of SOx

intensity ascribed to carbon atoms located in γ and β positions and in the ether moiety have been reported.34,35 Surprisingly, the amount of oxygen on the Au surface does not increase after EDOT adsorption, despite the presence of two oxygen atoms in the molecule (Figure 3). Finally, it is worth noticing that X-ray absorption spectra acquired in correspondence of the C1s carbon edge (not shown) suggest that no preferential orientation of the adsorbed molecules is present.

**EDOT Adsorbed from Solution on Au NP Surfaces.** A similar experiment employing Au NPs has been carried out to search for any different behavior. It is well-known that the bottom-up approach for the preparation of metal NPs requires the presence of a suitable encapsulating agent during the synthesis to control the growth of the NPs and to avoid the formation of a larger metal core during the purification procedures and subsequent storage. However, the encapsulating agent can severely hamper the interaction of the metal core with the external environment since it can form a surrounding layer around the core. As the present study is focused on the interaction of EDOT derivatives with Au, any presence of the encapsulating agent is particularly detrimental. For this reason, a synthetic procedure was employed to remove the encapsulating agent without affecting the metal core size (see Experimental Methods). As a consequence, aggregates have been deliberately formed. Since all the purification steps have been carried out close to room temperature, the enlargement of the metal cores does not take place. The final product consists of a finely divided powder; high solubility of the powder is not an essential requirement since Au NPs should be deposited in solid form on a substrate to carry out the characterization through photoemission. Two different sizes of 3.5 and 14 nm have been selected, taking into account that the NPs possess a polyhedral shape and that the surface-to-volume ratio increases when the size of the NPs decreases. As a consequence, the fraction of atoms in correspondence with vertexes and edges increases with the reduction of NP size. The 14 nm Au NPs possess a relatively low surface-to-volume ratio, while this value is particularly high in the case of 3.5 nm Au NPs. It is worth noticing that the concentration of vertexes and edges on the NP surfaces as well as the size of the terraces are supposed to strongly influence the reactivity of the NPs toward a number of different species.

When EDOT is adsorbed from aqueous solutions, the photoemission spectra of the S 2p core levels show three doublets, similarly to that observed in the case of Au polycrystalline surfaces (Figure 1 and Supporting Information Figure S-3). Spectra of 3.5 and 14 nm Au NP samples are rather similar, although the fraction of sulfur species ascribed to the thiol molecule or sulfur atoms is slightly more abundant in the case of 3.5 nm Au NPs. As for the C 1s core level, the peak is located at the same position observed in the case of the Au polycrystalline surface (Figure 2 and Supporting Information Figure S-3). The line shape of 14 nm Au NPs is similar to that previously reported, while the broad tail located at higher binding energy is absent in the case of 3.5 nm Au NPs. Similarly to the case of the polycrystalline Au substrate, bare Au NPs show some traces of contamination from adventitious carbon since the samples were not prepared in ultrahigh vacuum. However, the extent of this phenomenon does not prevent us from drawing meaningful considerations from the C1s spectra. It is worth noticing that oxidized Au species are absent both in the pristine 3.5 and 14 nm Au NP samples and after EDOT deposition. Hence, the reactions taking place during the adsorption step cannot be ascribed to the oxidized Au NP surface.

**Thiophene Derivatives Adsorbed from the Vapor Phase on Au(111) Substrates.** It is well-known that the solvent plays a key role in the adsorption process from solution. To study the system independently of the medium and, at the same time, to overcome the problems due to contamination during sample handling, which can induce spurious contributions to the measured spectra, similar photoemission experiments have been carried out under inert conditions by exposing a clean Au(111) single-crystal surface, in ultra high vacuum, to the molecular vapors of EDOT, bi-EDOT, and TET.

In the case of EDOT, at saturation exposure (ca. 105 L), the S 2p spectra still show three doublets (Figure 1c), a broad and asymmetric C 1s core level peak (Figure 2c), while oxygen is absent (Figure 3).33 Similar results have been observed also in the case of bi-EDOT at saturation exposure (Figure 1d). In the case of TET, the S 2p spectra show only two doublets (Figure 2d). The absence of the

![Figure 1. S 2p core levels of the different thiophene derivatives. Fitted voigt doublet components are shown: Sat is associated to atomic S, Sthiolate/Sn to the formation either of thiolate species or of poly-S units, Sthiolate/Sn to the formation of SOx groups. Au, Au vap., and Au sol. refer to electrogensed films on polycrystalline Au, films grown from the vapor phase on Au(111), and film grown from the 10 mM aqueous phase on polycrystalline Au (24 h dipping time), respectively.](image-url)
The doublet located at the lowest binding energy may be ascribed to the different molecular structure: in the case of TET, the positions of the EDOT ring are functionalized by thiophene rings, while in the case of EDOT and bi-EDOT the outermost R positions are occupied by hydrogen atoms. It is worth noticing that when the outermost R positions of an EDOT trimer are functionalized by phenyl rings the results do not evidence any peak ascribed to thiol molecules or sulfur atoms.35,36 Similarly to the previous cases, the C 1s core level spectra for EDOT, bi-EDOT, and TET exhibit a relatively broad and asymmetric peak (Figure 2c–e), and again oxygen is not detected on the surface.

Table 1. Binding Energy Values of the Fitted Components in Photoemission Spectra

<table>
<thead>
<tr>
<th>sample</th>
<th>S 2p_{3/2} components (±0.1 eV)</th>
<th>thiophene species</th>
<th>thiols/cluster of S atoms</th>
<th>S atoms</th>
<th>oxidized S species</th>
<th>C 1s components (eV)</th>
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<td></td>
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<td>EDOT — solution phase</td>
<td></td>
<td>163.6</td>
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<td>14 nm Au NPs</td>
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<td>161.2</td>
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<tr>
<td>3.5 nm Au NPs</td>
<td></td>
<td>163.6</td>
<td>162.1</td>
<td>161.1</td>
<td>-</td>
<td>284.8</td>
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<tr>
<td>EDOT — vapor phase</td>
<td></td>
<td>163.5</td>
<td>162.2</td>
<td>161.1</td>
<td>-</td>
<td>284.2</td>
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<td>BiEDOT — vapor phase</td>
<td></td>
<td>163.2</td>
<td>162.0</td>
<td>161.1</td>
<td>-</td>
<td>284.1</td>
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<tr>
<td>TET — vapor phase</td>
<td></td>
<td>163.8</td>
<td>162.1</td>
<td>-</td>
<td>-</td>
<td>284.1</td>
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<tr>
<td>PEDOT 160 s deposition  time</td>
<td></td>
<td>163.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>285.6</td>
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<td></td>
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<td></td>
<td>286.5</td>
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<td>PEDOT 0.03 s deposition  time</td>
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<td>162.0</td>
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aData taken from ref 18.
The adsorption of thiophenes proceeds much more slowly than previously reported for alkyl thiols, though under (Figure 4a). The adsorption of thiophenes, as briefly outlined in the Introduction, moreover, the formation of elemental sulfur has been reported for thiol molecules, but only in a few cases for thiophene derivatives. The presence of a small amount of oxygen well below the stoichiometric value that holds for EDOT derivatives, or even its total absence, suggests the cleavage of the C_{aromatic}—O bonds and the consequent release of the —O—CH_{2}—CH_{2}—O— moiety. The opening of the aromatic ring and the corresponding formation of thiol species, as well as the rupture of C_{aromatic}—O bonds, are further supported by the C 1s line-shape: the major component is located at the binding energy usually associated with films based on polythiophenes, although similar C 1s spectra have been observed in the case of alkyl chains, and shakeup effects are possible.

Previous reports show that monomeric thiophene derivatives are thermally desorbed significantly below room temperature, whereas in our case the thiophene-containing thin film, spontaneously adsorbed from aqueous solution onto polycrystalline Au substrates, survives thorough rinsing with ultrapure water at room temperature. This suggests the formation of oligomeric or polymeric species at the surface.

**SERS Experiments.** To support the observations in an independent way, SERS measurements have been performed with EDOT and other thiophene derivatives adsorbed on an electrochemically roughened polycrystalline Au surface from dilute aqueous solutions. The measurements have been performed both in situ, that is, during the adsorption in aqueous solution, and ex situ, that is, after withdrawing the substrate from the solution. The results obtained are shown in Figure 4.

The intensity of the Raman peaks increases with increasing dipping time, without reaching a steady state even after 24 h (Figure 4a). The adsorption of thiophenes proceeds much more slowly than previously reported for alkyl thiols, though under different experimental conditions. Although a complete and reliable assignment of the vibrational spectral features of thiophene derivatives in thin films has not been reported so far, on the basis of a large number of experimental infrared and Raman spectra and theoretical calculations, main assignments can be made. The major bands in the range 1350—1600 cm\(^{-1}\) can be attributed to the stretching vibrations of the thiophene ring. They are broad and not well-resolved, which is characteristic for polymeric films. The peaks ascribed to the C—H stretching vibrations of aromatic and methylene moieties, usually located between 2850 and 3100 cm\(^{-1}\), are absent in our spectra. We have also studied the spectra of thiophene, 3-methylthiophene, and EDOT after a short dipping time of 5 min (Figure 4b). Each of the investigated molecules exhibits a strong signal due to thiophene ring stretching vibrations in the range 1350—1600 cm\(^{-1}\) in their SERS spectra, reflecting the successfulness of the short adsorption process and sensitivity of the measurement setup. However, the surface spectra of thiophene and EDOT do not show any C—H stretching vibrations due to methylene units, and the spectrum of 3-methylthiophene does not show any aromatic C—H stretching vibrations. On the other hand, stretching vibrations ascribed to methyl C—H bonds in 3-methylthiophene are well evident around 2850 cm\(^{-1}\). The Raman spectra acquired employing liquid EDOT, thiophene, and 3-methylthiophene show well-evident peaks located between 2850 and 3100 cm\(^{-1}\) (see Supporting Information Figure S-4) ascribed to C—H stretching vibrations; in addition, the EDOT spectrum shows peaks located between 800 and 1100 cm\(^{-1}\) that can be ascribed to the presence of the ether moiety. However, a precise comparison between spectra acquired on Au surfaces and those acquired on pristine molecules is not at all straightforward since the positions and intensities of the different peaks could be significantly affected by
the adsorption on the Au surface, also taking into account that selection rules are operative.

The results suggest the release of the ether moiety from the EDOT molecule. To confirm this conclusion, experiments similar to those previously reported have been carried out using SO3-EDOT. This molecule possesses a relatively long alkyl chain bound to the ether moiety. If the ether moiety is preserved after the adsorption on the Au surface, strong bands ascribed to C–H stretching should be visible in the Raman spectra in the proximity of 3000 cm⁻¹. Actually, the spectrum of SO3-EDOT after 24 h adsorption is very similar to that of EDOT, with C–H stretching bands being absent (Figure 4c). In addition, the molecule possesses a SO₃ group at the end of the alkyl chain. This functional group exhibits a strong band associated to the C–SO₃⁻ stretching, normally located at ca. 800 cm⁻¹. In the case of SO3-EDOT, this band is absent, suggesting once more the release of the ether moiety. As a control experiment, a simple thiol molecule, namely, MESNa, has been adsorbed on the Au surface in the same experimental conditions; the molecule has been selected taking into account that it is well-known that the molecule is intact on the surface after the adsorption. In this case, the C–SO₃⁻ stretching band is well evident in the Raman spectra (inset in Figure 4c).

**Electrogenerated PEDOT.** In the case of the longest deposition time (that is, 160 s), the C 1s core level spectra (Figure 2g) show the presence of three singlets that can be ascribed to PEDOT. Additional components located at higher binding energy, fitted employing two broad singlets, can be ascribed to the doped form of PEDOT or to shakeup effects. As for the S 2p core level, the spectrum exhibits a doublet (Figure 1g) ascribed to PEDOT together with additional components located at higher binding energy similarly ascribed to the doped form of PEDOT or to shakeup effects. It is worth noticing that the doping process occurs concomitantly with the deposition step.

In the case of the shortest deposition time (that is, 0.03 s), the spectra are significantly different. In particular, the C 1s peaks show a main peak together with additional components located at higher binding energy (Figure 2f), fitted employing two broad singlets. The overall line shape of the spectra suggests the presence of an oligo- or polythiophene derivative whose structure lacks the oxygenated moiety. The additional components are once more ascribed to the doped form of an oligo- or polythiophene or to a shakeup effect. For the S 2p core level, the main S 2p₁/₂ peak at 163.5 eV is ascribed to thiophene species (Figure 1f). In addition, another two doublets at lower binding energy are well evident; as in the case of EDOT derivatives, these peaks can be ascribed to thiol molecules or a cluster of sulfur atoms and to atomic sulfur, respectively. Additional features, located at higher binding energy, are ascribed to the presence of oxidized sulfur species, similarly to those observed in the case of EDOT adsorbed on the Au polycrystalline surface from aqueous solution.

The intermediate deposition times, that is, 0.06, 0.25, 1, 3, and 10 s, exhibit C 1s and S 2p spectra whose features are in between the two extreme cases previously reported (data not shown). In particular, the longer the deposition time, the smaller the features ascribed to thiol molecules or sulfur atoms in the S 2p spectra. In addition, the C 1s spectra show a progressive transition from a line shape typical of an unsubstituted oligo- or polythiophene to that of PEDOT, whose maximum is located at higher binding energy.

The film effective thickness has been estimated on the basis of the attenuation of the Au 4f₇/₂ photoemission signal. In the range 0.03–10 s, the dependence of the thickness on the electrogeneration time is satisfactorily linear. This result is compatible with those previously reported for other polythiophenes in different experimental conditions. In the case of the longest deposition time, the underlying Au substrate is so deeply buried that the Au 4f₇/₂ signal cannot be detected. However, the linear relationship between deposition time and thickness is confirmed by AFM measurements (Figure 5).

An additional experiment has been carried out to verify if the adsorbed layer is desorbed during the first instants of the PEDOT electrogeneration process. A Au polycrystalline electrode has been dipped for five minutes in a 10 mM EDOT aqueous solution containing 0.1 M NaBF₄. SERS results previously reported evidence that a thin layer of thiophene-based material is deposited even for such a short dipping time. The electrode was then removed from the EDOT solution, thoroughly rinsed with ultrapure water, and inserted in an electrochemical cell containing only the supporting electrolyte. A +1.0 V potential step, close to that observed during the PEDOT electrodeposition, was applied for 10 s. Finally, the electrode was thoroughly rinsed with ultrapure water and dried in air.

The results show that the resulting S 2p and C 1s spectra are similar to those previously reported for the EDOT film deposited on polycrystalline Au from 10 mM aqueous solution. This demonstrates that the applied potential, close to that measured during the electropolymerization process, does not lead to the desorption of the thiophene-based layer deposited at open circuit potential and that the reaction/dissociation process of EDOT does not depend on the application of the potential.

4. CONCLUSIONS

The adsorption process of EDOT exhibits a peculiar behavior: a decomposition reaction coupled with oligomerization takes place instead of a simple self-assembly process. Differences in the spectral features for the different Au substrates, namely, Au(111) in ultrahigh vacuum conditions, Au polycrystalline surfaces, and Au NPs possessing different sizes, are well evident. However, the conclusions about the behavior of EDOT are quite similar. This also holds for different EDOT derivatives, namely, bi-EDOT, TET, and SO3-EDOT. Hence, the reactivity can be reasonably extended to many other EDOT derivatives and, most likely, to...
thiophene derivatives bearing ether moieties in the 3 and/or 4 positions.

These results have been fruitfully employed to better understand the nature of the interface between electrogenerated PEDOT and Au substrates. When a Au polycrystalline electrode is dipped in aqueous solution of EDOT derivatives, the adsorption of the molecules takes place together with rupture/oligomerization reactions. During the electropolymerization, the applied potential does not induce the desorption of the thin film. The result suggests that an interface layer between bulk PEDOT and the Au substrate is formed during the electropolymerization. The formation of this layer has not been reported so far; its presence must be considered to give a correct rationale for the properties of the PEDOT layer in different practical applications.

The mechanisms of the surface reactions cannot be understood in detail on the basis of the present work, but it should be noticed that, although traditionally Au has been considered an inert metal, its catalytic properties have recently aroused much interest. They are directly related to the coordination number of the Au atoms on the surface, that is, to the width of the terraces and to the consequent density of different kinds of surface defects. As an example, the Au surface can effectively catalyze the oxidation of alcohols and unsaturated hydrocarbons. As for thiophene derivatives, bond ruptures induced by metal surfaces (dehydrodissulfurization reactions) have been reported to occur on transition metals such as Pt. However, there are only very few reports in the case of Au, normally dealing with unsubstituted thiophene; the decomposition of the thiophene ring adsorbed on Au has been reported to lead to alkyl thiols and atomic sulfur. In addition, chemisorption of thiophene derivatives, especially at the defect sites on the metal surface, may lead to a strong perturbation of the electronic structure of the thiophene derivatives and induce spontaneous oligomerization, as has been previously observed in vacuum at low temperature on Fe and Ni. On the other hand, direct evidence of the scissoring of the C–O bonds, as found in this work with EDOT derivatives, constitutes a novelty.

## ASSOCIATED CONTENT

Supporting Information. Representative AFM image of Au polycrystalline surface, typical galvanostatic polymerization curve, 3.5 nm Au NP photoemission core level spectra, Raman spectra of liquid thiophene, 3-methylthiophene, and EDOT. This material is available free of charge via the Internet at http://pubs.acs.org.

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