

SPECTROSCOPIC STUDY OF THE CHEMISORPTION PROCESSES OF THIOPHENE DERIVATIVES ON NOBLE METAL SURFACES

Fabio Terzi,¹ Laura Pigani,¹ Chiara Zanardi,¹ Renato Seeber,¹ Luca Pasquali,² Stefano Nannarone^{2,3}

¹ *Dipartimento di Chimica, Università di Modena e Reggio Emilia, Via Campi 183, 41100 Modena, Italy, fabio.terzi@unimore.it*

² *Dipartimento di Ingegneria dei Materiali e dell'Ambiente, Università di Modena e Reggio Emilia and CNISM, Via Vignolese 905, 41100 Modena, Italy, luca.pasquali@unimore.it*

³ *Laboratorio Nazionale TASC, INFN-CNR, s.s.14, km 163.5 in Area Science Park, 34012 Trieste, Italy,*

Thiophene and derivatives – substituted thiophenes, oligomers and polymers – have been studied for many years due to their importance in practical applications, such as organic electronics, electrochemical sensors, catalysis, corrosion protection and antistatic coatings [1-4]. In most cases, thiophene and derivatives are under the form of thin films adhering to a substrate, with a thickness ranging from that of a single monomolecular layer, as in the case of Self Assembled Monolayers and Lagmuir-Blodgett films, to few microns. In most cases, the nature of the interface between the organic layer and the underlying substrate plays a major role in determining the final properties of the material. In this frame, the study of the adsorption of simple thiophene derivatives on planar surface constitutes a fundamental step.

Among the large number of possible thiophene-based molecules, 3,4-ethylenedioxythiophene (EDOT, Figure 1) has emerged as one of the most important monomer, since the relevant polymers possess particularly interesting properties, such as high conductivity, stability in the oxidised form, low oxidation potential, low band gap, high regioregularity, transparency when prepared under the form of thin films [1-4]. Surprisingly, relatively poor attention has been paid to a detailed investigation of the adsorption and reactivity of EDOT on metal surfaces.

Our group recently demonstrated the possibility to prepare composite materials with quite interesting peculiar properties, consisting of noble metal nanoparticles entrapped in a PEDOT polymeric matrix [5,6]. The interface between the metal surface of the NPs and the polymeric matrix also in this case plays a crucial role in determining the performance of the whole system [5,6].

In view of these considerations, in the present study the adsorption of EDOT on metal substrates has been investigated by a multitechnique approach. Au and Pt surfaces have been chosen since these metals constitute the substrates of choice in many applications, such as electrochemical sensors and devices for organic electronics. EDOT molecules have been adsorbed on these metals and the resulting modified substrates have been characterised using high resolution X-ray Photoemission Spectroscopy, Near Edge X-ray Adsorption Fine Structure and spectroscopic ellipsometry. In addition, the kinetics of the adsorption of EDOT has been followed *in situ* by means of Surface-Enhanced Raman Spectroscopy. Similar Raman experiments have been carried out also using other monomers, i.e. thiophene, 3-

methylthiophene, 2,5-dimethylthiophene, SO₃-EDOT and 2-mercapto-ethanesulfonic acid (see Figure 1), in order to support the interpretation of the spectra.

The results suggest that noble metal surfaces are not inert with respect to thiophene derivatives; in particular, thiophene derivatives possessing electron-donating groups, such as EDOT and SO₃-EDOT, seem to be particularly reactive. XPS and NEXAFS spectra suggest that EDOT forms ultrathin films on Au and Pt surface and a partial decomposition of EDOT molecules occurs, as shown by the presence of two and three S2p peaks on Pt and Au substrates, respectively. This conclusion is also supported by C1s spectra and by the absence of O1s peaks. Similar results are also obtained when the experiment is performed on an ultraflat surface, namely Au(111), in ultra high vacuum conditions. SERS spectra evidence the formation of an organic coating, most likely based on a polythiophene, which slowly grows on the Au surface. The vibrations ascribed to -O-CH₂-CHR-O- moieties seem to be absent in the case of EDOT and SO₃-EDOT molecules, suggesting the rupture of C-O bonds. On the other hand, other derivatives, such as simple thiophene and 3-methylthiophene, seem to be adsorbed without bond breaking, the molecules lying flat on the surface. Finally, ellipsometry has been employed to measure the thickness of the EDOT film and the relevant optical properties. The results, as drawn out from a suitable fitting procedure, support the conclusions previously reported.

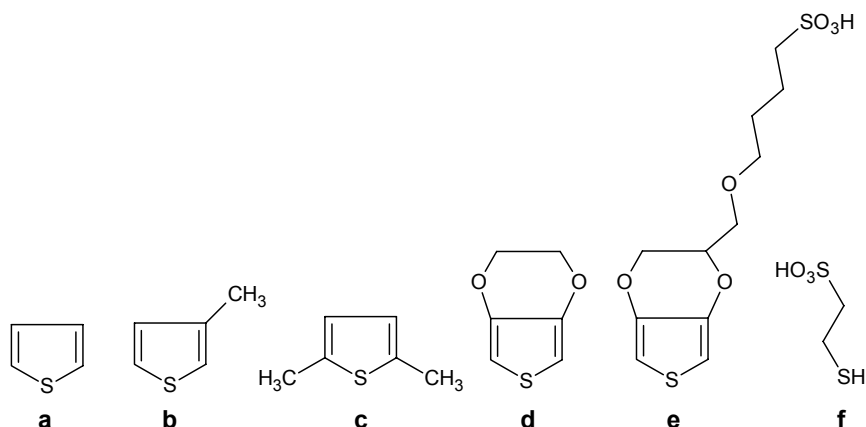


Figure 1. Structures of the investigated molecules (a: thiophene; b: 3-methylthiophene; c: 2,5-dimethylthiophene; d: EDOT; e: SO₃-EDOT; f: 2-mercaptoethanesulfonic acid)

References

1. Groenendaal L., Jonas F., Freitag D., Pielartzik H., Reynolds J. R., *Adv. Mater.* 2000, 12, 481
2. Kirckhmer S., Reuter K., *J. Mater. Chem.*, 2005, 15, 2077
3. Pigani L., Foca G., Ionescu K., Martina V., Ulrici A., Terzi F., Vignali M., Zanardi C., Seeber R., *Anal. Chim. Acta*, 2008, 614, 213
4. Martina V., Ionescu K., Pigani L., Terzi F., Ulrici A., Zanardi C., Seeber R., *Anal. Bioanal. Chem.* 2007, 387, 2101
5. Terzi F., Zanardi C., Martina V., Pigani L., Seeber R., *J. Electroanal. Chem.* 2008, doi:10.1016/j.jelechem.2008.03.009
6. Zanardi C., Terzi F., Pigani L., Heras A., Colina A., Lopez-Palacios J., Seeber R., *Electrochim. Acta* 2008, 53, 3916